WHITE PAPER

Moisture-Induced Performance Changes in High-Performance Polymers: Challenges and Mitigation

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Abstract

Moisture absorption can be a destructive phenomenon to polymer-based components in oilfield assets, thus there is a need to examine its effect on the integrity and performance of industrial high-performance polymers.

This whitepaper discusses the impact of moisture absorption on polymer components used in the oil and gas industry, outlining the mechanisms by which moisture penetrates and affects these materials. It further examines how moisture absorption affects mechanical properties, increases gas permeability, and induces microcracks. Attention is given to 3D-printed polymeric parts, where manufacturing-induced microstructures can exacerbate moisture diffusion. Strategies for mitigating moisture-related degradation, such as surface protection, optimized printing parameters, and material selection, are also discussed to enhance the durability and performance of polymer components in harsh environments.

Background

Many polymers naturally absorb water, with some superabsorbent types being highly valued for advanced applications in fields like medicine and construction. However, when thermoplastics absorb moisture, it can alter both their processing characteristics and their properties. In the oil and gas industry, storage units, vessels, and transportation pipes operate at high pressures and temperatures. Offshore assets are constantly exposed to high humidity due to seawater. These components are subjected to high-level strain, and often, they are stretched to a point where water ingression may occur. Furthermore, as internal surface areas increase due to the inherent voids, there is an increased risk of material degradation owing to the interaction with saline fluids like seawater (LeBlanc et al., 2023).

Moisture absorption, which can also be referred to as water absorption, is the capacity of a particular material to absorb moisture from its surroundings. Polymers absorb water to an extent and the degree to which they absorb moisture is determined by the type of polymer, the ambient conditions, that is, temperature, humidity, etc., and time of interaction with its environment. The absorbed moisture causes several problems in the material by plasticization and hydrolysis. Other than dimensional alterations, material properties, such as mechanical properties, can be affected by moisture absorption.

High-performance polymers provide several benefits over other materials, such as strength, wear resistance, improved chemical resistance, excellent weight reduction, insulation, and aesthetics. Most of these polymers are produced as composites for improved mechanical performance. The mechanical performance of fibre-reinforced composites relies on the strength and modulus of the fibres, as well as the strength and chemical stability of the matrix. While these factors are crucial, the effectiveness of the bond between the matrix and fibre is key. In essence, the overall performance of composite materials hinges on a strong interface between the two components, thus, the knowledge of material-environment interactions is critical during material design.

Moisture absorption weakens the matrix-reinforcement interface in high-performance polymers, leading to degradation of the bond and reduced mechanical performance. This can result in swelling, microcracking, and compromised structural integrity over time. Polymers with low water absorption levels and low thermal expansion are categorized as dimensionally stable polymers. Conversely, absorbed moisture can sometimes act as a plasticizer, decreasing the glass transition temperature and strength of the material. Although the effect of moisture absorption is often reversed, irreversible effects can happen, which may appear as alterations in tensile strength, elasticity, and impact strength.

Mechanism of Moisture Absorption

In polymers, it is widely known that moisture alters the functional properties. At room temperature and above, water acts as a softening agent, positioning its molecules between micro-level chains. On the other hand, at cryogenic temperatures, wet samples exhibit higher stiffness than dried counterparts (Startsev et al., 2020). Most polymers absorb water at different rates, however, not all of them exhibit property alterations. Studies have shown that property changes occur when water molecules are connected to macromolecules in polymers by hydrogen bonds. In other words, polymer chains with stronger polar groups bind with water through hydrogen bridges. Some of the examples of these polymers are the ketone group (C=O) or the sulphone (O=S=O) polymers. However, there are restrictions; the presence of oxygen atoms on both sides of a ketone group acts as a barrier to hydrogen bond formation. An example is PEEK which contains ketone groups, fitted with oxygen atoms at both ends of the chain (Baschek et al., 1999).

Water is absorbed by the polymer as free and bound water. Free spaces within the polymer chain are filled with free water, which means it does not alter the volume of the material. Contrarily, the formation of new bonds between water molecules and molecular chain of the polymer can make bound water increase the volume of the material. The bound water is also responsible for the reduction in glass transition temperature. When polymers experience prolonged exposure to water and high temperature, free water begins to form hydrogen bonds with the chains of the material, converting into bound water.

