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Degradation pathways of amine-cured epoxy novolac and bisphenol F resins under conditions of high pressures and high temperatures

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Abstract

Significance of the study:

The ever-rising energy demands are driving the petroleum industry to explore fossil fuels from geologic formations that show conditions of abnormal high pressures and high temperatures, universally known as HPHT conditions [1]. Conditions of HPHT in the downhole oilfield applications are of major concern because of the high demands of the materials involved, and the presence of seawater in the pipeline liquids makes corrosion a pervasive issue across the industry. Furthermore, the HPHT fields encompassing a gas phase, a hydrocarbon phase, and a seawater phase, combined with high temperature and high-pressure conditions, can result in extensive coating degradation and defects. In general, this extremity of the HPHT zone tends to accelerate the material degradation processes, forcing early and costly replacements. For this reason, process equipment, wells, tanks, and pipelines in the HPHT zones are often protected with high-performance epoxy-based anti-corrosive coatings.

However, the durability and/or degradability of these highly cross-linked coating systems under the HPHT conditions (including the gases such as N₂ and CO₂, combined with a mixture of hydrocarbon fluids and artificial seawater) are rarely reported in the open literature and the underlying mechanisms remain largely unexplored. Furthermore, Rapid Gas Decompression (RGD), i.e., when depressurization to ambient conditions takes place during emergency shutdowns, can also lead to failures (e.g., crack initiation and growth in cross-linked networks) caused by the fast release of HPHT phases dissolved in the coating. Consequently, in the present study, the largely unexplored degradation pathways for amine-cured epoxy novolac (EN) and bisphenol F (BPF) epoxy resins at HPHT are investigated under lower limits of HPHT.

Strategy of the investigation:

The present work has two aims. Firstly, to understand the degradation behavior of an amine-cured epoxy novolac (EN) and an amine-cured bisphenol F (BPF) epoxy coating under conditions of HPHT. Secondly, to assess the interaction of the three HPHT phases with the two coating networks. The formulations considered are epoxy-based coatings, consisting only of a resin (base) and a curing agent. In particular, the exclusion of pigments, fillers, and additives allows a more accurate description and interpretation of the resin degradation pathways. Furthermore, when developing a coating formulation, the resin system is the

principal ingredient. This study is the first step towards developing an efficient and high-performing epoxy formulation for HPHT conditions, keeping in mind the wide variety of chemical reactions that can be used for the curing of epoxy resins.

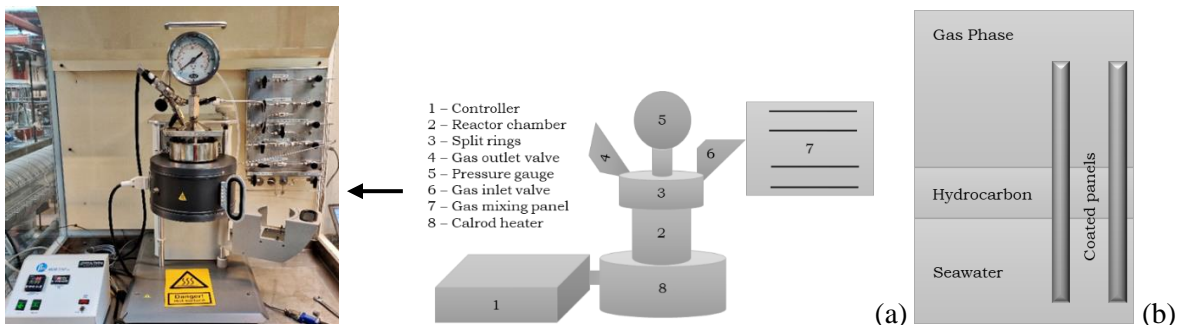


Fig. 1. (a) Schematic illustration (with photo) of the HPHT reactor and (b) coated panels positioned inside the pressure chamber [after 2].

The HPHT conditions were simulated in a batch-like reactor (Fig. 1) encompassing the three major phases viz. a gas phase comprising a mixture of nitrogen (N_2) and carbon dioxide (CO_2), para-xylene (PX) representing the hydrocarbon phase, and 3.5wt% NaCl solution as the seawater phase at high pressures (130 bars) and high temperatures (180 °C). Using a DEN 438 epoxy novolac resin (functionality, $f = 3.6$) as the base and a mixture of DEAPA adduct and MXDA adduct amine hardeners as curing agents, an epoxy novolac (EN) coating was formulated. Similarly, using EPON 862 ($f = 2.1$) as the base and Amicure PACM cycloaliphatic amine as the hardener, a Bisphenol F (BPF) coating was prepared. For both EN and BPF, the functional group stoichiometric ratio as well as the curing conditions, were selected to agree with the commercial grade formulations available for HPHT applications.

Major findings and results:

After the HPHT exposure, SEM analysis figured the changes in surface topography and cross-section of the coating networks. EDX analysis determined the elemental composition at the exposed surface, and cross-sectional line mapping analyzed the depth of penetration of HPHT components into the coating network. FTIR confirmed the chemical modifications of the curing agents and analyzed the chemical changes in the crosslinking before and after HPHT exposures. Lastly, the DSC measurements estimated the change in glass transition temperature, supporting the overall coating degradation pathways for EN and BPF.

