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Sulfonated SEBS Membranes for HVAC Systems

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Summary: A series of partially sulfonated SEBS(polystyrene-b-poly(ethylene-r-butylene)-b-polystyrene) was synthesized. The sulfonation degree of the sulfonated SEBS, that reacted with acetyl sulfate, was characterized by FT-IR and elementary analysis. Water permeability, water sorption (which strongly affect proton conductivity), and DSC (to determine the amount of bound water and free water) were investigated for application of sulfonated SEBS for HVAC system. It was observed that increasing sulfonation degree water permeability, water sorption, and bound water content increased. It revealed that sulfonation of SEBS membrane contributes to elevate hydrogen bonding between water vapour and hydrophilic polymer.

Keywords: HVAC system; membrane; SEBS; sulfonation; water vapor transmission rate(WVTR)

Introduction

Membranes composed of hydrophilic polymers have been used in heating, ventilating and air conditioning systems to improve control of humidity while reducing energy cost. Systems function by allowing transfer moisture between a humid air stream to a relatively dry one. One of the functions of a HVAC(heating/ventilation/air conditioning) system in a building is to exhaust air to the atmosphere and simultaneously replenish the exhausted air with fresh air. It is necessary to adjust the temperature of the fresh air to approximately the same temperature and humidity of the exhausted air before introducing it into the building. This requires additional cooling or warming of the fresh air and the addition or removal of moisture, at a significant energy cost. In addition, this ventilating process frequently employs moving parts in the apparatus which requires periodic maintenance. In order to minimize energy and maintenance costs, it is desirable to provide a static heat and moisture exchanging core for simultaneously and continuously effecting both heat and moisture exchange between two air streams. An inexpensive water-conducting membrane having mechanical strength is desirable in order to provide an improved operating lifetime for such core.[1] In U.S. Pat. No. 5,348,691 McElroy et al. disclose a humidifying device wherein water is transported across a membrane composed of a perfluorocarbonsulfonic acid polymer or a polystyrenesulfonic acid.[2]

It is our object of this study to produce a membrane which allows the transfer of water between two gas streams separated by the membrane. The membrane must be mechanically stable and free of porosity and pinholes which would allow clogging by contaminants.

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Experimental

Materials

The polymer used in this study was polystyrene-b-poly(ethylene-r-butylene)-b-polystyrene triblock copolymer(Mw ~ 50,000 and 30% styrene contents) purchased from Kraton Polymers and purified by dry in vacuum oven at 60 °C before use. The sulfonating reagent was acetyl sulfate, which was prepared from the reaction of acetic anhydride with concentrated sulfuric acid (98%). 1,2-dichloroethane(DCE, Dae-jung chem., Korea) as a solvent to dissolve SEBS and isopropyl alcohol as a termination agent was used.[3]

Preparation of Acetyl Sulfate

Acetyl sulfate was prepared the following proportions.[4] Acetic anhydride (152.6 ml = 164.8 g = 1.62 moles) was cooled to −10 °C. Concentrated sulfuric acid (56.16 ml = 103.0 g = 0.998mols) was added slowly so that temperature would not exceed 0 °C. The viscous reagent was allowed to warm to 10 °C and an aliquot was taken for sulfonation. It must be kept below 0 °C or used immediately.

Sulfonation of the Block Copolymer

10 g of SEBS dissolved in 150 ml DCE was stirred at 55 °C under nitrogen ambient for 3 h.[5,6] In order to control the degree of sulfonation, the required amount of acetyl sulfate was added slowly using dropping funnel. The solution was stirred for 3 h and then 10 ml of IPA was added to stop the reaction. Sufonated SEBS washed with deionized water several times until neutral pH of the sewage was obtained.

Preparation of Membranes

A solution of sulfonated SEBS in THF solvent was prepared and filtered. Concentration of the solution was 8 wt%. The filtered solution was poured into a glass dish and placed at room temperature until complete evaporation of the solvent. Residual solvent was evaporated under vacuum at 60 °C. The membrane was obtained as a transparent flat-sheet shape.

Characterization

The sulfonation degree of sulfonated SEBS was also evaluated quantitatively by an element analysis and calculated by the next equation:

$$\text{sulfonation degree } (mol\%) = \frac{moles\ of\ sulfonic\ acid}{moles\ of\ stylene\ in\ SEBS} \times 100$$

