



The role of polymers in the CO₂ transportation infrastructure: experimental characterization and model analysis

Introduction

The continuous increase in anthropogenic carbon dioxide (CO₂) emissions is widely recognized as the primary driver of global climate change, making Carbon Capture and Storage (CCS) a key technology for achieving decarbonization targets, particularly in hard-to-abate industrial sector [1]. The large-scale implementation of CCS relies not only on efficient capture technologies but also on safe, reliable, and cost-effective transport systems capable of conveying captured CO₂ to storage or utilization sites.

Pipeline and marine transport are the most suitable options for large-scale CO₂ transfer, depending on transport distance and capacity. To maximize transport efficiency, CO₂ is generally handled under dense-phase conditions. Pipelines typically operate with supercritical CO₂ at 10–20 MPa and near-ambient temperature, whereas marine transport employs refrigerated liquid CO₂ at 15–20 bar and temperatures between approximately –30 °C and the triple point [2,3].

Polymeric materials play a fundamental role in the integrity of CCS transport infrastructures. Thermoplastic polymers are increasingly used as internal liners and barrier layers to protect metallic pipelines against corrosion and reduce CO₂ permeation, while elastomers are widely employed as seals, gaskets, and O-rings to ensure leak-tight operation. The long-term reliability of these components is therefore critical for the safety and efficiency of CCS systems.

Compared with conventional hydrocarbon gases, CO₂ exhibits high solubility in many polymers, leading to swelling, plasticization, and changes in their thermal, mechanical, and transport properties [4,5]. The absorbed gas increases polymer chain mobility and free volume, reducing the glass transition temperature and potentially affecting dimensional stability, barrier performance, and sealing efficiency [6]. In elastomeric components, exposure to high-pressure CO₂ may also induce Rapid Gas Decompression (RGD), one of the most critical degradation mechanisms in CCS applications. During rapid depressurization, dissolved CO₂ cannot diffuse out of the polymer fast enough, resulting in gas supersaturation, cavity nucleation, blistering, crack propagation, and ultimately seal failure [7,8]. To improve the resistance of elastomeric seals to RGD, reinforcing fillers such as carbon black are commonly incorporated into rubber formulations. Besides enhancing stiffness and mechanical strength, carbon black influences the microstructure of the polymer network, modifying CO₂ sorption and diffusion behavior and, consequently, the material's resistance to RGD damage.

This work combines experimental characterization and predictive modeling to investigate the behavior of commercial elastomers exposed to dense-phase CO₂ under conditions relevant to CCS transport. CO₂ sorption, swelling, diffusion, and permeability are experimentally evaluated over a broad range of temperatures and pressures. The experimental results are interpreted using the Lattice Fluid/Non-Equilibrium Lattice Fluid (LF/NELF) equations of state to describe CO₂ sorption and polymer swelling [9–11], while gas transport is analyzed through the Standard Transport Model (STM), which couples penetrant solubility with concentration-dependent diffusivity [12]. The resulting integrated framework provides a predictive tool for assessing the performance of polymeric liners and sealing materials, supporting material selection and the design of reliable CCS transport systems.

Method and/or Theory

The materials characterized in this study for the CO₂ sorption and permeations include commercially available elastomeric polymers, such as EPDM, HNBR and FKMs, commonly employed in CCS transport systems.

CO₂ sorption experiments were carried out over the temperature range of 5–45 °C using a fixed-volume, variable-pressure apparatus based on the pressure-decay technique. In each experiment, the polymer sample was placed inside a high-pressure cell connected to a calibrated gas reservoir, which was initially charged to the desired pressure. The amount of CO₂ absorbed by the polymer was determined from the pressure decrease recorded during equilibration, while the corresponding diffusion coefficients were evaluated by fitting the transient sorption curves using Fick's diffusion model [13,14]. On the other hand, CO₂ permeability was conducted using the constant-pressure method (ASTM D3985–17),



employing gas chromatographic (GC) analysis of the permeate stream, in a home-made permeation set-up.

The experimental sorption data were interpreted through thermodynamic models based on the Lattice Fluid (LF) equation of state for rubbery polymers and the Non-Equilibrium Lattice Fluid (NELF) model for glassy materials, both obtained by solving the polymer–penetrant phase equilibrium problem [9–11]). These models accurately describe CO₂ uptake over the range of pressures and temperatures relevant to CCS applications, including cryogenic conditions down to –50 °C and pressures up to 100 bar.

$$\mu_i^{pol}(T, p, \Omega, \rho_{pol}) = \mu_i^{gas}(T, p) \quad (1)$$

Gas transport was subsequently analyzed using the Standard Transport Model (STM), in which permeability is described by coupling penetrant solubility with concentration-dependent diffusivity through the kinetic mobility coefficient and the thermodynamic factor.

