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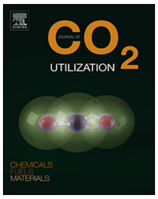

Facile synthesis of CO_2-selective membrane derived from butyl reclaimed rubber (BRR) for efficient CO_2 separation

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ABSTRACT

Butyl reclaimed rubber (BRR) was used as a novel precursor in the fabrication of a rubber membrane for CO_2 separation. Fully de-vulcanized BRR without impurities was produced from waste tire by regeneration. The properties of BRR were evaluated via systematic investigation of a number of experimental variables, and the effects of these variables on the molecular structure and the CO_2 separation performance of the membrane were assessed. The BRR-derived membrane was fabricated by simple solution-coating on an Al_2O_3 support. The effect of the fabrication parameters, such as the solvent type, polymer concentration (8–12 wt%), and curing temperature (room temperature to 100 °C). The results indicate that the CO_2/N_2 separation performance of the BRR-derived membrane prepared with a low concentration ($<$ 10 wt%) of coating dope in toluene solvent and cured at room temperature is competitive with that of membranes reported in previous studies due to the *cis*-isoprene structure. The CO_2/N_2 ideal selectivity of 11.6, coupled with a CO_2 permeability of 86.9 Barrer, obtained with the 8RD-T25 membrane is comparable to that of a commercial rubber membrane. Furthermore, the use of BRR would decrease the use of non-renewable resources and aggregation of waste, with reduced environmental impact.

1. Introduction

Studies have investigated alternative separation methods to diminish the emission of carbon dioxide (CO_2) from power plants into the atmosphere. These methods include absorption [1,2], pressure swing adsorption [3,4], and membrane-based separation technology. The separation of CO_2 from N_2 in commercial CO_2 capture systems is generally achieved by membrane technology [5,6]. The membrane process is prospectively practical because of its attractive advantages, such as high stability and efficiency, ease of operation, and low maintenance costs [7,8]

Several gas separation mechanisms can be applied for CO_2/N_2 separation depending on the membrane structure; these mechanisms include molecular sieving in inorganic porous membranes and solution diffusion in polymer membranes (or dense).

However, the molecular sieving mechanism in membrane processes for CO_2/N_2 separation is expensive and energy intensive due to close kinetic diameters of CO_2 (3.3 Å) and N_2 (3.64 Å). In contrast to porous membranes, efficient CO_2/N_2 separation can be achieved through the solution-diffusion mechanism in dense membranes due to the condensability of CO_2. Amerongen et al. [9] prepared and explored different rubber-derived polymer membranes and evaluated their solubility; the results indicate a strong, linear correlation between gas solubility (S) and critical temperature (T_c):

$$\ln S = a + b \times T_c \tag{1}$$

where a is the overall sorption capacity, and b is the slope of the trend line; this equation characterizes the increase in penetrant solubility in the polymer with increasing gas condensability [as determined from the critical temperature (T_c)]. CO_2 should exhibit high solubility because of its higher critical temperature (304 K) than other gases (for example, 33 K for H_2 and 126 K for N_2).

As shown in Table 1, the slopes of the plots obtained for some glassy- and rubbery-based membranes were calculated using Eq. (1)

Abbreviations: BRR, butyl reclaimed rubber; RTR, reclaimed tire rubber; NR, natural rubber; PB, polybutadiene; PDMS, poly(dimethylsiloxane); BR, butyl rubber; SBR, styrene-butadiene rubber; FT-IR, Fourier transform–infrared spectroscopy; XRD, X-ray diffraction; SEM, scanning electron microscopy; TGA, thermal gravimetric analysis; T, toluene; X, xylene; N, *N*-methyl pyrrolidinone

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Nomenclature

Notation

T_g	glass transition temperature (°C)
T_c	critical temperature (°C)
T_d	decomposition temperature (°C)
P	permeability of the membrane (Barrer)
S	gas solubility (cm^3 (STP)/cm^3 atm)
a	overall sorption capacity (vol%)
b	slope, the ratio of the gas solubility and gas condensability (cm^3 (STP)/cm^3 atm K)
Vr	volume fraction of polymer in a swollen network in equilibrium with pure solvent (vol/vol)
Vs	mole volume of the solvent (cm^3/mol)
dp	transmembrane pressure difference (cmHg)
dt	time difference (s)
V	volume of the downstream chamber (cm^3)
L	effective thickness of the membrane (cm)
A	effective area of the membrane (cm^2)
T	temperature (K)
Δp	difference in the pressure between upstream and downstream (atm)
κ	transport coefficient ($mol^2\,m^{-4}\,s^{-1}\,Pa^{-1}$)
p_0	gas pressure on the feed side (Pa)
k_1	sorption rate constant ($mol\,m^{-2}\,s^{-1}\,Pa^{-1}$)
C_{real}	real concentration of the coating dope (wt%)
W_0	wet weight of membrane (casting dope) (g)
W_i	dry weight of membrane (g)

