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SYNTACTIC AND COMPOSITE FOAMS

Comprehensive analyses of syntactic foam behaviour in deepwater environment

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Abstract Over the past 10 years, numerous studies were performed to better understand the behaviour of the glass syntactic foams used as thermal insulation of pipes for deepwater production. The obtained results outlined some specific behaviour of polymeric syntactic foams reinforced by glass microballoons in service conditions: both water uptake and mechanical stress have a key impact on thermal properties. This article focuses first on the wet behaviour of glass syntactic foams. The effect of water is investigated to better model the nature of water diffusing in syntactic foams with and without a topcoat protection. Secondly, the effect of hydrostatic pressure on coated structure is addressed by using a confined compression test. As polymer material is bonded to the steel surface, it is not submitted to pure hydrostatic loading but to non-spherical loading in the vicinity of the pipe. The confined compression test is then chosen to represent these non-spherical loadings of material. The rupture of glass microballoons is monitored by acoustic emission for different matrices and attempts are made to quantify the resulting acoustic emission signals by comparison with prior tomography results. These experimental analyses provide a better understanding of the main factors affecting the functional properties of syntactic foams.

Introduction

Over the past ten years, numerous studies were performed to better understand and discuss degradation mechanisms of syntactic foams due to combined effects of pressure, temperature gradient, and water ingress [1–4].

Nevertheless, many of the studies were conducted on small samples of material, often for convenience aspects. Some of them revealed some specific behaviours of syntactic foams, for instance, the effect of the nature of water (sea water or natural water) [5] or the detrimental effect of combined solicitations (for example, the combination of pressure loadings under temperature and water environment) [6].

All these results outlined the need to have full-scale thermal testing protocols and facilities to study the behaviour of thermal insulation coating systems on lengths of pipes under simulated service conditions. Some experimental facilities were developed to directly measure thermal properties [7]. More recently, some full-scale prototype tests were modelled to address their global long-term behaviour. These tests took into account the water ingress and the highly non-linear ageing behaviour of syntactic foams [8].

Nevertheless, some behaviours need to be more accurately understood to better describe and then model these systems. This article will investigate two of these particular behaviours of syntactic foams: the first part addresses the behaviour of syntactic foams when aged in different environments and the second part investigates the foams' response under non-isotropic mechanical conditions.

Context

Increasing demand for oil and optimistic estimation of reserves in deepwater sustain the development of offshore

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deepwater fields. Above \$80/barrel, there would be an economical interest to produce oil in difficult conditions (for example, shale oil, harsh offshore environment) [9]. For these reasons, the ultra deepwater (3000 m water depth) is becoming one of the next issues.

The production of oil in ultra deepwater faces lots of challenges. Amongst others is flow assurance which requires the use of thermally managed systems [10]. Due to multiphase flow in flowlines and risers, and consequently possible wax and hydrates formation, thermal insulation of subsea pipelines has become increasingly important. This thermal insulation is used to maintain fluid temperature from subsea completion to floating platforms above a given temperature, around 40 °C, to facilitate the flow.

One of the first approaches was to place insulation materials in the annulus of pipe-in-pipe systems, but these systems are expensive and heavy to install. Alternative systems were therefore developed based on steel pipe surrounded by insulation materials without external steel pipe. In this case, the insulation, mainly based on polymeric material, must withstand the high pressure, water ingress, and high internal and low external temperatures.

Several technologies were developed:

- independent modules placed around the steel pipe (Fig. 1); the syntactic foam is then in contact with water on all its surface: on the one hand, cold water on the outer surface and on the other hand, hot water near the steel surface. This system was used amongst others for the development of Girasol field [11].
- multilayer coatings including syntactic foam layer for insulation (Fig. 2). In this case, only the external surface of the system is in contact with water. This solution was used, for example, for the insulation of Bonga production steel catenary riser [12].

Each of these technologies has pros and cons. Some are easier to manufacture (modules), others easier to manipulate (coated pipes). The ageing conditions are different in terms of temperature and environment. These different points outlined the need for characterisation of the behaviour of the materials.

