

Catching CO₂ with certified thermoplastic polymer materials

The durability, safety and performance of soft-sealing materials is paramount to ensure the leak-free transport and storage of carbon dioxide, especially in extreme environments which may be encountered in carbon capture and storage.

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Background

With the adoption of the EU Green Deal, the Climate Law and proposals supporting energy and climate targets for 2030, carbon capture and storage (CCS) set of technologies are currently identified as a pivotal role in the decarbonization of industrial sectors such as cement or steel plants and power plants, as well as a means to produce low-carbon blue hydrogen. Recent US and EU administration funding announcements show an unprecedented momentum in the number of projects yet to be sanctioned, including an acceleration of R&D investments.

This three-step technology does have an important part in reducing greenhouse gas emissions and achieving world net-zero targets; however, there remains several obstacles to mass and rapid adoption of this key asset. Possible barriers revolve around leakages, safety, and public acceptance.

One of the biggest perceived risks stemming from CCS operation has been the potential for leakages of CO₂ during operations and transportation. However, the estimated values for



CO₂ pipelines failure rates are in the same range of those reported for hydrocarbon pipelines.^[1] From the source to the sequestration of CO₂ on both onshore and offshore depleted oil and gas wells or saline aquifers, it is necessary to transport and transfer CO₂ in a safe and reliable way whether in its gaseous or liquid state.

Long-distance transport of large CO₂ volumes can be done through onshore or subsea pipelines in its gaseous form or via CO₂ carriers when liquified. Pipeline transport of CO₂ through populated areas requires attention be paid to design factors, overpressure protection, and leak detection. On the other

hand, CO₂ transportation by ship has several similarities to liquefied petroleum gas (LPG) transportation by ship.^[2]

To ensure safe transport and storage as well as prevent leakage of CO₂ greenhouse gas from various components in the value chain, e.g., valves, wellheads, compressors, pumps and loading systems, soft sealing materials and their durability are often scrutinized. Established sealing and material companies such as Omniseal Solutions are often asked about assessing the behavior of these sealing materials and their integrity when exposed to 100% CO₂.

Material categories

Soft sealing materials can be split into two sub-categories: elastomers and thermoplastics, with each exhibiting different behaviors because of their intrinsic properties.

According to published technical papers, elastomeric seals can undergo severe degradation, i.e., chemical ageing, swelling, and blistering with "impure CO₂" blends containing SO_x, NO_x, O₂, H₂S and Brine.^[3] CO₂ at high pressure can diffuse and dissolve in elastomeric materials. The initial sorption of CO₂ into elastomers results in swelling, which changes their mechanical and physical properties. The most important effect during the sorption is the reduction in T_g, often called plasticisation. Furthermore, blistering of elastomeric seals is caused by absorption/diffusion of CO₂ at high pressure often creating catastrophic failure when depressurized - called Rapid Gas Depressurisation (RGD) or Explosive Decompression (see Figure 1).

With elastomer seals, it is not always possible to provide a straightforward summary of what makes an elastomer RGD resistant or high performance in CO₂ applications. Rather, it is more practical to rank the elastomeric seals by their relative resistance to RGD.^[3]

For thermoplastic polymer materials, evaluation is a little more straightforward, in which one considers their higher modulus and thus their higher resistance to fracturing or blistering from RGD. This



Fig. 1: Schematic showing the events leading to blistering of polymers when depressurized after being exposed to a high-pressure CO₂ ^[3]

is done to an extent that RGD testing of thermoplastics are not required by oil & gas industry standards such as NORSOK M-710 and ISO 23936-1. However, CO₂ could impact multiple physical properties of thermoplastics (creep resistance, crystallinity, sorption, swelling) that could eventually affect their ability to seal.

Creep and Crystallinity^[4]

At low temperatures and pressure, CO₂ will not have an impact on creep resistance and crystallinity of polymer materials. However, if both are exposed to higher temperatures (approx. 300°C) and pressures (ANSI class 2500 and higher), the CO₂ will have a thermal annealing effect on the material, both improving creep resistance and crystallinity. If only exposed to high temperatures but at ambient pressure, the tensile creep resistance will be improved but without a large impact on crystallinity. Depending on temperature and pressure, the crystallinity for a polymer exposed to supercritical CO₂ will increase considerably. At a temperature of 290°C, the increase will be moderate (10-15%) compared to ambient conditions. However, if exposed to a temperature of 330°C, which is above the melting temperature of a polymer material,

the expected increase is higher (up to 53% increase compared to the as-received polymer).