The model was validated against the experimental measurements and subsequently employed to predict the effect of pressure, temperature, and penetrant concentration on CO₂ transport properties [13,15].

Decompression damages are, instead, evaluated using a purpose-build autoclave with two borosilicate windows for visual inspection on which elastomers were exposed to liquid CO₂ (58 ± 2 bar) at room temperature and sequentially perform rapid gas decompression (RGD) tests. To properly evaluate the effect of degassing, the samples were left for at least one night to be fully saturated with CO₂ before initiating the degassing process, as suggested by the characteristic times of diffusion obtained from sorption data.

Results

Figure 1 highlights the relationship between CO₂ transport properties and Rapid Gas Decompression (RGD) resistance in elastomeric materials. As shown in Fig. 1a, both EPDM and HNBR exhibit a non-monotonic dependence of CO₂ permeability on temperature. In agreement with the solution–diffusion mechanism, permeability results from the combined contribution of CO₂ solubility and diffusivity, whose relative importance changes with temperature. At temperatures close to ambient, permeability remains nearly constant because the increase in diffusivity compensates for the decrease in solubility. Upon cooling, permeability increases as the higher CO₂ density enhances gas sorption, making solubility the dominant contribution. At the lowest temperatures, however, permeability decreases again as the polymer progressively approaches a glassy state. In this regime, the sharp reduction in diffusivity, associated with the increase in glass transition temperature relative to the test temperature, outweighs the effect of solubility. Although CO₂-induced plasticization gradually lowers the glass transition temperature as gas penetrates the polymer, the downstream side of the specimen remains in the glassy state because of the lower CO₂ concentration, thus controlling the overall permeation process.

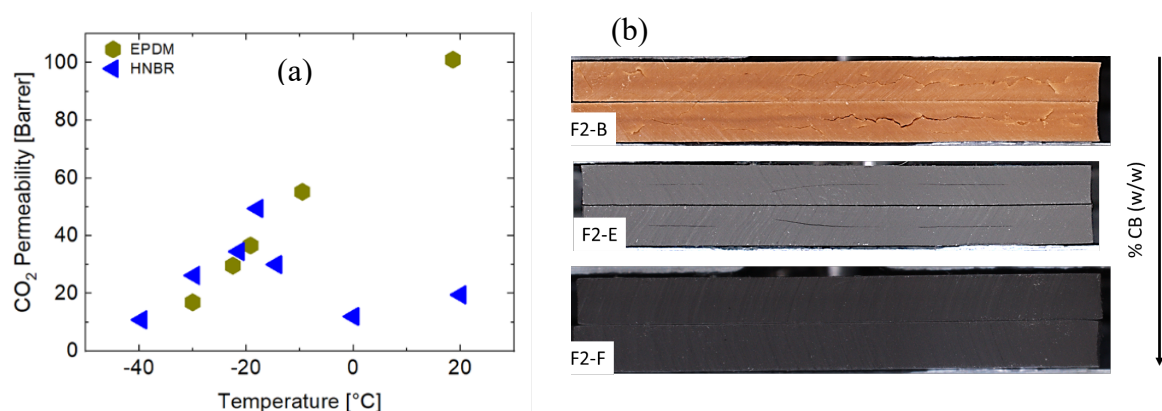


Figure 1 (a) Experimental permeability data (symbols) at 20 bar coupled with Standard transport model (lines) for EPDM and HNBR; (b) Blister formation in FKMs as a function of liquid CO₂ depressurization on different FKMs with increasing content of carbon black.



The influence of transport properties on material durability is reflected in the RGD experiments (Fig. 1b). Carbon black (CB) reinforcement markedly improves decompression resistance by reducing CO₂ uptake, increasing the stiffness of the elastomer, and limiting crack initiation and propagation. As the CB loading increases, blister formation is progressively suppressed and the damage morphology changes from extensive internal cracking to virtually defect-free specimens. These observations confirm that both the CO₂ transport behavior and the elastomer formulation play a key role in determining the reliability of sealing materials operating under dense-phase CO₂ conditions.

Conclusions

This work provides a comprehensive experimental and modeling investigation of CO₂ sorption, transport, and decompression behavior in thermoplastic and elastomeric polymers for CCS transport applications. The combined LF/NELF thermodynamic framework and Standard Transport Model accurately describe CO₂ sorption, swelling, diffusion, and permeability over a wide range of operating conditions, providing a reliable predictive tool for material selection. The results demonstrate that CO₂ transport is governed by the interplay between solubility and diffusivity, leading to non-monotonic permeability trends at low temperatures and highlighting the role of CO₂-induced plasticization in controlling gas transport. For elastomeric seals, RGD resistance is strongly affected by both transport properties and material formulation, with carbon black reinforcement significantly reducing gas uptake, limiting damage evolution, and improving decompression resistance. Overall, this study establishes clear relationships between polymer composition, transport behavior, and durability, providing useful guidelines for the design of reliable liners and sealing materials for dense-phase CO₂ transport.

