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CO₂ Permeability in HNBR: Insights for CO₂ Transport Applications

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ABSTRACT

Carbon capture, utilization, and storage is a crucial short-term strategy to mitigate climate change. Once captured, CO₂ needs to be transported to storage sites, and to ensure efficient transport, it is typically compressed into a liquid or supercritical fluid. These conditions can alter the properties of materials used during the transport stage. A HNBR, a commonly used elastomer in oil and gas applications, is investigated in this work in terms of its CO₂ permeation properties. The plasticization effect of CO₂ plays a key role, as it can shift the glass transition temperature, leading to peculiar permeability behavior at high-pressure. Thermodynamic modelling is also effectively applied, describing the observed trends.

1 | Introduction

Global warming, primarily driven by greenhouse gas (GHG) emissions, is an urgent issue. Climate change has caused significant damage, including reduced resource availability and increased frequency and severity of extreme weather events. The Intergovernmental Panel on Climate Change (IPCC) has set a target to limit GHG and CO₂ emissions in the atmosphere, aiming to cap the global temperature rise at 1.5°C by 2050 [1]. Carbon capture, utilisation and storage (CCUS) has emerged as a crucial short-term strategy for reducing CO₂ emissions and mitigating climate change [2]. In CCUS processes, CO₂ is captured from large point sources and transported via ships or pipelines to underground storage sites or storage tanks for reuse. To make the transport process efficient, CO₂ needs to be compressed and transported as a liquid or supercritical fluid [3]. These

severe conditions may alter the properties of materials employed throughout the transport supply chain.

Polymers are widely used in CO₂ transportation infrastructure as materials for pipeline coatings, liners, gaskets, O-rings, and packings, thanks to their low density and high corrosion resistance. Selecting proper polymeric materials, compatible with the dense CO₂ stream, is essential to achieve reliable and safe modalities of carbon transport [4, 5].

CO₂ absorption may cause plasticization, which can alter the polymer's glass transition temperature, thereby affecting its mechanical properties. Under supercritical conditions, CO₂ can show extraction capacities, potentially removing additives and plasticizers in a de-plasticizing effect. Furthermore, CO₂ uptake is likely to determine relevant swelling in polymers, eventually

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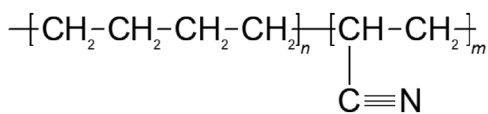


FIGURE 1 | HNBR chemical structure.

leading to geometrical mismatches due to volume expansion, changes in long-term performance, and altered CO₂ transport properties across the polymer phase.

Understanding the effects of CO₂ on polymeric materials under high-pressure and cryogenic liquid conditions is critical to assess their suitability for such demanding applications.

2 | Materials and Methods

2.1 | HNBR

Hydrogenated nitrile butadiene rubber (HNBR) is a synthetic rubber known for its excellent mechanical properties (Figure 1).

HNBR consists of both saturated and unsaturated monomers of butadiene and acrylonitrile (ACN) monomers. Showing good chemical resistance and low cost, HNBR was one of the most commonly used elastomers in the oil and gas industry. In this work, the HNBR polymer samples used were characterized by the presence of 35% carbon black, a common filler used to enhance mechanical performance and durability.

2.2 | Glass Transition Temperature Change

Glass transition of the polymeric sample was determined by differential scanning calorimetry (DSC), using the equipment DSC2500 (TA Instruments). To account for the shift in the glass transition caused by CO₂ uptake, the sample was exposed to CO₂ until complete saturation. Subsequently, the sample was removed from the CO₂ atmosphere and desorption begins: DSC analysis was performed at different times, weighing the sample beforehand. The glass transition was thus determined for each CO₂ concentration datapoint.

2.3 | Sorption Test

Experimental analysis of CO₂ sorption was conducted according to the pressure decay method using the BELSORP machine as the analytical instrument. A known mass of polymer sample was evacuated to remove gas residues, and then placed in a sample holder of calibrated volume, immersed in a thermostatic bath to control the temperature. Upon exposure to CO₂, a pressure sensor monitors the pressure variations caused by CO₂ sorption into the polymer. After a sharp initial pressure drop, which gradually leveled off, the equilibrium was reached. Solubility was calculated through the application of a mass balance and the Peng-Robinson equation of state to account for the deviation from ideal gas behavior.

2.4 | Permeation Test

The permeation of carbon dioxide in the polymer was assessed using the constant pressure technique in compliance with ASTM D3985-17 [6], in a setup developed in-house at SINTEF. In this setup, the polymer sample was placed between two compartments of a permeation cell with a diameter of 47 mm. The upstream side was exposed to a constant pressure of CO₂, while the downstream side was maintained at atmospheric pressure, and argon was used as sweep gas. The gas supply on both sides was controlled by means of mass flow controllers. The gas composition on the permeate side was measured using a micro-GC (Agilent 990) equipped with a thermal conductivity detector (TCD). A thermostatic bath (Julabo FP50) was employed to maintain a stable and uniform temperature throughout the experiments.