Polymer materials tend to have an increase in creep in tension over time in ambient temperatures (see Figure 2). When exposed to the above-mentioned conditions, this creep behavior in tension will decrease, as can be seen in Figure 3. In both graphs, M-15 describes regular polymers, while M-111 is a modified polymer. Similar to the change in crystallinity, the biggest impact on the creep

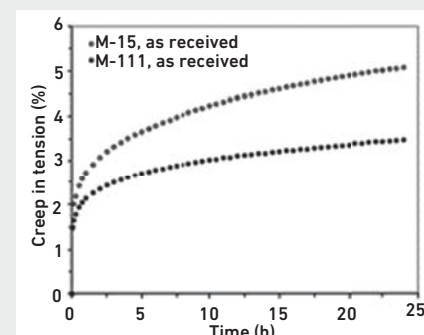


Fig. 2: Evolution of creep in tension (4.83 MPa stress, 23°C) over time, for regular polymer (M-15) and modified polymer (M-111)

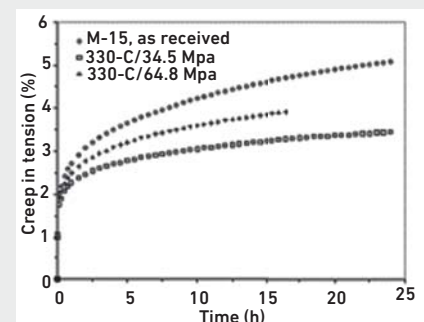


Fig. 3: Evolution of creep in tension (4.83 MPa stress, 23°C) over time, for regular polymer (M-15) before and after 34.5/64.8 MPa CO₂ treatment for 2h at 290°C



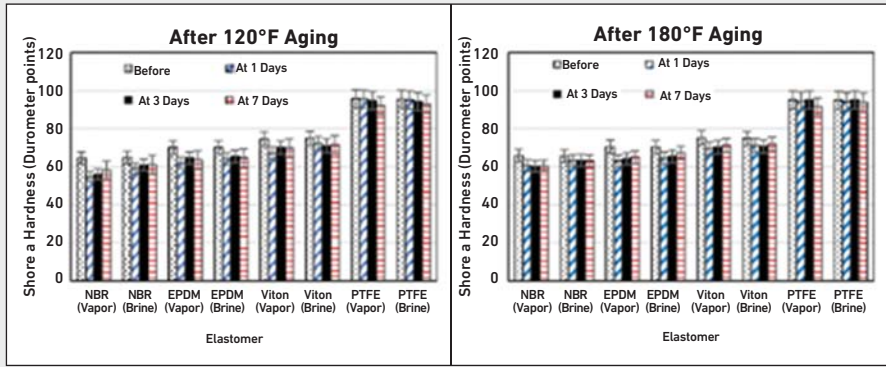


Fig. 4: Impact of aging on the hardness of different elastomers/thermoplastics (left: ageing in 49 °C, and right: ageing in 82 °C)

resistance of the polymer is seen at a temperature of 330°C, while exposed to a high pressure.

Sorption and Swelling^[5]

Essential to the measurement and comparison of sorption and swelling with respect to any fluids in materials is the partial molar volume (PMV). It is the PMV of CO₂ sorbed in the polymer, which will indicate whether the polymer material is submissive to sorption and subsequently swelling, when exposed to CO₂.

Experiments on this topic have shown that the polymer material has significantly large PMV values, after being exposed to CO₂ at temperatures of 40–80°C. The high degree of crystallinity of the polymer material (crystallinity weight fraction = 0.51), induces rigidity in the polymer structure and could explain these large PMV values, since mobility of the solvent molecules is limited; thus, they cannot fully eliminate the voids created during the sorption process. Generally, it can be deduced that the sorption and crystallinity increase along with the pressure

and temperature. However, the PMV values will decrease with increasing pressure but at constant pressure due to increased elasticity.

Diffusion and Permeation^[6]

Experimental tests on the permeation of CO₂ through a polymer over a temperature range of 30–116°C indicate that the CO₂ molecules do not significantly interact with the polymer but move through pre-existing channels and voids. As discussed already in the previous section, the high degree of crystallinity in the polymer material results in a considerable sorption as an effect of CO₂ permeation.

Ageing^[7]

CO₂ in the presence of brine reacts with water to form the weak carbonic acid H₂CO₃, which possibly

influences the performance of the polymer material. CO₂ will therefore also have an impact on the ageing of this material, either in vapor phase or in brine (2% salinity) and through affecting various physical properties such as hardness, tensile strength and strain. The statements discussed below are a result of experiments at a constant high pressure of 6.9 MPa and varying temperatures of 49°C and 82°C.