The water uptake was measured by immersing the membrane coupons into deionized water at 30 °C for at least 1 day, then removing the samples and blotting the membrane surface to remove any excess water, and finally, promptly weighing them on a microbalance. The water uptake was expressed as follows:

$$W(\%) = \frac{(W_w - W_d)}{W_d} \times 100$$

where, W_d and W_w are the mass of the dry sample and the mass of the water-swollen sample, respectively. The amount of free water in fully hydrated SSEBS membranes was determined by differential scanning calorimetry(DSC) measurements. A wet membrane which has frozen was hermetically sealed in a sample pan. A DSC module was purged with nitrogen and quenched down to −30 °C with liquid nitrogen and then heated to +30 °C at a heating rate of 5 °C/min. The free water contents in total water can be calculated by:

$$\text{free water content} = \frac{\text{measured enthalphy}}{\text{water enthalphy } (335\ \text{J/g})} \times \text{water uptake } (\%)$$

The thermal degradation behavior of the SSEBS membranes was measured using a TGA at a heating rate of 20 °C/min from 30 °C to 600 °C. The water permeation property was tested by gravimetric(dish) method (ISO 2528) to determine of water vapor transmission rate(WVTR) that is the steady state rate at which water vapor permeates through a film at specified conditions of temperature and relative humidity. Values are expressed in g/m^2/24 hr in metric (or SI) units. The mechanical strength of SSEBS membranes

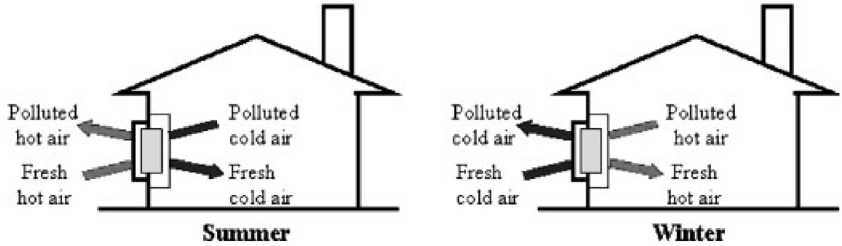

Figure 1.
Basic principle of ventilation.

were tested by universal testing machine(UTM).

Results and Discussion

A series of partially sulfonated SEBS were synthesized and the sulfonation degree of sulfonated SEBS reacted with acetyl sulfate was characterized quantitatively by a FT-IR and quantitatively by an elementary analysis.[8–10]

Figure 3 compares changes in spectra before and after sulfonation. The band centered around 1200 cm^{-1} is due to asymmetric stretching vibration of sulfonate groups produced by sulfonation. The absorbencies at 1038 and 1105 cm^{-1} can be ascribed to the vibrations of phenyl rings substituted with sulfonate groups and sulfonate anions attached to phenyl ring. The ratio of sulfonation which expresses the efficiency of employed sulfonic acid decreased with increasing amount of acetyl sulfate as shown Table 1. As more acetyl sulfate was added, the concentration of sulfonated group in the obtained sulfonated SEBS was increased. However, the sulfonation degree actually obtained was quite lower than the expected value when taking into account the amount acetyl sulfate added.

The membrane was obtained as a transparent flat-sheet shape with various brown colors. As presented at Figure 4, the colors of membranes become darker by increasing sulfonation degree.

The water content and water state in the sulfonated polymers are very important factors that directly affect proton transport across their membranes. Generally, it is believed that protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H_3O+, H_5O_2+, and H_9O_4+ in the water medium. In a fully hydrated state, sulfonated polymers may dissociate immobile sulfonic acid groups and mobile protons in aqueous solution. Then, the free protons move through a localized ionic network within

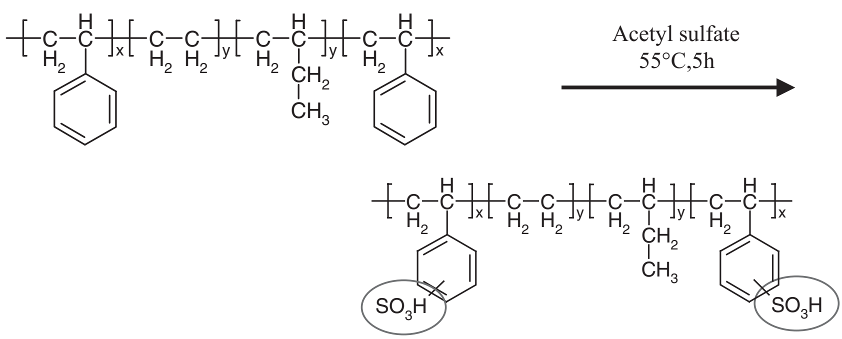

Figure 2.
Reaction scheme for sulfonation of SEBS.[7]

