Removal of Pyridine from Water by Pervaporation Using Filled SBR Membranes

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ABSTRACT: Styrene butadiene rubber (SBR) was efficiently cured (crosslinked) by using sulfur to accelerator ratio less than unity. This cured SBR was further compounded with carbon black filler (grade N330) with three different doses i.e., 5, 10, and 20 wt % of filler to form three different filled and crosslinked membranes, i.e., SBR5, SBR10, and SBR20. These filled rubber membranes and one unfilled but efficiently cured membrane, i.e. SBR0, were used for pervaporative removal of pyridine from its mixtures with water. The filled membranes were found to show better selectivity and mechanical properties but lower flux than the unfilled membrane. All of these membranes showed reasonably good range of flux and pyridine selectivity. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1330–1334, 2011

Key words: efficient vulcanization; filled membrane; pervaporation; pyridine–water mixtures; flux selectivity; activation energy

INTRODUCTION

Pervaporation (PV) is a second-generation membrane process in which liquid mixtures to be separated are allowed to pass through a dense membrane under reduced pressure. In this process, separation takes place by preferential sorption and diffusion of one of the components through the membrane. In recent times, apart from dehydration of organics, PV has been extensively tried for removal of traces of organics such as pyridine from water.

Pyridine is an important solvent and catalyst. It is frequently found in effluents from rubber and plastics, petrochemicals, and some other organochemical industries such as pharmaceuticals and agrochemicals.[1] The recovery of pyridine from outflow is an important problem because it is often necessary to reuse relatively expensive chemicals. Membranes made from glassy polymers have been tried[2–4] for separation of pyridine from water. Despite easy availability and processing, rubber membranes are not tried for this kind of separation because of its poor selectivity. PV membrane made from PDMS rubber has been reported to preferentially permeate water from the mixtures of picolines, and water though it showed sorption selectivity for picolines.[5] Amorphous structure with extensive free volume and flexible chain configuration make most of the rubber membranes permeable to water despite its organophilicity. However, efficiently crosslinked rubber membranes have been reported to show preferential organic permeation.[6]

Most of the rubber membranes are crosslinked (cured) by sulfur and accelerator. During sulfur crosslinking, it forms mono, poly, and cyclic sulfur-bonded structures in the rubber matrix.[7] Among these three types of bondings, the mono sulfur bondings contribute to high selectivity of the membranes.[6] Hence, for producing effectively cured rubber membranes, monosulfide linkages must be increased at the expense of poly or cyclic sulfur linkages, which contribute little to effective crosslinking as required for restricted permeation and hence high separation factor of the cured membranes. "Efficient vulcanization" with sulfur to an accelerator ratio of 1.5 : 6.0 results in maximum extent of monosulfide linkages as required for effective curing and hence selectivity of the rubber membranes. Above this ratio there is little change in amount of monosulfide linkages. However, the selectivity as well as strength of the rubber membranes can further be improved by incorporating reinforcing fillers in the rubber matrix to produce filled rubber membranes.

The effect of fillers on transport properties of the filled membranes have been reported by various authors. The transport of permeant through filled membranes depends on the nature of the filler used and its compatibility with the polymer matrix. If the filler is compatible, it will occupy the free volume of the polymer and the permeants will transport through a tortuous path, whereas incompatible

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fillers create voids in the polymer–filler interface and transport occurs through this void space.[8] In most of these cases, silicon rubber membranes have been filled with zeolite for selective organic permeation from its aqueous mixtures.[9–11] In the present work, efficiently crosslinked SBR have been compounded with different doses of reinforcing carbon black fillers of high surface area to obtain filled rubber membranes of improved selectivity achieved through chemical crosslinking by efficient vulcanization and physical crosslinking through filler incorporation. The incorporation of fillers not only improves the organic selectivity of the membranes but also improves the mechanical strength of the otherwise soft rubber membranes. These filled membranes have been used for removal of pyridine (0–11 wt % pyridine in water) from water.

EXPERIMENTAL

Preparation of PV membranes

SBR of grade 1702 as obtained from Tyre Corporation of India, West Bengal, was used for preparation of membranes. Carbon black of N330 grade used for compounding the rubber was obtained from the same company. The rubber was masticated, swelled in toluene for 24 h, followed by addition of the required amount (5, 10, and 20 phr) of carbon black with mechanical stirring of the dispersion for 24 h. Sulfur (crosslinker, 1.5 phr) and accelerator (6 phr) was then added and the compounded mixture was stirred for another 8 h. From this rubber dispersion, membrane was cast on a smooth and clean glass plate, and it was air-dried overnight at ambient condition.