Permeability is calculated as follows:

$$\mathcal{P}_i = \frac{\dot{n}_p y_{i,p} l}{A \Delta f_i} \quad (1)$$

where \dot{n}_p is the molar gas flow permeate side, $y_{i,p}$ is the gas concentration in the permeate flow, A is the sample area, l is the thickness of the polymer, and Δf_i is the driving force of the process, defined as the difference in fugacity between the upstream and downstream side.

2.5 | Permeability Modelling

Permeability analysis was also conducted, making use of thermodynamic modelling. Based on prior solubility estimates and modelling, the standard transport model was here applied [7].

The diffusive mass flux across the membrane can be written as follows:

$$J_i = -\rho L_i \omega_i \nabla \left(\frac{\mu_i}{RT} \right)_{T,P} \quad (2)$$

where ρ is the polymer density, ω_i is the mass fraction of the gas L_i is a kinetic factor that depends on CO₂ concentration in the polymer, μ_i is the chemical potential of the penetrant.

Permeability of species i in a polymeric phase is defined as:

$$\mathcal{P}_i = \frac{J_i l}{p_i^u - p_i^d} \quad (3)$$

Where $p_i^u - p_i^d$ is the partial pressure difference between the upstream and the downstream of the polymer.

By combining Equations (2) and (3), one can write:

$$\mathcal{P}_i = \frac{1}{p_i^u - p_i^d} \int_{p_i^d}^{p_i^u} L_0 e^{\beta \omega_i} S_i z_i dp_i \quad (4)$$

S_i is the solubility and z_i is the compressibility factor of the gas. The only two adjustable parameters are the infinite dilution mobility coefficient L_0 , that is linked to the polymer fractional free

