Effect of sulfonation and diethanolamine addition on the mechanical and physicochemical properties of SEPS copolymer

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Abstract. Modification techniques have been developed to achieve changes in the processing of polymers, and modification of their mechanical, thermal and morphological properties, as well as their hydrophobicity and conductivity. Sulfonation improves ion conductivity, antistatic behaviour, hydrophilicity and solubility of the polymers. These characteristics are related to the presence of sulfonic groups in the polymer matrix. This research project focuses on the evaluation of mechanical, physical and chemical properties of membranes that are based on a sulfonated Styrene-Ethylene-Propylene-Styrene (SEPS) copolymer. The membranes were functionalized with diethanolamine at 5, 15 and 30% w/w, to separate carbon dioxide. FTIR and XRD analyses were used to characterize the membranes. The sulfonated-loaded membrane with 15% of diethanolamine showed the best results in each characterization.

1. Introduction

Sulfonation processes are used to introduce sulfonic acids into polymers and modify properties such as ion conductivity, to increase their hydrophilicity and to improve polymer solubility. Sulfonated polymers have a wide range of applications. They are used as membranes for fuel cells, for electrodialysis, to exchange resins and in gas separation. [1,2]. Incorporation of polar groups by sulfonation favors water uptake, thus increasing conductivity and inducing stronger interactions with polar feed gases such as CO2. These properties are typical of polymers that are commonly used in fuel cells and gas separation, respectively. Polymers with aromatic rings are more susceptible to experience sulfonation. This has been demonstrated with sulfonated polyethertherketones (SPEEKs), polystyrene copolymers [3], polyimides [4], polyphenylenesulfides, polycarbonate [5], Poly (phenylene oxide) [6], and polysulfones. The properties of the modified polymer are strongly affected by the degree of sulfonation. For instance, selectivity for CO2 separation of Poly (2,6-dimethyl-1,4-phenylene oxide) (PPO) can be increased from 16.7 to 33.2 in sulfonated brominated PPO membrane with a 19.7% degree of sulfonation (DS) [7].

The copolymer that is used for this application is composed by a soft, rigid block known as block copolymer, which confers stability and rigidity. The Styrene-Ethylene-Propylene-Styrene (SEPS) is composed by two styrene blocks and an ethylene and propylene block that confers impact resistance and elasticity, respectively. SEPS is resistant to UV radiation at high temperature and it is stable during its production process. The purpose of this work is to study the effect of sulfonation and diethanolamine on the mechanical and physicochemical properties of SEPS membranes to evaluation of material stability in carbon dioxide separation [8].
2. Methodology

2.1. Materials
Styrene-Ethylene-Propylene-styrene (SEPS) copolymer was kindly donated by Kraton®. Diethanolamine was purchased from Sigma Aldrich to be used as a carrier agent to functionalize the membranes and improve carbon dioxide separation.

2.2. Preparation of the membrane
A solution of 5 grams of SEPS copolymer was prepared in 100mL of dichloromethane and then mixed with a sulfonating agent. The sulfonating agent was prepared in 100mL of dichloromethane at 0°C in an ice bath; 4.73mL of acetic anhydride were then added, along with 2.68mL of sulphuric acid after 10 minutes. The solution was left to rest for an additional 10 minutes. The solution was reacted for a certain time and then stopped with methanol. The obtained product was removed and washed with de-ionized water until neutralization. The sample was dried in an oven at 75°C [9,10].

The sample was dissolved in toluene. The solution was loaded with 5, 15 and 30% w/w (DEA) and stirred until obtaining a stable, clear solution. They were then transferred to a petri-dish until it was completely dry [9,10]. Polymer membranes were obtained with DEA (Loaded membranes LM) at different concentrations and with sulfonation (Sulfonated membranes SM). Moreover, the effect of DEA was determinate about sulfonated membranes (Sulfonated-loaded membranes SLM). All samples obtained were evaluated with respect to unmodified membranes (UMM).

2.3. Characterization of the membranes
Contact angle was determined from images that were previously taken when measuring the angle of a water drop on the surface of each membrane. This analysis was carried out at room temperature [11]. Mechanical properties like tensile strength, deformation resistance and Young’s modulus were determined for each membrane using a EZ-S Shimadzu [11]. FTIR analysis was used to identify the sulfonic groups that are present in the membranes at different times. It was also used to establish the different functional groups, such as sulfonic and amines. A Scanon FTIR-8400 equipment was used to perform Fourier Transformed Infrared Spectroscopy (FTIR) in a frequency range between 4000 and 400cm⁻¹ to determine the composition of each type of modified membrane [11]. An X-Ray Diffraction (XRD) analysis was carried out using a PW3373/00 Cu LFF DK332001 equipment with a copper anode, 45kW voltage and 40mA current. It was used for determining the structural characteristics of the unmodified and 15% sulfonated-loaded DEA membranes [11].