Characterization of the membranes

In this work, the rubber membranes have been filled with three different doses of fillers and modified with varied degrees of crosslinking to improve its selectivity. Hence, these membranes were characterized by verifying the compatibility of the fillers with the rubber and the extent and nature of crosslinking in the membrane matrix by FTIR, SEM, mechanical properties, and measurement of crosslink densities by physical and chemical methods.[12]

Permeation studies

Pervaporation experiment

Pervaporation experiments of pyridine–water mixtures with the filled rubber membranes were carried out in a batch-stirred cell[13] with adjustable downstream pressure that was maintained at 1 mm Hg by the liquid (mercury) column method, using a manometer. The feed compartment of the pervaporation cell was equipped with a stirrer to ensure adequate mixing of the liquid feed to eliminate any concentration or temperature gradient. Effective membrane area (A) in contact with the feed mixture was 19.6 cm^2 and the feed compartment volume was 150.0 cm^3. The pyridine–water mixtures in contact with the membrane were allowed to equilibrate for approximately 3 h for the first experiment and 1 h for the subsequent experiments with different feed compositions. When the steady state was reached, the permeate was collected in traps immersed in liquid nitrogen. Permeation flux (J) was

$$J = \frac{W}{At} \quad (1)$$

calculated by dividing the amount of total permeate (W) by the time (t) of experiment and area of the membrane from eq. (1).

The PV experiment was performed at a constant temperature by circulating constant temperature water around the jacket of the PV cell. The pyridine content of the permeate was determined by an Abbe-type digital Refractometer (model no. AR600, MISCO, Cleveland, OH) at 25°C temperatures for all the samples. The pyridine selectivity of the membranes were evaluated in terms of separation factor (α_{pv}) from eq. (2) as given below

$$\alpha_{PV} = \frac{y_{Pyridine}/y_{water}}{x_{Pyridine}/x_{water}} \quad (2)$$

Here, y_i and x_i are weight fractions of component i (pyridine) in permeate and feed, respectively.

The performance of the membrane was also evaluated in terms of two other important parameters, i.e., permeation separation index (PSI) and enrichment factor (β) as obtained from eq. (3) and eq. (4), respectively. The reproducibility of permeate compositions and fluxes were within ±5%.

$$PSI = J_{pyridine}(\alpha_{PV} - 1) \quad (3)$$

$$\beta = \frac{Y_{Pyridine}}{X_{pyridine}} \quad (4)$$

Here, $J_{pyridine}$ is flux of pyridine from the membrane; $Y_{pyridine}$ and $X_{pyridine}$ are permeate and feed concentration of pyridine.

RESULTS AND DISCUSSION

Permeation studies

Effect of feed concentration on pyridine separation

Figure 1 shows the variation of wt % of pyridine in permeate against wt % of pyridine in feed for
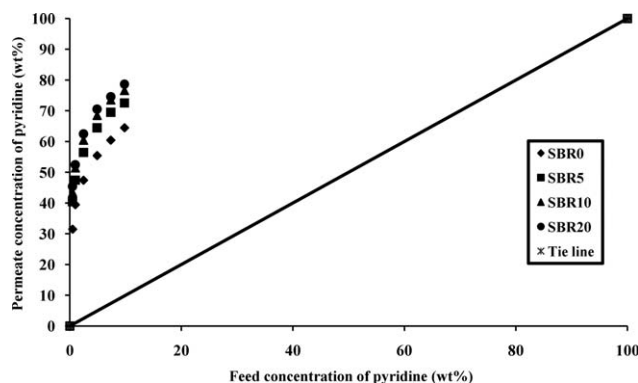
Figure 1 Variation of permeate concentration with its feed concentration at 40°C for SBR membranes: ◆, SBR0; ■, SBR5; ▲, SBR10; ●, SBR20.

Figure 2 Variation of pyridine and water flux with feed concentration of pyridine at 40°C for SBR membrane; ◆, SBR0pyr; ■, SBR5pyr; ▲, SBR10pyr; ●, SBR20pyr; *, SBR0water; ×, SBR5water; +, SBR10water; −, SBR20 water.

separation of pyridine from water with SBR-0, SBR-5, SBR-10, and SBR-20 membranes. It appears from these McCabe-Thiele-type *xy* diagrams that these filled rubber membranes show high pyridine separation over the used concentration range (0.48–9.79 wt % pyridine in feed) without any pervaporative azeotrope. It is also seen that for the same feed concentration, the separation characteristic of the membranes increase from SBR0 to SBR20 with increasing filler loading.