Fig. 1 Insulation modules system (CRP doc)

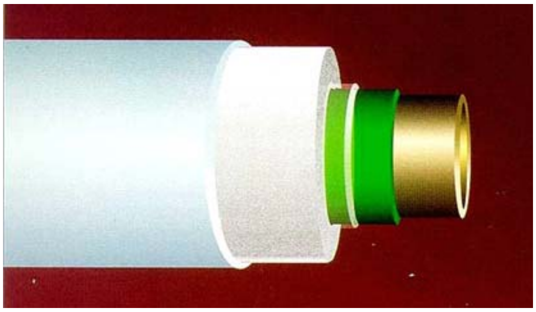

Fig. 2 Five-layer insulation system (Socotherm)

Experimental

Materials

The effect of ageing environment has been studied on a commercial syntactic foam whose matrix is an epoxy-hardened by an anhydride curing agent. This resin has been reinforced with sodium-borosilicate glass micro-balloons with a density of 0.38 g/cm^3 and a 55% volume fraction. Some pure epoxy/anhydride resin samples have also been manufactured in the laboratory.

The effect of a topcoat on the ageing of the foam has been studied on epoxy syntactic foam samples embedded in pure resin (Fig. 3). To reduce the amount of water ingress into the foam, the chosen pure resin has a formulation with well-known properties and, in particular, low water ingress. This resin consisted of a mixture of difunctional epoxy resin (diglycidyl ether of bisphenol A—DGEBA) and an amine hardener (4,4′-methylenebis(3-chloro-2,6-diethylaniline—MCDEA) at stoichiometric ratio. This formulation has been chosen because its satisfactory ageing characteristics and especially the diffusion coefficients of water are well known. The thickness of the epoxy coat was around 2 mm (Fig. 3).

The mechanical testing was conducted on foams with different matrices: polypropylene (PP), polyurethane (PU) and epoxy (EP). The three foams were filled with glass micro-balloons of same density 0.38 g/cm^3. The samples were machined into a cylinder with dimensions of 10 mm diameter and 10 mm height (Fig. 4).

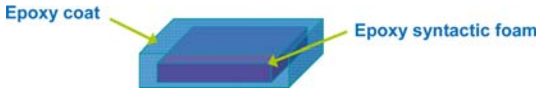

Fig. 3 Bi-layer samples

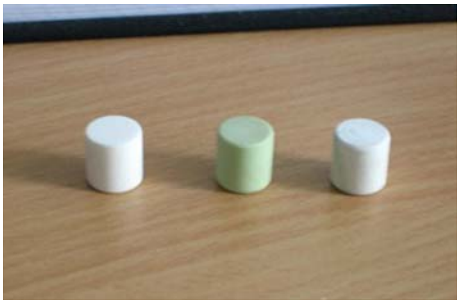

Fig. 4 Syntactic foam samples for compression test

Characterization methods

Gravimetry

Isothermal ageing tests were performed at 80 °C in deionised water, in natural sea water and in 90% relative humidity in an oven. All tests were conducted at 80 °C. The sizes of the samples were 50 × 50 × 2 mm^3. The percent water uptake (%mass gain) was calculated following the ASTM D570 (mass gain determined on blotted dry samples normalised by the initial mass).

Compression test

The non-isotropic condition has been applied using a confined compression set-up (Fig. 5). The strain rate was the same for all experiments: 5×10^{-3} mm/min. For monotonic tests, the load was increased up to 25 MPa for rigid matrix (epoxy) and 20 MPa for soft matrices (PU, PP). The tests were performed at room temperature (295 K).

Results and discussion

Wet behaviour of syntactic foams

The mass gain of pure epoxy-anhydride samples aged at 80 °C in deionised water, in natural sea water and in 90% relative humidity is presented in Fig. 6. The sigmoidal form of the curve reveals a two-step phenomenon: the first step corresponds to the plasticization of the resin by water molecules and the second one is attributed to the degradation of the polymer. This latter phenomenon was checked by drying aged samples. The final weight was less than initial unaged one, proving the degradation. This two-step behaviour is generally represented by the Langmuir law, which takes into account not only the diffusion into the material but also other phenomena like degradation which give these abnormal results. In the case of an epoxy hardened by an anhydride, the degradation in hot water classically occurs by hydrolysis of the ester functions [13]. The study of the degradation of the resin was nevertheless not the main issue of this article. Thus, focus was on the first step where the diffusion kinetics in the resin have been similar in both liquid environments. As expected, the mass gain in 90% relative humidity is lower, and corresponds more or less to 90% of water uptake in liquid [14].

The results on syntactic foams are more surprising (Fig. 7). The liquid water uptake behaviour is very sensitive to the environment. First, regarding sea and deionised water, the weight uptake was the highest for deionised water, whereas the sea water exhibited a smaller weight increase. This could be explained by the water activity [15]. The parameter a_w is the ratio between the vapour pressure of water in a media (for example, salt water) and the vapour pressure of pure water in the same conditions. Its value is 1 for deionised water and 0.75 for NaCl saturated solution.

