



Polymers in Carbon Capture, Utilization, and Storage

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Carbon dioxide has a critical point (31°C, 73.8 bar) that is easily reached experimentally. In its supercritical state, CO₂ possesses solvent-like qualities exacerbated by gas-like diffusivities and liquid-like densities. Its solvation power is easily tunable by altering its temperature and/or pressure. Carbon dioxide can be used as a polymer processing aid due to its appreciable solubility and plasticization effects. It readily diffuses into polymer matrices and expands the free volume between the polymer chains, thus allowing for modification. It has been used in such areas as polymer foaming, polymer particle formation, polymer welding, polymer surface modification (including immobilization of molecules into the surface layer) and polymer/drug solid dispersions. Large-scale polymer foaming can be accomplished by using CO₂ as a blowing agent. The processing conditions dictate the bubble size and distribution, thus the mechanical strength.

Background on CO₂ Interactions with Polymers

Since CO₂ has a relatively high saturation value in polymers, it causes them to swell at high pressure. If pressure is then released quickly, it causes cooling

and foaming. These phenomena may cause permanent damage to polymer pipes, seals, gaskets, and other parts. Damage then leads to insufficient properties and cracking, foaming, leaking, and rupture.

Experimentally, it is easy to adjust the density of CO₂ anywhere from near that of ambient air density up to near that of liquid water. Also, CO₂ can be tuned to be in three distinct phases (gas, liquid, or solid) or its supercritical state. This leads to a plethora of different uses for this simple gas; see Figure 1 for its phase diagram and Figure 2 for a plot of its density at different isotherms. The modified Benedict-Webb-Rubin equation of state¹ was utilized to make a plot of CO₂ density at various isotherms. This equation takes in to account that CO₂ is non-ideal at high pressures. At the lower temperatures on the plot, the transition from gas to liquid (25°C) and from gas to supercritical fluid (31.1°C) can clearly be seen with an increase in pressure due to the drastic increase in the CO₂ density. It is harder to compress CO₂ when it is at higher temperatures due to the increased internal energy, therefore the density is lower at higher temperatures.

The CO₂ solubility in polyolefins varies widely based on which side groups are present and what intermolecular forces are prevalent. Chemically, Polyethylene (PE) is the simplest polyolefin due to having hydrogen

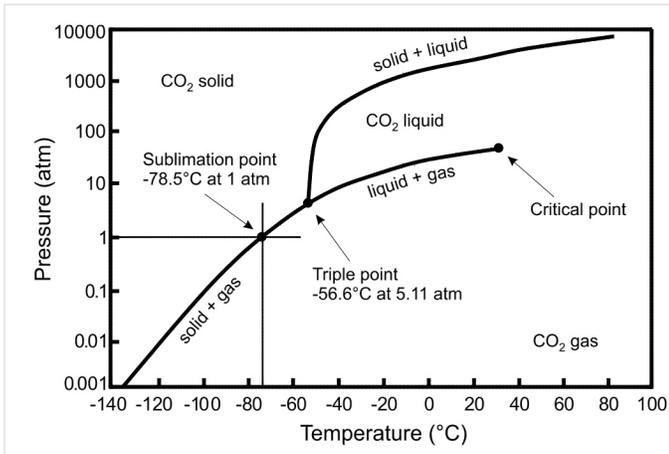


Figure 1. CO₂ phase diagram²

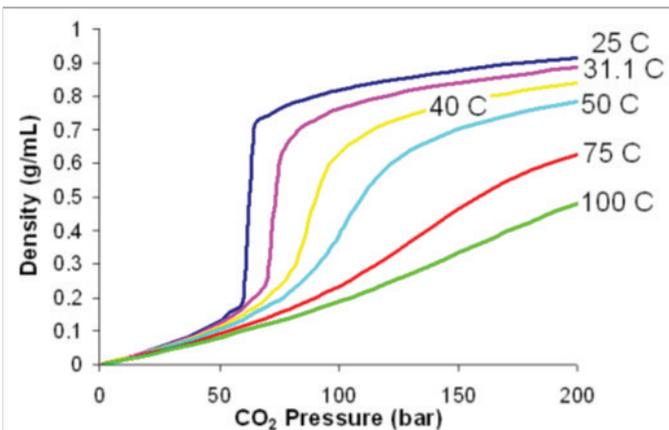


Figure 2. Density versus CO₂ pressure at various isotherms

as its only side group, and it is used prevalently in composite pipeline inner and outer liners. Even though the polymer is simple, there are still many different grades of PE based on molecular weight, branching, cross-linking, density, and crystallinity. A PE with less polymer backbone branching packs more tightly. This leads to higher density and a higher volume fraction of crystallinity. Carbon dioxide has a higher solubility in the amorphous areas of the polymer than it does in the crystalline regions, due to steric hindrance.

