



Measurement of Adhesion Strength of Methane Hydrates to Wall



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Abstract

One of main risks in natural gas transport is formation of hydrate deposits in pipelines and sealines. In order to mitigate this problem, a possible solution could be to apply an appropriate inner coating, avoiding adhesion of hydrate particles to the pipe wall. With this purpose, different commercial coatings were characterized with traditional laboratory methods (roughness, water contact angle and diiodomethane contact angle) and performed adhesion force test with model hydrates (THF hydrates) at atmospheric pressure. Nevertheless, such measurement conditions are far from the real field conditions. Therefore, in order to assess the technology, a new experimental tool was developed to perform adhesion stress measurements on hydrocarbon hydrates under more representative operating conditions. The results of these measurements clearly show that the tests carried out with model systems at room pressure may provide misleading outcomes.

Keywords: Methane hydrate; Adhesion; Flow assurance; Coating

Introduction

Clathrate hydrates, or gas hydrates, are water-based solids physically resembling ice. Excellent review monographs on the subject are available [1,2]. The formation of hydrates in oil and/or gas transport system in presence of water, operating at sufficiently low temperatures and high pressures, can lead to complete obstructions. Therefore, especially for subsea development, it is necessary to provide for storage, transportation and injection of additives to prevent hydrate formation.

In order to avoid the massive injection of chemicals, an appropriate internal coating could counteract adhesion of hydrate particles to the inner wall of pipe. While a large literature exists on the preparation and characterization of coated surfaces, very little / ambiguous information is available in the literature about hydrates adhesion is concerned. For this reason, different coatings were selected to investigate their ability to mitigate hydrate adhesion [3].

To assess the coatings performances two different tests were performed and compared:

- A. an adhesion test with a model hydrate (water + THF)
- B. an adhesion test with natural gas hydrates under representative conditions.

Materials

Experimental activity was focused on four different commercial coatings; their selection was based on data sheet provided by the manufacturers. Selected coatings belong to two types of polymers: Poly Tetra Fluoro Ethylene (PTFE) and Fluorinated Ethylene Propylene (FEP). In addition, a reference carbon steel substrate was investigated, in order to compare the results with respects to a bare material. Selected Polymeric Coatings are produced by two different manufacturers, hereinafter referred to as "A" and "B". Two A coatings and two B coatings were examined. Their color code make reference to the composition (Black and blue ones are PTFE based, while green ones are FEP based).

Materials Characterization

A preliminary surface characterization was carried out in terms of roughness and water and diiodomethane contact angle. These data was collected to investigate the possible correlation with the adhesion performances.

Surface average roughness

Measurement of roughness was performed by an optical 3D Microscope (Alicona Infinite Focus, Alicona Imaging GmbH, Raaba/Graz, Austria). This device combines the low depth of

field of an optical microscope with vertical scanning, traversing across the surface of the sample, to provide high resolution and high depth of field topographical images with a large field of view. Vertical resolution and lateral resolution are 10nm and 400nm, respectively.

Contact angle

Hydrophobicity and oleophobicity of the surfaces were evaluated by means of the demineralized water contact angle (WCA) and Diiodomethane contact angle (DCA), respectively. Sessile drops for measurement were positioned on surfaces by means of a micro pipette (max. 20µl) and images of drops were taken by means of Nikon D90 equipped with macro objective (Nikon DX AF-S NIKKOR 18-105mm 1:3.5- 5.6G ED). Sample were positioned on a horizontal support. Collected pictures have been analyzed by means of the software Image J version 1.4.3.67 with a dedicated plug in: "Contact Angle version 0.2.0" levelled surface.

Adhesion Test on Thf-Based System

Room temperature adhesion measurements have been performed with a tool derived from the work of Smith et al. 3 After hydrate formation, a dynamometer (Sauter FK 100max 100N, precision 0,5%FSR), installed on a slide, pushed the cuvette to detach the hydrate from the substrate and record the peak force reached during the operation.

Adhesion Test on Methane Hydrate

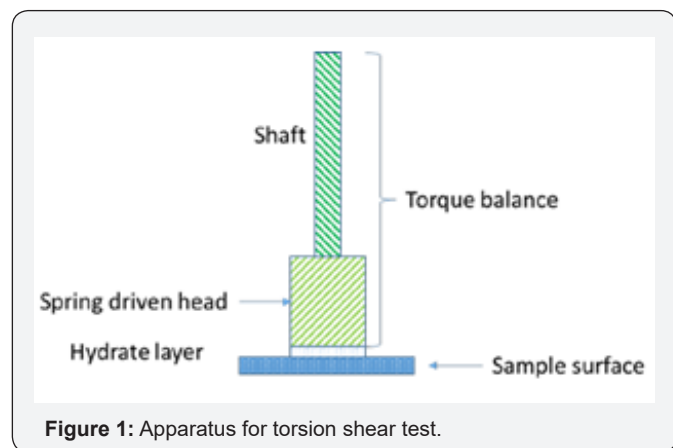


Figure 1: Apparatus for torsion shear test.