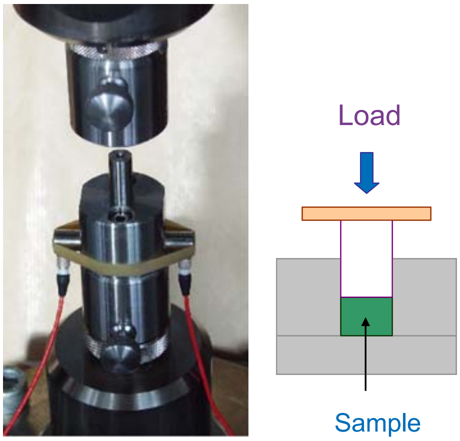

Fig. 5 Confined compression set-up

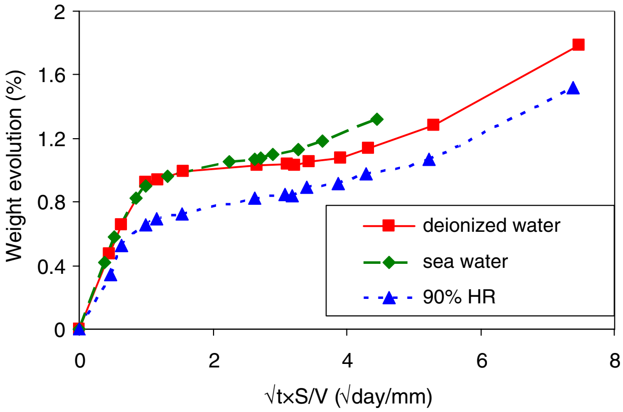

Fig. 6 Weight gains comparison of pure epoxy-anhydride aged in three environments

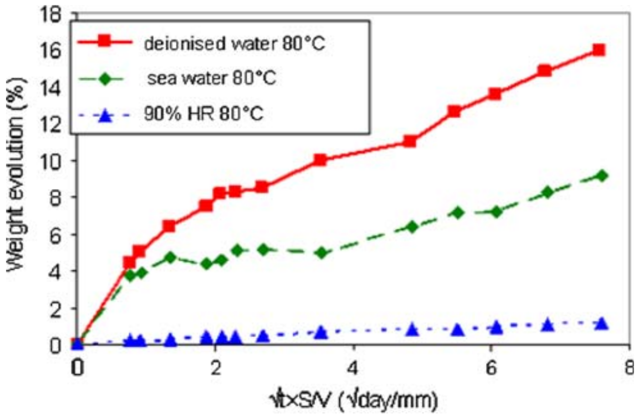

Fig. 7 Weight gains comparison of epoxy syntactic foam aged in three environments

Due to the chemical products generated during ageing, and especially when water molecules segregate to the glass–matrix interface, there is a difference between the activity of water in the ageing solution (a_s) and the activity of water inside the material (a_m). This difference creates an osmotic pressure:

$$\Pi = \frac{RT}{V_m} \ln \frac{a_s}{a_m}$$

where V_m is the molar volume of water.

This equation shows that a higher activity of the ageing solution leads to a higher osmotic pressure, inducing then a bigger interface gap, thus promoting a higher level of water ingress.

The second surprising result concerns the water uptake in 90% relative humidity. In this case, the weight gain is very low, not equivalent to 90% of the water uptake of the foam in an aqueous environment.

As insulation material is often protected by a pure polymer layer, these results make us wonder what kind of ageing medium is in contact with the foam. Indeed, as the coating layer acts as a membrane, the water diffuses through it at a molecular state. Then the following question arises regarding the behaviour of the syntactic foam in relation to these diffusing molecules: is it equivalent to liquid or relative humidity environment?

Some prototype samples were manufactured to simulate the foam embedded in pure resin which protected it from a direct contact with the liquid. These samples were aged in hot water (80 °C) for around 400 days. The weight uptake curve (Fig. 8) shows a regular increase up to almost 4% during the test duration.

This test has been modelled using the sample geometry and the diffusion properties of each material determined from absorption results in similar conditions (Figs. 7, 8). The sample has been meshed with 3D elements and the water absorption simulation has been based on two hypotheses: (1) the diffusion in pure epoxy follows a Fick law [16] and (2) the diffusion in syntactic foam follows a Langmuir law in the case of liquid water or a Fick law in the case of relative humidity.