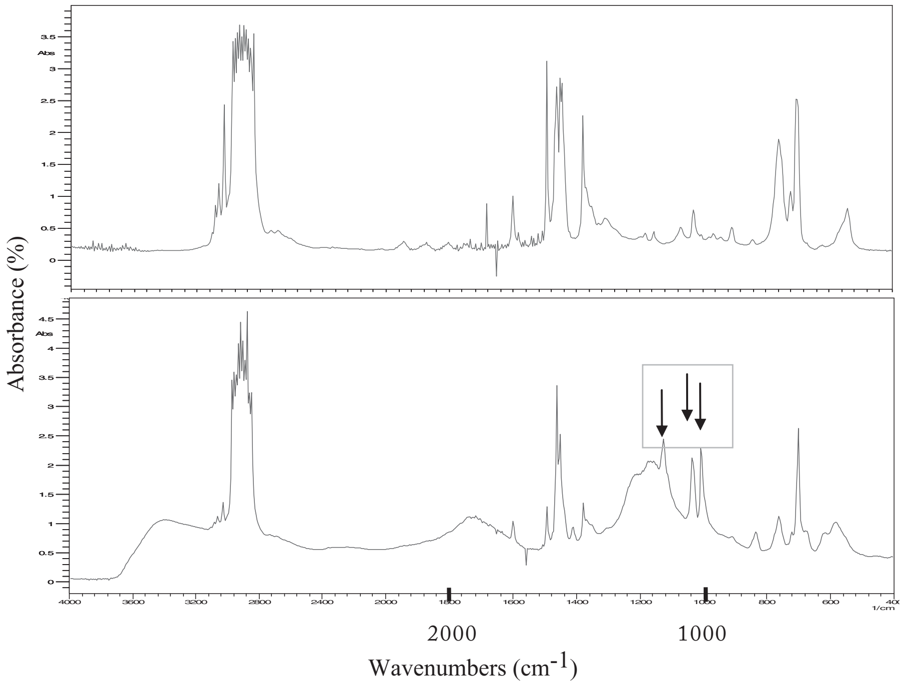

Figure 3.
FT-IR spectra of SEBS before and after sulfonation.

Table 1.
Designation of sulfonated SEBS membranes with defferent sulfonation degree.

Sample	Amount of acetyl sulfate (mol%)	Sulfonation degree (mol%)	The ratio of sulfonation (%)
SSEBS-1	4.8	26.7	65.1
SSEBS-2	9.7	37.2	38.3
SSEBS-3	14.5	47.2	32.4
SSEBS-4	19.4	58.0	35.0
SSEBS-5	24.2	46.2	23.3
SSEBS-6	29.0	56.2	23.2

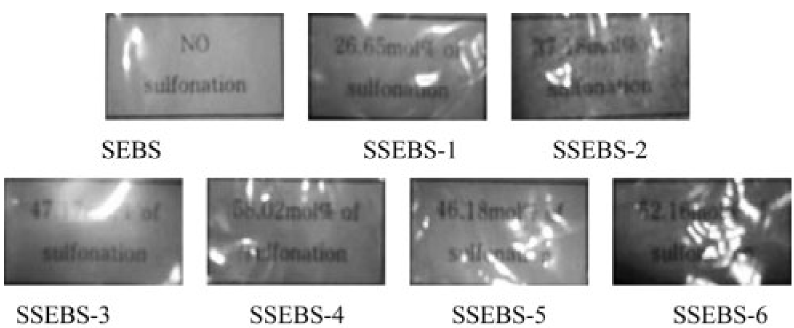

Figure 4.
Membranes with various sulfonation degree.

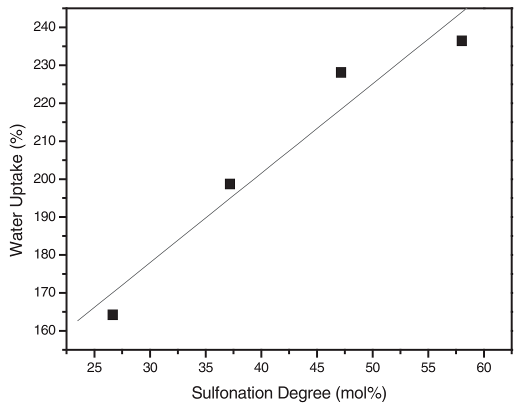

Figure 5.
Effect of sulfonation degree on water up take of the membrane.

fully water-swollen sulfonated polymer membranes.[11,12] Accordingly, the proper water content level should be maintained in sulfonated polymer membranes in order to guarantee high proton conductivity that can be bonded with water vapor.[13–15] Figure 5. shows water uptake of SSEBS membrane with different sulfonation degree.

In a DSC curve, a single peak around 0 °C stands for an endothermic peak corresponding to the heat of fusion of free water-the same transition temperature as bulk water. The amount of free water in the SSEBS membranes was obtained from an integration of the endothermic peak area. Then, the amount of bound water was calculated from the difference between the total water and the free water. Table 2 summarizes the amount of free water and bound water.