A new system for methane hydrate adhesion measurements at representative conditions was designed and built based on the principle of a torsion shear test 21. The apparatus, schematically described in Figure 1, is set up inside an autoclave to allow the formation of a methane hydrate adhesive layer between a fixed plate (sample surface) and the spring-driven head of the torque balance. As the hydrate is formed the shaft is rotated and the angular position of the shaft at the hydrate detachment is recorded. This value gives a quantification of the force needed to remove the hydrate from the surface. The comparison of measured values gives a rank of the materials with respect to

hydrate adhesion. To avoid spurious hydrate detachment from the balance, the head surface was toothed to maximize adhesion.

The autoclave has been equipped with instruments and devices that allows to:

- control the temperature imposed to the sample;
- observe and acquire the methane hydrate formation on the sample by a video-endoscope located close the sample area;
- Observe and acquire the measurements of the rotation during the torsion shear test by a video-endoscope located close the measurement area.
- The value of shear stress is derived by means of the following equation

Where T_{mmmm} is the maximum tangential shear stress, M is the measured torque, D_e the external diameter (25mm) of the annulus and D_i the inner diameter (20mm) of the annulus.

Result

Surface characterizations

Surfaces were characterized by means of surface average roughness, water contact angle and diiodomethane contact angle (Table 1). Obtained values of roughness can be similar. Only two samples are slightly different: A-green and B-black. In particular A-Green shows a sponge-like surface morphology and a S_a roughness slightly greater.

Table 1: S_a roughness. In the bracket the ranking of roughness starting from high value.

Surface	Mean [µm]	RMS [µm]	RE [%]
Carbon steel (reference)	2,23	0,056	2,49
A-Blue (5)	2,09	0,001	0,04
A-Green (1)	3,25	0,106	3,26
B-Black (2)	2,87	0,017	0,59
B-Green (4)	2,13	0,004	0,19

Interfaces interactions between coated surfaces and polar and non-polar liquids were assessed, respectively, by means of water contact angle (WCA) and Diiodomethane contact angle (DCA) measured with sessile drop method. Measured contact angles are in good agreement with literature. No significant deviation from typical values was found for PTFE based coating, and only a small underestimate was found for

THF hydrates adhesion tests

Adhesion tests on THF system were repeated on each surfaces 5 times. The carbon steel case and B samples cases were not reported because not all hydrates was detached from the coating and because of the over-range measured with the instrument.

Methane hydrates adhesion tests

Adhesion test on methane hydrate, performed in auto-claves with the torque balance, were repeated 3 times for each material.

Table 2: Shear stress measured on hydrate THF adhesion test and on methane hydrate adhesion test.

Shear Stress [Kpa]	Carbon Steel	A Green FEP	A Blue PTFE	B Black PTFE	B Green FEP
THF hydrate detachment	289	19	97	181 (*)	89 (*)
High-pressure apparatus	> 130	22	18	6	38

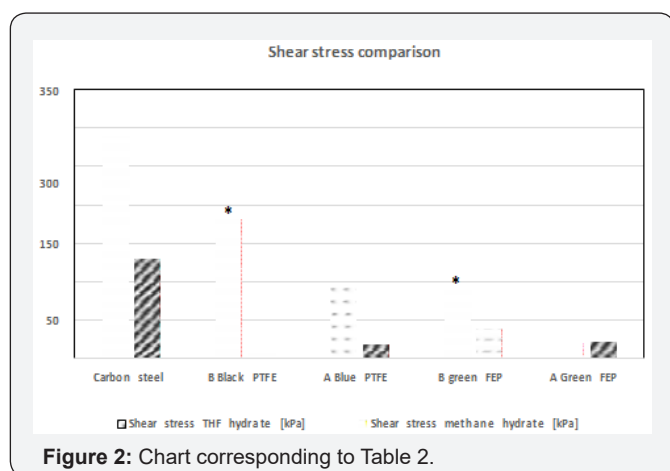


Figure 2: Chart corresponding to Table 2.

Conclusion

Tests were performed to investigate the capability of different commercial polymeric coatings to reduce the adhesion

Total detachment of the hydrate was also verified. Shear stress was calculated by means of eq.1. A comparison of results obtained by the two different methods are reported in Table 2 (Figure 2).

of methane hydrate on the inner surface of pipelines. In order to reach this goal a new test system was designed and built to measure the adhesion force of a hydrocarbon hydrates at high pressure.

The results were compared with adhesion tests performed on a THF model system, showing that the latter can underestimate the performance of coatings with respect to the results achieved under more representative conditions and also lead to inaccurate rankings.

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