Greek letters

ν_c	cross-linking density (mol/cm^3)
χ	polymer–solvent interaction parameter
λ	wavelength of X-ray radiation (Å)
θ	diffraction angle (°)

and carefully compared with those from literature survey [10–15]. Rubbery polymer-based membranes with natural rubber (NR), polybutadiene (PB), and poly(dimethylsiloxane) (PDMS) exhibited higher slope values ($15.6–22.6 \times 10^{-3}\ K^{-1}$) than glassy-based membranes ($6.8–15.6 \times 10^{-3}\ K^{-1}$). This finding could be attributed to the high chain flexibility of rubbery polymers when the operating temperature is higher than T_g and when no specific interactions exist between the polymer chain and the condensable gas, resulting in high gas solubility. Thus, rubbery polymer-based membranes are considered a sorption-enhanced polymer membrane for penetration of gas molecules with high condensability [16–18]. However, given that most rubbers can be classified as linear or straight-chain polymers, rubber membranes must be cross-linked during preparation to improve its selectivity in practical applications [19,20]. Thus, the use of cross-linking additives should be considered when preparing rubber membranes, but this technique is costly and requires a complex preparation process.

Reclaimed rubber is an important additive used to manufacture assorted rubber and exhibits many advantages despite that it is a product of waste tire rubber [21–26]. These advantages include (1) ease of mixing with other materials, (2) low-energy consumption for processing, (3) facilitated curing due to the retained cross-linked compounds, and (4) cost saving. Furthermore, the transformation of waste material into a new product is desirable from the viewpoint of material recycling. This approach would be potentially cost and energy efficient due to the production of high-value/functional products from waste [27–32]. In our previous study [33], we evaluated the feasibility of adopting reclaimed tire rubber (RTR) as precursor for the direct synthesis of gas separation membranes without adding cross-linking agents. The RTR-derived membrane mainly consists of NR (60% to 69%; the remaining 30% to 40% is synthetic rubber) and show competitive gas permeability (PCO_2 = 9.9–38.4 Barrer; PO_2 = 2.1–11.5 Barrer) but low gas selectivity (CO_2/N_2 = 6.57–9.97; O_2/N_2 = 1.77–2.14).

Table 1

Slope of the correlation between the solubility vs critical temperature for various different polymer membranes.

Membrane	b ($\times 10^{-3}\,K^{-1}$)	References
Polyetherimide	14.8	[13]
poly(urethane-urea)	14.8	[14]
Poly(vinylidene fluoride)	6.8	[15]
Amorphous polyethylene	15.6	[10]
Natural rubber	17.6	[10]
1, 2-Polybutadiene	22.6	[12]
poly(dimethylsiloxane)	15.6	[11]

Therefore, this study mainly aims to provide a novel precursor for fabricating CO_2 separation membranes by using butyl reclaimed rubber (BRR). To the best of our knowledge, the effect of the stereoisomerism structure of the polymer precursor on membrane performance was not investigated in the previous study. Compared with membranes containing NR, those fabricated using synthetic rubbers, such as BR, styrene–butadiene rubber (SBR), and PDMS, are predicted to show higher selectivity and thermal stability [20,34]. BRR was used due to its recyclability and material properties. In this work, we aim to determine the optimal conditions for preparation of BRR-derived membranes with effective CO_2 separation performance. Based on a systematic investigation of the properties of BRR through thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD), we found that the *cis–trans* isomerism structure of isoprene is a key factor in optimizing the separation performance of the membrane. The ratio of *cis* and *trans* isomerism was dependent on the degree of decrosslinking. The high ratio of *cis* isomerism in the matrix could increase the amount of rubber dissolved in the solvent compared with that of *trans* isomerism, thereby enhancing the gas transport flux in the membrane.

2. Materials and methods

2.1. Butyl reclaimed rubber and chemicals

BRR from local markets was used as the polymer precursor in this study. The BRR was regenerated from butyl-based inner-tire via a thermo-mechanical reclaiming process, involving a higher degree of desulfurization and impurity removal. Fig. 1 shows photographic images of the BRR, which is an amber and translucent rubber. Toluene was purchased from Riedel-deHaën. Xylene was obtained from J.T. Baker®. *N*-methyl pyrrolidinone (NMP) were obtained from Mallinckrodt Chemical, Inc. The porous α-Al_2O_3 discs with 23 mm diameter and 1.4 mm thickness purchased from Ghana Fine Ceramics (Taiwan).

2.2. Preparation of BRR-derived membrane

The BRR-derived membranes (aBRR-bc) were fabricated with different loading weights of BRRs (a), different types of solvents (b) and