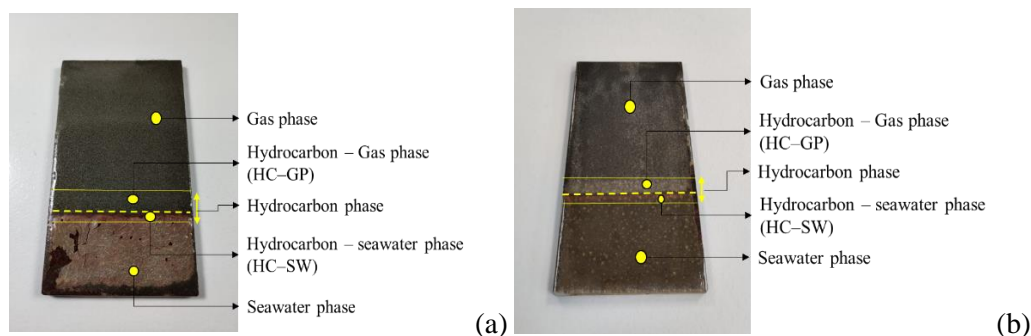


Figure 2: Non magnified photographs of (a) BPF, and (b) EN coatings after HPHT exposure showing the three resultant zones: GP–gas phase zone, the hydrocarbon exposed zone showing two subzones HC-GP (hydrocarbon-gas phase) and HC-SW (hydrocarbon-seawater interface), and SW–seawater exposed zone [after 2].

Each of the three HPHT phases interacts differently with the coating networks. The gas-phase exposed zone remained predominantly intact for both EN and BPF after exposure to the HPHT environment. Thus, the high-pressure N_2 and CO_2 had no detrimental effects on the networks. However, para-xylene uptake resulted in a free volume increase i.e., a significant lowering of the glass transition temperature (T_g).

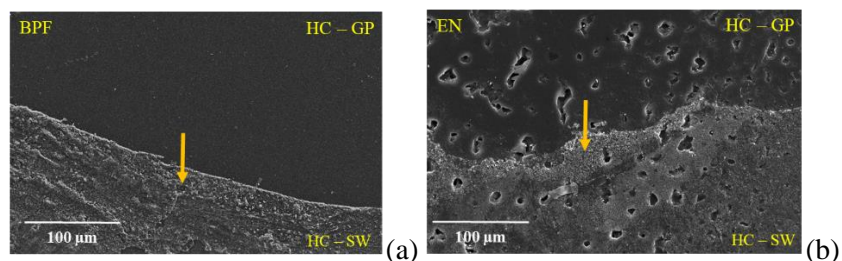


Figure 3: The underfilm corrosion that led to deposition of red-colored iron oxide is observed for both EN and BPF on the surface of HC-SW zone after HPHT exposure [after 2].

This softening phenomenon enhanced the resin chain mobility at the hydrocarbon-seawater interphase, allowing higher diffusion rates of seawater and CO_2 gas to the steel-coating interface with clear signs of coating degradation. The synergistic action of seawater and CO_2 at the steel-coating interface triggered an underfilm-corrosion resulting in iron oxide precipitates. Furthermore, simulation of Rapid Gas Decompression (RGD) uncovered the role of RGD in the iron oxide formation process for both EN and BPF coatings. Lastly, the seawater phase induced small blisters in the EN coating, whereas for BPF, a complete loss of adhesion between the coating and the substrate was observed. FTIR analysis highlighted that physical degradation of coatings is dominant over chemical degradation under conditions of HPHT. Each of the three phase interactions, effects of high temperature and high-pressure, and the transport phenomena of HPHT components through EN and BPF networks will be discussed in detail. It is well

known that the high aromaticity of epoxy-based networks often provides the characteristic thermal stability and barrier resistance. However, the present study highlighted that HPHT conditions with aromatic hydrocarbons as one of its phases proved detrimental for EN and BPF resin networks.

Brief summary and conclusions:

A closed batch-like reactor (autoclave) was used to simulate high pressure and high temperature (HPHT) conditions, and assess the degradation pathways for EN and BPF amine-cured anticorrosive coatings. The gas-phase-exposed zone remained unaffected for EN and BPF networks. Para-xylene interactions at HPHT led to increased chain motion that served as the initiation point for the CO₂ and seawater permeation into the EN and BPF networks. As a result, anodically dissolved iron from the steel-coating interface solidified as iron oxides at the HC–SW exposed surface. Minimal yet sufficient water uptake, generating blisters and macro pinholes in the case of EN, was observed in the seawater-exposed zone. On the other hand, water molecules permeated to the steel-coating interface in the BPF network, resulting in an almost complete loss of adhesion under HPHT conditions. In summary, the present findings promote a need to formulate superior epoxy-based anti-corrosion coatings for a spectrum of downhole oilfield applications. Moreover, the current research findings keep the potential to assist the most anticipated CO₂-resistant coatings designed for the next-generation Carbon Capture and Storage (CCS) domain.

References:

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