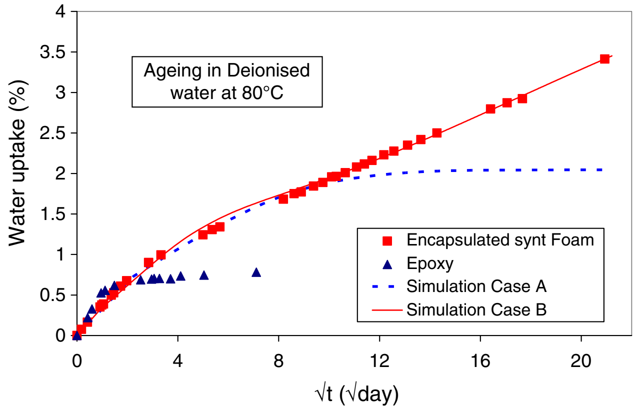

Fig. 8 Comparison of the experimental and simulated weight gains of bi-layer samples. The two simulated combination of hypotheses for bi-layer sample: Case A: Fick diffusion on water in epoxy and Fick diffusion of relative humidity in foam, Case B: Fick diffusion on water in epoxy and Langmuir diffusion of water in foam

The comparison between experimental results and the two simulated curves shows that the water absorption behaviour of the syntactic foam in the protected samples is related to ageing of foam directly in liquid water.

These results suggest that, even when protected by a topcoat, the ageing mechanisms of syntactic foams are the same than in liquid water. Nevertheless, thanks to its lower diffusion coefficients, the topcoat will reduce the diffusion of liquid medium into the foam and then reduce the ageing kinetics.

Behaviour under non-hydrostatic conditions

In this section, the mechanical behaviour of a multilayer coating system is addressed (Fig. 2). A structure of this type is commonly composed of a steel pipe and a 5-layer insulating coating comprising several material types: solid polymers thermoset and thermoplastic, syntactic foam, each layer having a different functionality. First of all, the steel surface is covered with an adhesive which links the coating layer to steel. This adhesive is a fusion-bonded epoxy. When the coating material is polypropylene based, an intermediate layer is necessary to link epoxy material to PP. This function is fulfilled by a modified PP layer which can mix with the PP layer on the one hand and also chemically react with epoxy material on the other hand. The third layer is a PP pure layer between modified layer and PP syntactic foam material. The main layer is the syntactic foam layer, which is several tens of millimetres thick. Its main function is to provide insulation between hot

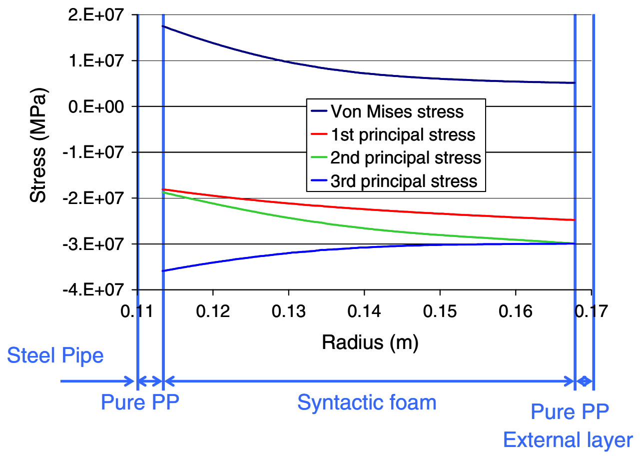

Fig. 9 Simulated stresses repartition in the syntactic foam when the insulated pipe is submitted to 30 MPa hydrostatic pressure

steel tube and cold sea water. The last layer is a pure PP layer (around few millimetres thick) which protects the foam from external damage during installation or during service. It also limits the diffusion of water into the syntactic foam.

Other materials are also used in the manufacture of an insulation coating. The manufacturing process varies with respect to design and material but all these kinds of structures must sustain non-isotropic conditions under external pressure. Indeed, the modelling of an insulated pipe under hydrostatic pressure reveals that the Von Mises stresses are not constant through the cross-section, suggesting that the loading is not purely hydrostatic (Fig. 9). Due to the link between the insulation material and the steel surface, the foam movement is restricted in the circumferential and longitudinal directions.

To compare the behaviour of syntactic foam with different matrices, a confined compression set-up has been used. This condition has been chosen to simulate the mechanical loading actually applied on the insulation coating when it is bonded onto the steel surface.