All of the above membranes have similar chemical crosslinking but they differ in the extent of physical crosslinking, which increases from SBR0 to SBR20. This may be the reason for the above order of separation characteristic.

Effect of feed concentration on flux, separation factor, PSI, and enrichment factor

Figure 2 shows the effect of feed concentration of pyridine on pyridine and water flux for all the SBR membranes at 40°C. It appears from this figure that with an increase in pyridine, concentration in feed pyridine flux increases linearly, whereas water flux remains marginally constant for all the membranes. It is also observed that the unfilled membrane shows much higher pyridine or water flux than the filled membranes, whereas for the filled membrane flux decreases from SBR5 to SBR20. In Figure 3, pyridine selectivity is plotted against its feed concentration with power regression (regression coefficient >0.9) at the same temperature for all the membranes. From this figure it is observed that pyridine selectivity decreases drastically with feed concentration. The increase in flux and decrease in selectivity with increasing pyridine concentration in feed for the pyridine–water binary mixture may be attributed to the plasticization of the organophilic membranes at high feed concentration of pyridine. Similarly, with
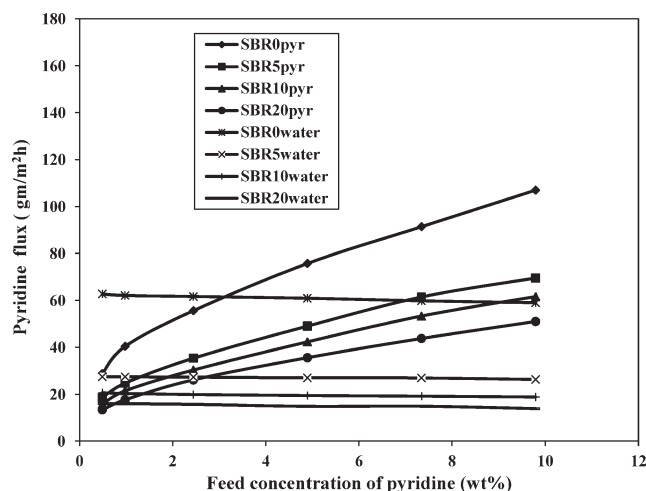
increasing filler loading (and hence physical crosslinking), free space in the rubber matrix decreases, resulting in lower flux but higher selectivity. In Figure 4(a), PSI and enrichment factor for pyridine is plotted against its feed concentration at the same temperature. Similar trend lines were also obtained for all of these flux, selectivity, PSI, and enrichment factor parameters at the two other PV temperatures, i.e., at 55 and 70°C.

Effect of filler loading on PSI and enrichment factor

In Figure 4(b), the effect of filler loading on PSI and enrichment factor is shown. From this figure it is observed that PSI decreases with filler loading whereas the enrichment factor increases up to 10 wt % filler loading and then the change of enrichment factor is marginal. With increasing filler loading, free volume in the rubber decreases and thus PSI also
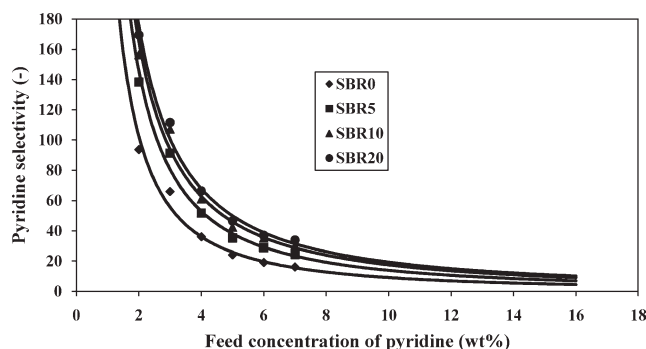