The hardness of a polymer is defined as the resistance of that polymer surface to indentation by a Shore A durometer. From general observation after several days, polymer hardness tends to drop from its original value, at all temperatures under study. However, this behavior is not observed in a polymer material, both in vapor and brine phase. Furthermore, there is a general increase in hardness irrespective of the temperature, due to chain growth or cross-linkage. It is detected that at a constant temperature, but with increased exposure time, the temperature inside the polymer will steadily increase, subsequently resulting in an increase in hardness and tensile strength (see Figure 4).

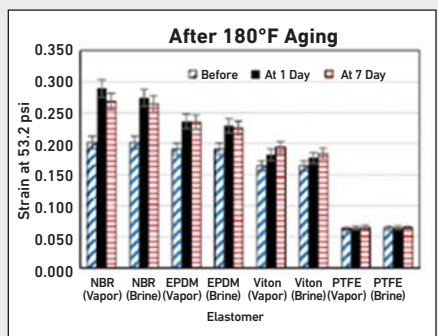
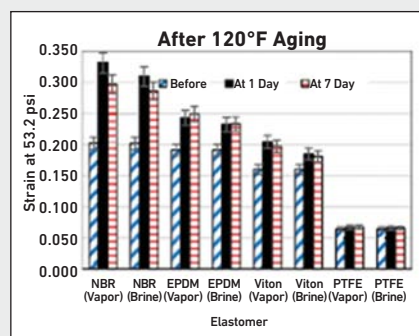


Fig. 5: Impact of aging on the strain of different elastomers in comparison with a polymer material, at a constant temperature (left: ageing in 49 °C, and right: ageing in 82 °C)

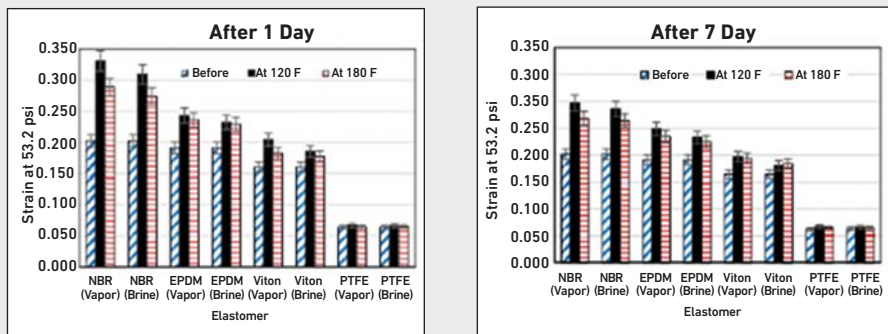


Fig. 6: Impact of ageing on the strain of different elastomers in comparison with a polymer material, with a varying temperature

Compression tests at low pressure (0.37 MPa) show that there is no impact on the strain when the polymer is exposed to CO₂ both in brine and vapor phase, independent of the temperature applied (see Figure 5).

Conclusively, the ageing impact of CO₂ on the physical and chemical degradation of a polymer material is relatively low, in comparison to elastomers, although CO₂ can be seen as the most damaging in comparison to other corrosive gases, such as H₂S and CH₄ (see Figure 6).

To provide a technology advantage to customers, Omniseal Solutions is continuously pushing the boundaries of possibilities of its proprietary thermoplastic

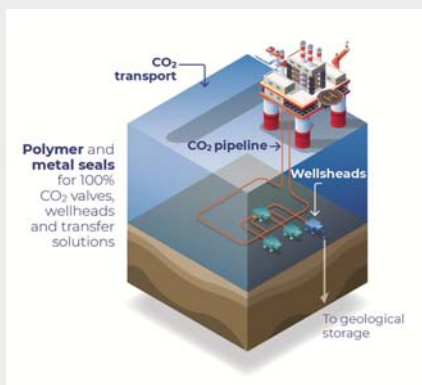


Fig. 7: Omniseal Solutions' polymer & metal seals within CCS value chain

polymer materials to address the needs for reliable and proven sealing solutions in extreme conditions (see Figure 7). In partnership with an Energy major, the Omniseal Solutions' technical team collaborated on a 100% CO₂ certification campaign of several of our proprietary thermoplastic materials that consisted of a bespoke immersion testing in compliance with the pass/fail

criteria of Norsok M-710, Edition 3.

The following are the test conditions (the selected pressure / temperature conditions ensure testing in liquid and supercritical CO₂):

- 100% CO₂
- 34.5 MPa [345 bar / 5000 psi]
- -46°C / RT / 97°C / 127°C
- up to 56 days

According to these test results, every selected material successfully passed the acceptance criteria per Norsok M-710, Edition 3, proving these materials are a better option compared to standard elastomers for sealing applications when exposed to CO₂. All third-party certificates are available upon request.

References

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