Figure 10 represents the compression curves of three syntactic foam materials, two with soft matrices (PP and PU) and one with rigid matrix (epoxy). These tests were conducted up to 250 MPa (320 MPa for epoxy), obviously a very high loading towards service conditions, in order to understand the overall behaviour of the material until rupture. After an initial increase of load, it can be observed that there is more or less a plateau which corresponds to the rupture of the microballoons. When all of the balloons are broken, there is compaction of the material and the load increases rapidly.

The acquisition of acoustic emission signals during these mechanical tests gives more information. Figure 11 presents the evolution of cumulative number of hits and absolute energy of acoustic signals versus load for each kind of syntactic foam. As the three graphs have the same scale, it is easy to compare the behaviour of each material. First of all, the soft matrices (PU and PP) lead to a progressive damage starting at a very low load for PU resin. PP foam shows a very low activity and very low cumulative energy. Rigid epoxy matrix leads to very differing behaviour. There is quite no noise up to a relatively high load when a sudden and great emission occurs. Due to the use of a threshold to eliminate the background noise during acoustic emission acquisition, some low-energy events are obviously missed but the comparison is relevant.

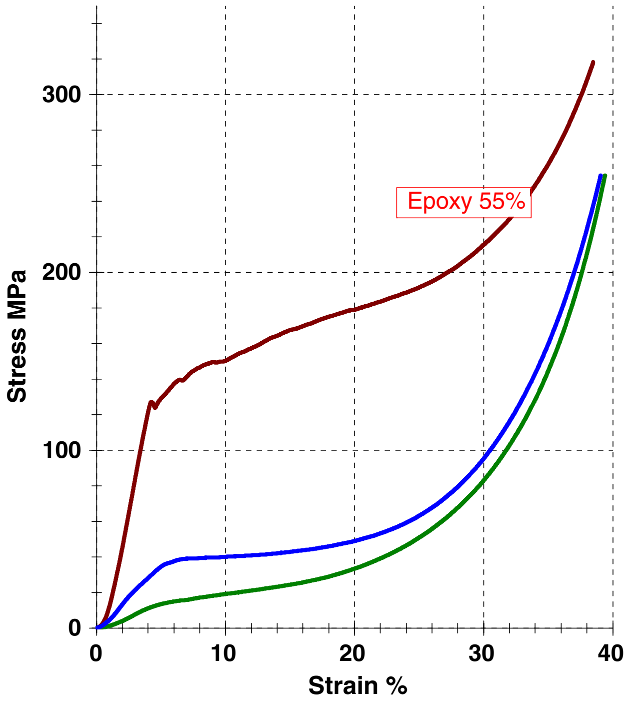

Fig. 10 Confined compression curves of syntactic foams

Above-mentioned differences can be complemented by observations performed by X-ray tomography on same materials during mechanical compression using confined test [17]. This study reported qualitative and quantitative study of broken microballoons at different levels of damage (interrupted tests at increasing load level). For soft matrices, the damage occurred progressively with increasing load and the biggest balloons broke first. For rigid epoxy matrix, there was no damage up to a load limit (around 100 MPa), above which the damage occurred suddenly through a shear process. In this latter case, the ruptures were not homogeneously distributed but located in bands, indicating that the rupture went from one balloon to its neighbour.

At this stage, acoustic emission events cannot be directly related to balloon microstructures; however, they