Figure 3 Variation of pyridine selectivity with its feed concentration at 40°C for SBR membrane; ◆, SBR0; ■, SBR5; ▲, SBR10; ●, SBR20.
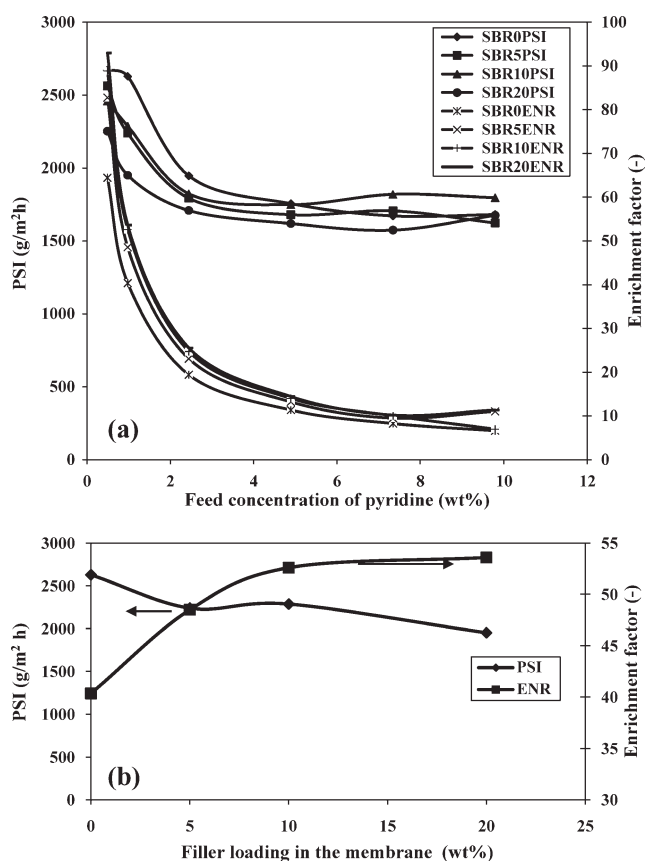
Figure 4 (a) Variation of PSI and enrichment factor of SBR membranes with feed concentration at 40°C; ◆, SBR0PSI; ■, SBR5PSI; ▲, SBR10PSI; ●, SBR20PSI; *, SBR0ENR; ×, SBR5ENR; +, SBR10ENR; −, SBR20 ENR. (b) Variation of PSI and enrichment factor (ENR) of SBR membranes with filler loading at 40°C; ◆, PSI; ■, ENR.

decreases. Further, increasing filler loading makes the membranes more selective to pyridine with higher enrichment factors.

Effect of feed temperature on flux and selectivity

It is evident from Figure 5 that both pyridine and water flux increase exponentially (with regression coefficient >0.9 for each of these curves) with temperature. However, for the same membrane, the rate of increase of flux is more for water than for pyridine due to smaller kinetic diameter of water. Thus, selectivity for pyridine decreases with an increase in temperature because of higher permeation rate of water. As shown in Figure 6, selectivity is seen to decrease linearly with temperature.

Effect of feed concentration on activation energy

Activation energy for permeation is calculated from the slope of the Arrhenius-type linear plot of logarithmic of flux (Q) against inverse of absolute temperature (1/T) from the following equation:
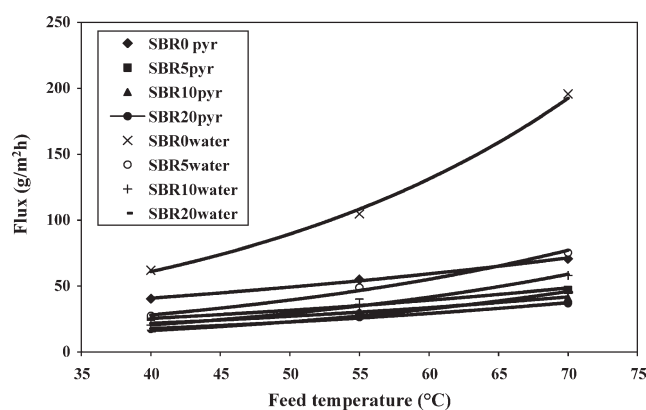

Figure 5 Variation of pyridine flux and water flux with feed temperature for SBR membranes. Feed concentration, 0.9797 wt % pyridine; ◆, SBR0Pyr; ■, SB5Pyr; ▲, SBR10PSI; ●, SBR20PSI; ×, SBR0 water; ○, SBR5 water; +, SBR10 water; −, SBR20 water.