In some cases, bound water can be classified into freezing-bound water and non-freezing-bound water, which is due to a weak or a strong interaction between water molecules and the polymeric matrix with polar and ionic groups. The amount of bound water in the SSEBS membranes increased considerably with increasing sulfonation degree while the amount of free water increased slightly. This implied that the bound water can be captured by the sulfonic groups in SSEBS membranes.

Water permeation property was examined with the SEBS membranes before and after sulfonation. It revealed that sulfonation of the membrane allows much more permeate of water vapour. The result was 477.7 and 30,095.5 g/m^{2}d, respectively and it should be tested for more samples depended on various sulfonation degree.

As appear in Figure 6, the first decomposition stage of SSEBS membrane which appear 5% weight loss was observed at 220–250 °C, where start the desulfonation process. Above 400 °C, the second decomposition of polymer main chain occurs.

Tensile strength and Elongation of SSEBS membrane increased with increasing sulfonation degree that means the rubbery parts of the copolymer become

Table 2.
Comparison of the water state of the sulfonated SEBS membranes with different sulfonation degree.

Sample	Water content (%)	Free water (%)	Bound water (%)	Ratio [bound]/[total]
SSEBS-1	164.2	91.4	72.8	44.3
SSEBS-2	198.7	95.7	103	51.8
SSEBS-3	228.1	96.7	131.4	57.6
SSEBS-4	236.4	97.2	139.2	58.8

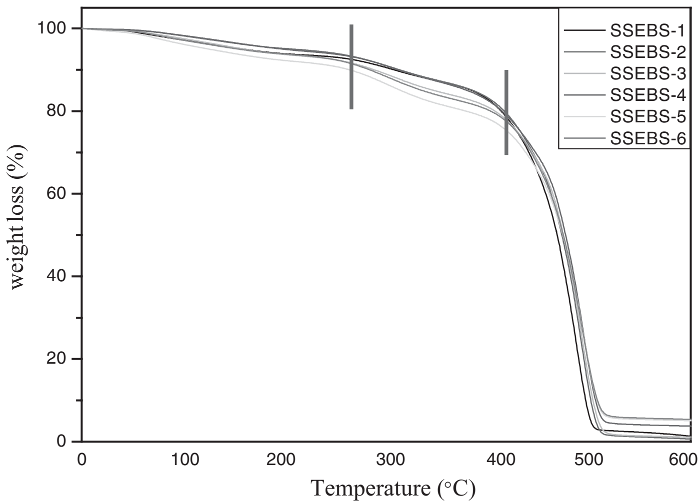

Figure 6.
TGA thermograms of Sulfonated SEBS.

more flexible due to the hanging sulfonic groups on the linear main polymer chain.

Conclusion

In the present study, sulfonated SEBS membranes were prepared to determine the effect of sulfonation degree on water sorption and water permeability for the application of HVAC systems. Water sorption and water permeability increased with increasing sulfonation degree. Especially, bound water contents in total water increased considerably with increasing sulfonation degree while the amount of

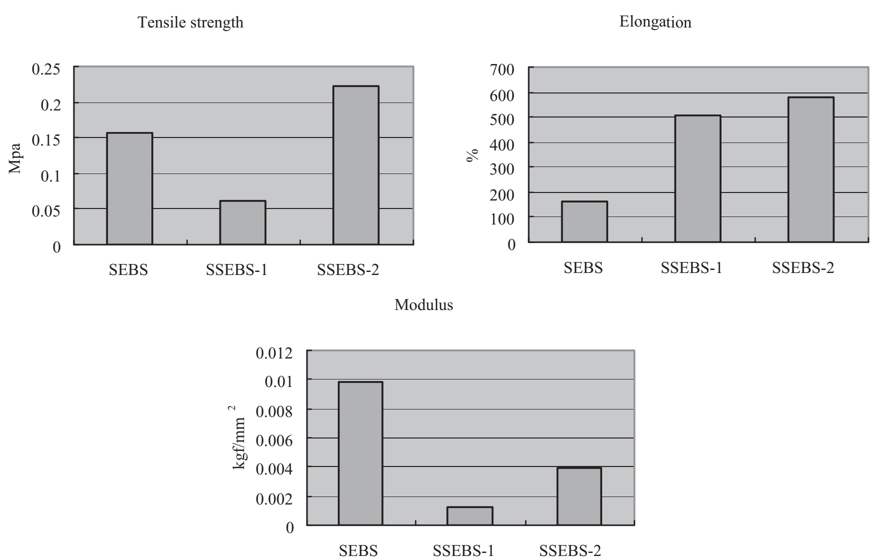

Figure 7.
The mechanical properties of sulfonated SEBS membranes.

free water increased slightly. It implies that the bound water might be captured by the sulfonic groups in SSEBS membranes and enhanced water permeability. The SSEBS membranes did not showed drastic decrease of mechanical properties and the membrane was suitable for the application of HVAC systems.

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