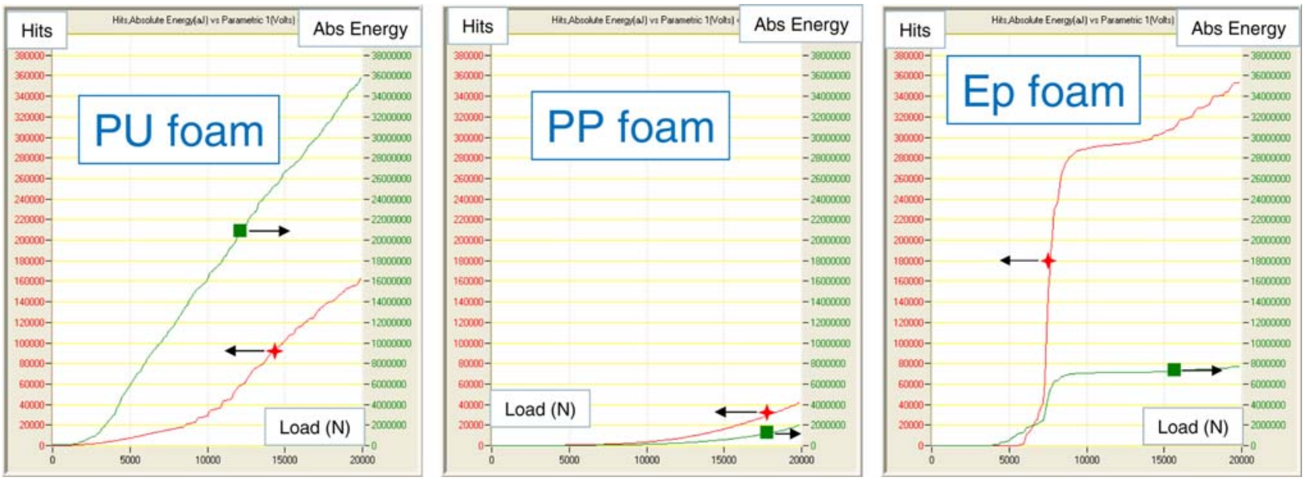

Fig. 11 Evolution of cumulative number of hits (✦) and absolute energy (■) versus applied load for the three kinds of syntactic foams

show similar trends than results obtained previously by other techniques [17]. Acoustic emission yields further information in microballoon damage under pressure. As it is an in situ method, it is possible to continuously record the events and then detect early damage appearance. This is not possible with X-ray tomography because this technique requires time to make a scan and then the mechanical test must be interrupted. Figure 12 represents an expanded view of the first part of compression curve on PP foam. This enlargement shows that the acoustic emission begins around 2000 N (25 MPa). This means that some degradation will be present in the material when pipes are installed at 3000 m water depth because hydrostatic pressure prevailing there is about 30 MPa. In addition, the early breakage concerns the large diameter microballoons, which are of primary interest for the insulation and buoyancy capabilities of the material [17].

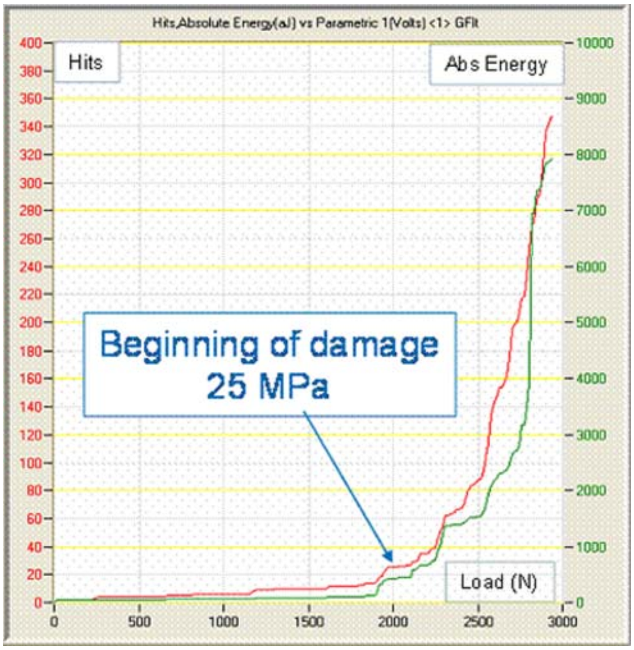

Fig. 12 Detection of the early damage on PP syntactic foam

Conclusions

The use of polymer-based syntactic foams reinforced with glass microballoons for pipeline insulation in deepwater requires a better understanding of their behaviour. These products present good ageing behaviour in relative humidity. As the foam layers are protected by a top layer on industrial structure (protective thermoplastic sheath), the influence of this protection was studied using foam samples embedded in pure polymer. The water absorption curves were modelled taking into account the geometry of the samples and the diffusion characteristics of each material. These results showed that despite the presence of the pure resin layer, the foam ages as in liquid water. There is no improvement of the ageing resistance of the foam.

Mechanical modelling of the insulated structure revealed that the mechanical stresses on the coating are non-homogeneous. A confined compression set-up was used to simulate this kind of loading. Acoustic emission monitoring was used during these compression tests and led to compare various syntactic foam materials. Soft matrices present continuous and uniform damage whereas brittle resins like epoxy withstand higher load with sudden and localised damage induced. During continuous recording of acoustic emission it is possible to detect early damage due to the first fractures of glass microballoons. As numerous different phenomena occur in syntactic foams during hydrothermal ageing, acoustic emission appears to be a powerful technique to study and evaluate the evolution of degradation processes during ageing.

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