$$\ln Q = \ln A - \left(\frac{E_P}{RT}\right) \quad (5)$$

Here, A is a preexponential factor and R is the universal gas constant. Thus, activation energy for permeation of pyridine and water could be calculated at several feed concentrations from similar plots. For each of these linear plots, by best-fit method, the values of regression coefficient were also found to be close to unity. Activation energy for permeation of both pyridine and water through filled SBR membranes at different feed concentrations of pyridine are shown in Figure 7. From this figure it is observed that activation energies of water remains marginally constant over the used feed concentration range of pyridine (0.48–9.79 wt %), whereas activation energy for pyridine permeation increases linearly up to approximately 6 wt % pyridine in feed, and thereafter the change is very small, signifying plasticization of the organic selective membranes by
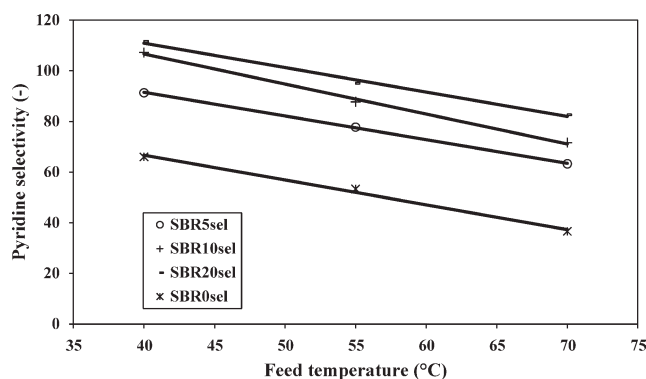

Figure 6 Variation of pyridine selectivity with feed temperature for SBR membranes. Feed concentration, 0.9797 wt % pyridine; ×, SBR0selectivity; ○, SBR5 selectivity; +, SBR10 selectivity; − SBR20 selectivity.
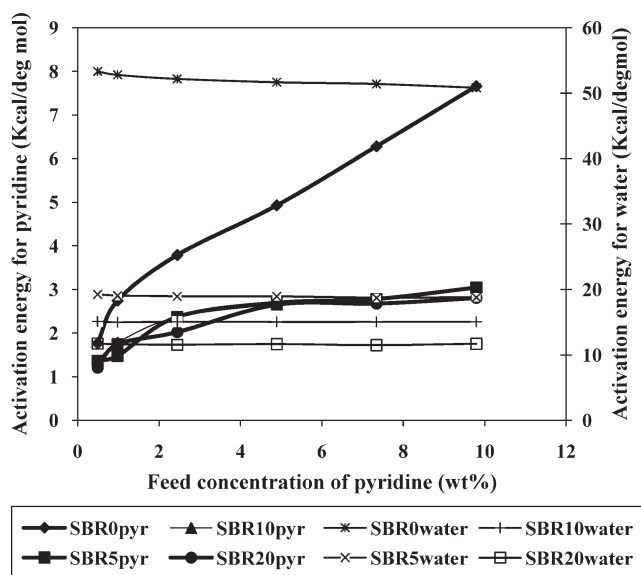
Figure 7 Feed concentration and activation energy of SBR membranes; ◆, SBR0pyr; ■, SBR5pyr; ▲, SBR10pyr; ●, SBR20pyr; *, SBR0 water; ×, SBR5 water; +, SBR10 water; □, SBR20 water.

pyridine. The membranes also show lower activation energy of pyridine than of water, as shown in the figure.

Effect of filler loading on activation energy

From Figure 7 it is also observed that for the same feed concentration, activation energy of both pyridine and water decreases with increasing filler loading. Activation energy is calculated from the slope, i.e., the rate of change of flux with temperature. The change of flux with temperature is less for a membrane loaded with filler due to restriction of movement of the otherwise mobile rubber chain also at higher temperatures. This may be the reason for highest activation energy of the unfilled rubber in which in the absence of any filler, the rubber chains show extensive mobility at higher temperatures and hence an increased rate of flux with temperature.

CONCLUSION

Efficiently crosslinked SBR rubber with maximum of monosulfide linkages as required for maximum aromatic selectivites have been prepared and further compounded with three increasing doses of reinforcing carbon black fillers. These crosslinked filled rubber membranes have been studied for pervaporative removal of pyridine from water at different compositions and temperatures. It has been observed that with increasing filler loading from SBR-5 to SBR-20, physical crosslinking increased manifold, resulting in increasing tensile strength and pyridine selectivities of the membranes. These rubber membranes will be extremely effective for preferential permeation of any organic having similar solubility parameter with these rubbers.

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