In reinforced polymers, such as carbon fibre reinforced polymers (CFRPs), the diffusion process is highly complex once it is driven by mass diffusivity of the individual constituent, that is, the polymer matrix and the reinforcement, volume fraction, and the constitutive orientation and morphology of the reinforcement within the polymer matrix. Due to the combined effect of high operating temperatures and increased humidity associated with offshore assets, components are typically exposed to hygrothermal effects that influence the glass transition temperature of the reinforced polymers, leading to increased internal voids, polymer chain expansion, and the introduction of microcracks in the matrix.

Impact of Moisture Absorption in Polymers

Actions such as stringing, under-extrusion, bubble formation and oozing are major associated effects of the presence of moisture in a filament during 3D printing. If the spool is not dry, one can expect a low print quality and weak components. Furthermore, variation in colour of the filament can also indicate absorbed moisture in the filament.

It is important to note that the impact of prolonged moisture exposure can be irreversible due to water affinity with specific functional groups present in the reinforcements (Brito et al., 2019). In general, as seen in Figure 1, the destructive alterations occur because of potential physiochemical interactions between the polymer matrix and reinforcement, and, consequently, the reinforcement fibre is displaced, leading to delamination of the composite and corresponding decrease in the functional properties of the material. This means that prolonged exposure to moisture can induce microcracks and weaken the bond between the matrix and reinforcement, resulting in delamination and structural failure. Water soluble additives can be extracted from the material due to moisture absorption and lead to loss of material integrity and performance. Therefore, it is essential to predict the moisture content with respect to time because the results obtained from this observation will enable further predictions of most susceptible regions to cracks and deformations capable of reducing the product quality, particularly in warm and humid environments.

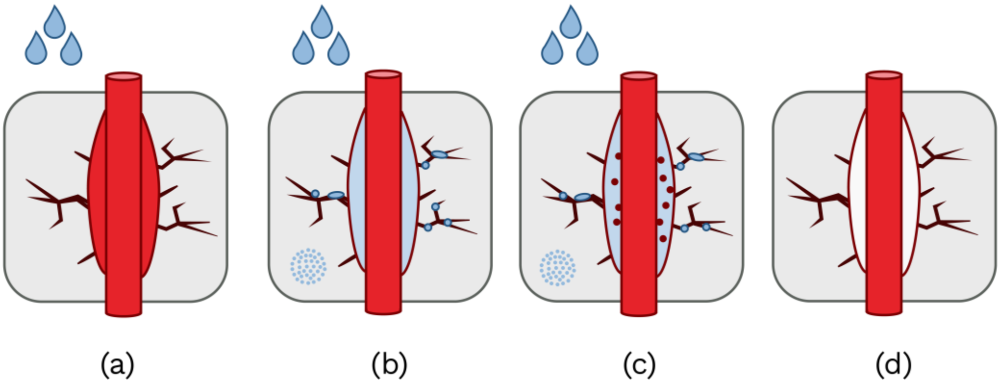

Figure 1: Delamination Process in a Polymer Composite caused by Moisture Absorption

Moreover, polymeric composites used in deep sea assets may experience different effects of moisture due to colder environments. The bound water within the polymeric material remains in its liquid state while occupying localized points in the material because there are no free spaces for phase transformation to occur. At lower temperatures, bound water may appear glassy-like in capillaries, microvoids and pores, causing an increment in internal stresses.

The absorption phenomenon is particularly detrimental to polymeric products. Moisture absorption can lead to increased gas permeability in high-performance polymers, reducing their effectiveness as barriers and potentially allowing the ingress of gases or fluids, which can compromise the integrity of seals, gaskets, and other critical components. The wet material is more permeable to gases. For example, moist PA6 CO_2 permeability is three times greater than dried PA6 (Krzyżak et al., 2013). The nature of plasticity also influences diffusivity. It is observed that elastomers exhibit higher CO_2 permeability than glassy polymers since rubbery polymers show larger diffusivity for non-condensable gas, which is based on their increased chain flexibility.