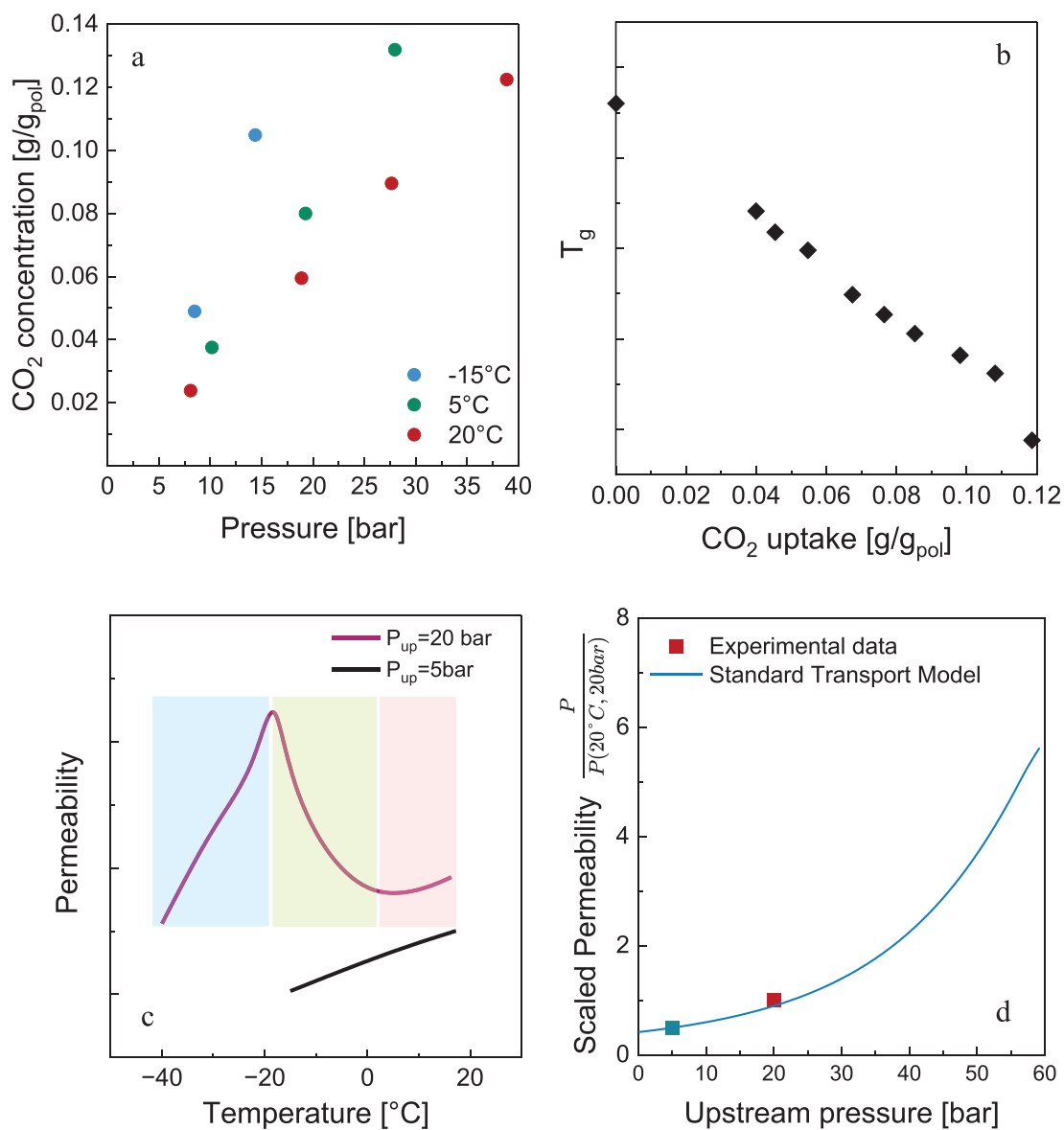


FIGURE 2 | (a) CO₂ solubility at -15°C, 5°C, and 20°C; (b) Glass transition temperature as a function of the CO₂ concentration in a HNBR; (c) Permeability trend as a function of temperature; (d) Permeability description by means of Standard Transport Model.

volume, and β , the plasticization factor that accounts for polymer swelling induced by the gas penetrant.

In the tested polymer, carbon black (CB) was present as a reinforcing agent. Being a non-permeable solid filler, CB typically decreases both the solubility and diffusivity of the gas within the polymer. To account for its effect, the permeability of the pure polymer is estimated using the following correction:

$$\mathcal{P}_{HNBR} = \frac{\mathcal{P}_{pol+CB}}{(1 - \omega_{CB})(1 - \Phi_{CB})} \quad (5)$$

where ω_{CB} is the weight fraction and Φ_{CB} is the volume fraction of carbon black in the polymer.

3 | Results and Discussion

The solubility of CO₂ in this HNBR at different temperatures is reported in Figure 2a, showing a linear increase with pressure, as it is typical of rubbery polymers. Figure 2c shows the permeability of CO₂ as a function of temperature at two different upstream pressure conditions: 20 and 5 bar. A significant difference in behavior is observed between these conditions, likely to be attributed to the effects of plasticization.

Focusing on the data at 20 bar, the permeability trend is non-monotonic and three distinct regions may be identified:

- From 20°C to 0°C: the values of permeability stabilize due to a balance between the effects of diffusivity and solubility. At these temperatures, the polymer is in an equilibrium rubbery state, and neither parameter dominates.

- From 0°C to −18°C: Permeability increases, primarily due to an increase of CO₂ solubility (and density). Being still a rubber, in this range, solubility becomes the dominant factor in determining permeability.
- From −22°C to −40°C: permeability decreases again as the polymer transitions to a glassy state, at least partially. This transition is characterized by a significant reduction in CO₂ diffusivity, as indicated by an increase of the time required to reach steady-state conditions.
 - At the beginning of the test, no CO₂ molecules are inside the polymer matrix, and the material is below its glass transition temperature. The reduction of the diffusion coefficient (or the increase in the time lag) outweighs the contribution of solubility, which levels off.
 - Over time, CO₂ molecules diffuse into the matrix, and after reaching a critical concentration [8], plasticization occurs, converting the polymer back to a rubbery state. Indeed, as one can see in Figure 2b, the glass transition temperature is decreased by the presence of CO₂ inside the polymeric matrix. However, at the downstream side, where CO₂ concentration is still negligible, the polymer remains glassy, and this portion governs the overall permeation process.

At 5 bar, the lower CO₂ uptake led to limited plasticization effects, and permeability follows a monotonic decreasing trend with decreasing temperature, as one would expect in the ideal case (no plasticization). Such a phenomenon can be attributed to the significant reduction in mobility (i.e. diffusivity) that prevails on the change in solubility. The standard transport model has been applied and tuned to describe the different behaviors. Figure 2b illustrates the model's description and prediction of permeability at 20°C. By appropriately selecting the parameters β and L_0 , the model allows for a good representation of permeability.

4 | Conclusions

The reported activity presents experimental and modelling findings on the permeation properties of CO₂ in one type of HNBR under different conditions. These results reveal critical insights into material performance, especially under challenging operating conditions relevant to CO₂ transportation, laying a foundation for optimizing the use of such materials in industrial applications. While these results show how an example HNBR has performed, the properties of HNBRs can be tailored by varying parameters such as filler content, crosslink system, and acrylonitrile content, as these parameters are likely to impact the behavior of the material in CO₂ applications. Future investigation will further explore the underlying mechanisms and broaden the scope to other elastomers.

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Conflicts of Interest

The authors declare no conflict of interest.

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