Thesis:

Study on accelerated exposure testing and thermal insulation for a Glass Fibre Reinforced Polymer in simulated Oil & Gas environment

Abstract

Polymer Matrix Composites (PMCs) are becoming widespread in the Oil & Gas industry. Their outstanding mechanical properties, along with their improved resistance to the corrosion compared to metals makes them a suitable candidate to overcome the physical limitations of traditional structural alloys, in particular for production pipelines and submerged structures in the offshore extraction of fossil fuels.

Oil & Gas industry is interested in employing PMCs as the structural material to make the exploitation of eXtreme High-Pressure High-Temperature (XHPHT) offshore reservoirs viable. There is not a single definition for XHPHT, but it refers to scenarios where materials will experience temperatures up to 200 °C and pressures reaching 140 MPa. These are very demanding conditions for polymer composite materials. These materials are expected to survive 25+ years in a harsh operative environment. PMCs are known to be affected by the seawater as the permeable polymer matrix undergoes plasticisation. Other ageing phenomena can be caused by the biological activity in the marine environment (biofouling), as well as chemical degradation due to the presence of CO₂ and H₂S in so-called "sour" reservoir or to the production chemical additives for boosting the *Enhanced Oil Recovery* (EOR). There is limited experience with composite materials in such specific applications, in particular for long term exposures. It is pivotal to gain enough understanding of how the material will age to judge if it is fit for purpose and economically sound. For most of the PMC composites, there is not enough confidence in how they would endure in those particular environments.

In this project, the focus was on mapping the evolution of the physical and mechanical properties of a Glass Fibre Reinforced Polymer (GFRP) composite, in relation to the progress of the absorption of fluids. The performance of the material was monitored while it was exposed to a basic simulated offshore Oil & Gas environment. The aim was to characterise how the properties of the materials evolve due to the fluid permeation at different temperatures, to evaluate the accelerated ageing effect. An extensive parallel testing campaign was carried out on both the epoxy matrix and the GFRP composite separately at increasing ageing stages. Gravimetric measurements were performed to calculate the diffusion coefficients when the composite is exposed to the seawater and an aromatic hydrocarbon mixture, to simulate production fluids. At the same time, Dynamic Mechanical Analysis (DMA) was used to measure the shift in the Glass Transition temperature.

Using an Arrhenius plot, the exponential relation between the seawater diffusivity coefficient and the exposure temperature was verified and the diffusivity coefficient values for the materials at a temperature of 4 °C, typical of offshore operative scenarios, were estimated at 0.23 and 0.05×10^{-13} m²/s for the neat epoxy matrix and the GFRP composite, respectively.

To monitor the evolution of mechanical performance, tensile tests on progressively aged material were performed. The materials appeared less prone to absorb the oil mixture and the effect on the mechanical performance on the epoxy matrix was limited. From the seawater exposure results, instead, it was possible to linearly correlate the loss in the GFRP tensile strength with the weight fraction of water absorbed. Time-Shift Factors were calculated with partial success, in order to estimate the accelerating effect of the higher temperature exposures on performance degradation.

Improved thermal insulation is beneficial towards the flow assurance of hot fossil fuel in offshore pipelines. Polymer foams are known for their low thermal conductivity which is related to their apparent density. The foam density is controlled during the foaming process, depending on the technology employed: usually, these foams are less dense than water. The possibility of adding a buoyant core to a pipeline structure, made by the polymer foam, would significantly reduce the structural loads at the top section due to the weight of the structure, thanks to the hydrostatic thrust.

By means of a *Chemical Foaming Agent* (CFA), an epoxy foam was successfully synthesised and tested for its mechanical properties, thermal conductivity and stability. An apparent density of 0.4 g/cm^3 and conductivity of $0.06 \div 0.07 \text{ W/(m \cdot K)}$ were obtained which are competitive with other commercial insulation systems A composite sandwich was prepared to evaluate its adhesion to a GFRP substrate. In this configuration, it can be used as thermal insulation for offshore composite pipes.