3. Analysis and discussion of results

3.1. Effect of sulfonation at different times using FTIR analysis
Figure 1(a) shows the infrared spectrum of three sulfonated samples. There, it can be observed that the sample exhibits the highest concentration of sulfonic groups after 60 minutes at 700, 1030 and 1150cm⁻¹. The sulfonic acid group (SO₃H) is regularly observed at 709, 1028, 1080, 1252 and 3440cm⁻¹. The peak at 1252cm⁻¹ is overlapping in the intensity of 1150cm⁻¹ and the peak at 3440cm⁻¹ overlaps at frequency 3420cm⁻¹ because of the presence of moisture. The peak at 1080cm⁻¹ is shifted to 1150cm⁻¹ due to the presence of the aromatic ring that reduces the symmetry and directly influences vibration frequencies. Asymmetric effort of the C=CH group caused by the benzene ring is observed between 3000cm⁻¹ and 3100cm⁻¹. Straining of the HCH group which is part of the polymer chain becomes evident at 1460 and 1490cm⁻¹ [3].

In addition, spectrum of the sulfonated-loaded membrane with 15% of DEA in Figure 1(b) shows the presence of sulfonic groups in the peaks at 888, 1067 and 1239cm⁻¹. Amino group is evidenced in slight peaks at 3500cm⁻¹. The same behaviour is observed in the membrane that was loaded with 30% of DEA. Figure 1(b) showed the same behaviour of each functional group in Figure 1(a). However,
FTIR analysis of the modified membranes can prove the presence of the different functional groups in their structures [3].

![Figure 1. (a) FTIR of the sulfonated samples at 30, 45 and 60min (b) FTIR of the modified membranes.](image)

### 3.2. Contact angle

Images of each type of membrane were taken for recognizing the contact angles. A water drop was placed on the membrane surface in order to identify the hydrophobic or hydrophilic properties of the material [12].

In Table 1, it is observed that all the membranes presented hydrophilic properties, since all angles are lower than 90 degrees. The angles decrease as concentration DEA increases. The sulfonated-loaded membranes have the smallest angle. Water molecules create more interaction with the amine groups on the membrane surface. This interaction is amplified by the porosity of the membranes, which allows a greater immersion of the drops into the material [12].

| Membrane    | Angle (°) |
|-------------|-----------|
| UMM         | 70        |
| LM 5% DEA   | 62        |
| LM 15% DEA  | 61        |
| LM 30% DEA  | 60        |
| SM          | 58        |
| SLM 5% DEA  | 54        |
| SLM 15% DEA | 53        |
| SLM 30% DEA | 53        |

### 3.3. Mechanical properties

The membranes were subjected to mechanical properties tests. Table 2 shows that the unmodified membrane presented the highest results because of its high density. Moreover, loaded membranes decreased their mechanical properties values.

| Sample       | Max. Strength (N) | Max. Tension (N/mm²) | Max. Deform (%) |
|--------------|-------------------|----------------------|-----------------|
| UMM          | 138.5             | 11                   | 2466.9          |
| LM 5% DEA    | 81.5              | 6.5                  | 1381.4          |
| LM 15% DEA   | 120.9             | 9.6                  | 1551.8          |
| LM 30% DEA   | 76.6              | 6.1                  | 1458.4          |
| SM           | 112.2             | 8.9                  | 2433            |
| SLM 5% DEA   | 93.2              | 7.4                  | 2071.7          |
| SLM 15% DEA  | 91.9              | 7.3                  | 2125.1          |
| SLM 30% DEA  | 77.8              | 6.2                  | 1308.3          |
Nevertheless, the loaded membrane with 15% of DEA showed the best results, followed by the sulfonated one. In the case of sulfonated-loaded membranes, the behaviour corresponds to a more notorious decrease in mechanical properties. By increasing the DEA load DEA, porosity of the membrane increases, leading thus to a decrease in the mechanical characteristics because of the decrease in density [11]. When DEA loads are added, it significantly benefits elongation of the material, which in turn causes a greater effect on elasticity of the membranes [13].

3.4. Analysis by X-ray diffraction (XRD)

The unmodified and 15% DEA sulfonated-loaded membranes were subjected to XRD test to evaluate the structural behaviour between unmodified and modified membranes by DEA impregnation.

As it is shown in Figure 2, the copolymer is amorphous and does not change with sulfonation and DEA load. At 18.0° the intensity of the peak changes in both membranes; the 15% DEA sulfonated-loaded membrane showed a decrease in intensity because of the distance between the polymeric chains and the free fractional volume (FFV) according to Bragg’s law [11]. The sulfonated-loaded membrane would present stronger interactions between polymeric chains that generate contraction in the polymer and increase porosity.

![Figure 2. X-Ray of an unmodified (sample 1) and 15% sulfonated-loaded membranes (sample 2).](image)

4. Conclusion

Copolymer of SEPS displayed excellent physical properties with positive values that are characteristics of membrane elongation. However, DEA sulfonated-loaded membranes exhibited the lowest results due to formation pores that decrease their resistance. DEA addition and sulfonation of SEPS copolymer increases the hydrophilic properties and the elongation characteristics of the material due to the porosity. All the same, it decreases the resistance to mechanical testing. Although the physic-chemical and mechanical properties were modified, the amorphous structure of the copolymer remained unmodified.

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