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References

- [1] A. Raza, R. Gholami, R. Rezaee, V. Rasouli, M. Rabiei, Significant aspects of carbon capture and storage – A review, *Petroleum* 5 (2019) 335–340. <https://doi.org/10.1016/J.PETLM.2018.12.007>.
- [2] L. Ansaloni, B. Alcock, T.A. Peters, Effects of CO₂ on polymeric materials in the CO₂ transport chain: A review, *International Journal of Greenhouse Gas Control* 94 (2020) 102930. <https://doi.org/10.1016/j.ijggc.2019.102930>.
- [3] S.T. Munkejord, M. Hammer, S.W. Løvseth, CO₂ transport: Data and models - A review, *Appl. Energy* 169 (2016) 499–523. <https://doi.org/10.1016/j.apenergy.2016.01.100>.
- [4] B. Schritterser, Characterization of the Rapid Gas Decompression Behavior of HNBR Based Rubber Master Thesis, (2010).
- [5] J. Sonke, W.M. Bos, S.J. Paterson, Materials challenges with CO₂ transport and injection for carbon capture and storage, *International Journal of Greenhouse Gas Control* 114 (2022) 103601. <https://doi.org/10.1016/J.IJGGC.2022.103601>.
- [6] H. Al Baroudi, S. Mori, K. Patchigolla, J.E. Oakey, Qualification of Elastomer Materials for CO₂ Pipeline Systems, 15th Greenhouse Gas Control Technologies Conference 2021, GHGT 2021 (2021). <https://doi.org/10.2139/SSRN.3817590>.
- [7] B. Schritterser, G. Pinter, T. Schwarz, Z. Kadar, T. Nagy, Rapid Gas Decompression Performance of elastomers – A study of influencing testing parameters, *Procedia Structural Integrity* 2 (2016) 1746–1754. <https://doi.org/10.1016/J.PROSTR.2016.06.220>.
- [8] X. Zhang, L. Zhang, Y. Li, C. Zhang, X. Liu, X. Wang, Development of Sealing Materials for CCUS Packers Resistant to Supercritical CO₂ and Analysis of Corrosion Mechanisms, *World CCUS Conference 2025* 2025 (2025) 1–5. <https://doi.org/10.3997/2214-4609.202522028/CITE/REFWORKS>.
- [9] F. Doghieri, G.C. Sarti, Nonequilibrium lattice fluids: A predictive model for the solubility in glassy polymers, *Macromolecules* 29 (1996) 7885–7896. <https://doi.org/10.1021/ma951366c>.



- [10] I.C. Sanchez, R.H. Lacombe, Statistical Thermodynamics of Polymer Solutions, *Macromolecules* 11 (1978) 1145–1156. <https://doi.org/10.1021/ma60066a017>.
- [11] R.H. Lacombe, I.C. Sanchez, Statistical thermodynamics of fluid mixtures, *Journal of Physical Chemistry* 80 (1976) 2568–2580. <https://doi.org/10.1021/j100564a009>.
- [12] M. Minelli, G.C. Sarti, Gas permeability in glassy polymers: A thermodynamic approach, *Fluid Phase Equilib.* 424 (2016) 44–51. <https://doi.org/10.1016/J.FLUID.2015.09.027>.
- [13] V. Signorini, L. Ansaloni, T. Peters, B. Alcock, M.G. Baschetti, M. Minelli, Characterization and Modeling of CO₂ Transport through Fluorinated Thermoplastics, *ACS Appl. Polym. Mater.* (2023). <https://doi.org/10.1021/ACSAPM.3C02056>.
- [14] Crank J., *The Mathematics of Diffusion*, Claredon Press - Oxford University Press, 1975, 2nd Ed. 79 (1957) 1267–1268. <https://doi.org/10.1021/ja01562a072>.
- [15] E. Ghiara, G. Lazzari, V. Signorini, L. Ansaloni, B. Alcock, M. Minelli, Cryo-compressed CO₂ sorption and diffusion in elastomers for the CO₂ transport chain: Examples of FKM, EPDM and HNBR, *Chemical Engineering Journal* 511 (2025) 161826. <https://doi.org/10.1016/J.CEJ.2025.161826>.