Moisture Absorption Levels of High-performance Polymers

As mentioned earlier, the amount of moisture absorbed is determined by the type of polymer, ambient conditions (such as temperature, humidity, and contact time), and any additives incorporated. For instance, nylon (PA) and polybenzimidazole (PBI) can absorb several proportions of their actual weight, while materials like polyetheretherketone (PEEK) and

Polyvinylidene Fluoride (PVDF) will absorb much less. Unfilled nylon can absorb up to 4% of its weight in normal conditions and up to 8% in high humidity, while polypropylene absorbs less than 0.01% submerged in water for 24 hours. Polytetrafluoroethylene (PTFE) has the least water absorption. Table 1 shows a comparison of water absorption levels in common high-performance polymers used in the oil and gas industry. Although moisture absorbed from the environment is not a huge concern, when moisture absorption reaches more than 1% or 2%+, this can result in significant dimensional changes to create concerns.

Table 1 – Water Absorption of Common Polymers Used in the Oil and Gas Industry (AIP Precision Machining)

Common Polymers	Min %	Max %
ABS – Acrylonitrile butadiene styrene	0.05	1.8
PA – Nylon Polyamide, 66 30% Glass Fibre	0.8	1.1
PAI – Polyamide-Imides (TORLON)	0.1	0.3
PBI – Polybenzimidazole (CELAZOLE)	0.4	5
PC – Polycarbonate, high heat	0.1	0.2
PE – Polyethylene, 30% glass fibre	0.02	0.06
PEEK – Polyetheretherketone	0.1	0.5
PEI – Polyetherimide (ULTEM)	0.2	0.3
PP – Polypropylene	0.01	0.1
PSU – Polysulfone	0.2	0.8
PTFE – Polytetrafluorethylene	0.005	0.015
PVC – Polyvinyl chloride, rigid	0.04	0.4
PVDF – Polyvinylidene fluoride (KYNAR)	0.03	0.05

Moisture Absorption in Additively Manufactured Parts

The effect of moisture absorption on additively manufactured components may yield severe implications based on the associated features of AM parts such as high porosity and partial bonded interfaces between subsequent layers. Various studies have reported that the tensile strength of additively manufactured ABS immersed in water reduced by approximately 30% (Kim et al., 2016). A 3D printed part made with PLA disintegrated after 60 days immersed in water (Kakanuru & Pochiraju, 2020). Furthermore, significant warping induced by moisture was observed in 3D printed continuous carbon fibre-reinforced nylon after conditioning the part in moisture (Kikuchi et al., 2020).

The rate of water absorption may be rapid at elevated temperatures, but the maximum amount absorbed reduces as temperature increases. Water diffusion through 3D printed parts may be more complex due to the resulting microstructure created during manufacturing, which includes multiple partially bonded interfaces. The impact of this intrinsic microstructure on diffusion rates has not yet been fully recognized, but it is critical for accurately predicting the rate at which parts absorb moisture until reaching equilibrium.

Conclusion – Keeping the Layers Dry

Exposure of polymeric parts used in oilfield assets to adverse environmental conditions can result in significant alterations in mechanical properties that include strength, stiffness, and ductility. One of the most typical destructive environmental agents is moisture. Polymer matrix composites characterized by continuous or short-fibred reinforcements incorporated in a polymer matrix can be subjected to different forms of degradation, especially when exposed to moisture and elevated temperatures. Moisture absorption in high-performance polymers at ambient and high temperatures occur at different rates, resulting in mechanical and thermomechanical changes. The extent to which a material may absorb moisture depends on the matrix and reinforcement material, the surrounding temperature, humidity, and the length of time the material is exposed to the adverse environment.

Significant reduction and mitigation of water absorption in 3D printed polymeric parts can be achieved in some ways: Firstly, hydrophobic coatings such as moisture-resistant coatings can be applied to provide protective barriers, reducing water ingress during service. Secondly, moisture absorption in additively manufactured parts can be reduced by optimizing printing parameters, such as nozzle diameter and printing speed, to minimize porosity and manufacture denser components, preventing moisture ingress. Thirdly, polymeric spools can be subjected to drying using temperature-sensitive dryers to extract inherent moisture from the material before printing. Another solution is adopting an effective material selection process. The use of polymers with lower water absorption rates, such as PEEK or high-performance polymers with ordered carbon or glass fibres, can inherently mitigate moisture penetration. Lastly, post-processing techniques, like annealing, can enhance surface integrity and reduce the volume of microvoids and partially bonded interfaces where moisture can accumulate.

To address the challenges of moisture absorption in producing 3D-printed high-performance non-metallic components, RusselSmith has implemented strategic measures, including a combination of pre-printing drying processes, custom printing parameters, and post-processing techniques, ensuring sustainable and durable end products.

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