Measuring the solubility of CO₂ in polymers can be performed at CCUS service conditions. There are three different types of experiments that can be

used to determine the solubility of gases in polymers: gravimetric, barometric, and frequency modulation. Within the gravimetric and barometric techniques, the measurements can be taken with simple instruments such as a balance or pressure transducer either while the polymer is in an autoclave or following its removal. Some of the other methods require highly specialized equipment like a magnetic suspension microbalance or a quartz crystal microbalance.

Modeling is also accurate in many cases if the polymer can be adequately described. Henry's Law is used for CO₂ gas at temperatures above the polymer's glass transition temperature (T_g). More complicated models, like the Sanchez-Lacombe Equation of State (SLEOS),³ are required if the CO₂ is supercritical. It is based on lattice-fluid theory that assumes that the polymer has a liquid-like (not rigid) structure that contains vacant spots in the lattice (free volume). This model is widely used because a) it allows for mixtures that include molecules with a wide variety of sizes, b) it is simple, c) the terms can be defined by the physical characteristics of the molecules present, and d) it can be accurately extended to high temperature and pressure.

Polymer Use in CCUS?

Recently, flexible composite pipe technologies have gained industry attention for their lower environmental impact, ease of installation, corrosion resistance, lower weight, uncomplicated end-fitting design, and ability to act as stand-alone structural line pipe that can be pulled through existing steel pipelines (for repurposing or rehabilitation). These pipes can also be spooled on reels, smaller drums, or subsea pallets.⁴ The weight advantage allows for use of smaller vessels for conveying and installing long lengths and ease of installation both onshore and offshore. End fittings can be installed onsite without welding. Some pipes have embedded fiber optics

for continuous monitoring, so they have minimal post-installation maintenance requirements.⁵

Polymer pipes often use high density polyethylene (HDPE) or polyphenylene sulfide (PPS) as pipeline liners in high-pressure distribution and transmission infrastructure. Polyamides (PA11 and PA12) and polyvinylidene fluoride (PVDF) are also commonly used as a liner material for composite pipes.⁶ Polytetrafluoroethylene (PTFE) is used for seals in mechanical compressors, and the elastomers Viton A and Nitrile butadiene rubbers (NBR) as seals and gaskets in valves.⁷

Other polymer materials are also used in the transmission of gases. Compressor stations, which require polymeric seals and gaskets, are located approximately every 40 to 70 miles of transmission pipeline. They are used to purify, compress, and cool the gas before its reentry back into the pipeline.⁸ Other polymer applications include diaphragms, O-rings, boots, flanges, gaskets, seals, valve seats, hoses, piston rings. For example, compressor valve plates and poppets valves are commonly made of PTFE or polyetheretherketone (PEEK), sometimes filled with glass or carbon.

Choosing and Testing Materials

Infrastructure materials for the CCUS market are expected to last multiple decades. Understanding how their properties change as they contact CO₂ at a range of different processing conditions is important. Choosing materials that are less affected by high pressure CO₂, and implementing safe operating conditions for those materials is necessary to ensure infrastructure reliability and safety. Initial material selection can be accomplished by taking the operating requirements into account, translating them to material selection criteria, then comparing them against known values for

polymer grades. The known values do not encompass all possible conditions, so long-term stress relaxation or creep, fatigue, or degradation mechanisms need to be better understood. This is where supplemental material information must be added through testing to ensure the reliability of the infrastructure. Testing includes in-situ conditions where CO₂ pressure, temperature and mechanical loading are all applied simultaneously. Other testing includes measuring in-situ swelling to see how materials geometrically change when in service. Finally, soaking materials and then characterizing them for mechanical or chemical degradation will enable understanding the degradation rate and pathway under a range of service conditions.

Why EWI?

EWI has the expertise, experience, and equipment to fully assess polymer materials in contact with gases expected in the CCUS market. A fully commissioned CO₂ lab is equipped with soaking autoclaves, a windowed autoclave, and electro-mechanical test stands with high pressure in-situ capabilities. Furthermore, EWI has polymer characterization equipment in-house to understand the microstructural, mechanical, thermal, and chemical changes that take place due to contact with high pressure CO₂. Testing polymers in service life or accelerated life conditions will allow for higher confidence of materials to perform reliably and safely in the CCUS market for decades to come.

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Note: Any reference to specific equipment and/or materials is for informational purposes only. Any reference made to a specific product does not constitute or imply an endorsement by EWI of the product or its producer or provider.

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