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This paper is a part of the hereunder thematic dossier
published in OGST Journal, Vol. 70, No. 2, pp. 215-390
and available online here

Cet article fait partie du dossier thématique ci-dessous
publié dans la revue OGST, Vol. 70, n°2, pp. 215-390
et téléchargeable ici

DOSSIER Edited by/Sous la direction de : **B. Dewimille**

Fluids-Polymers Interactions: Permeability, Durability
Interactions fluides polymères : perméabilité, durabilité

Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 2, pp. 215-390

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Oil & Gas Science and Technology – Rev. IFP Energies nouvelles, Vol. 70 (2015), No. 2, pp. 279-289
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DOI: 10.2516/ogst/2013211

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Dossier

Fluids-Polymers Interactions: Permeability, Durability
Interactions fluides polymères : perméabilité, durabilité

Evaluation of Long Term Behaviour of Polymers for Offshore Oil and Gas Applications

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Abstract — *Polymers and composites are very attractive for underwater applications, but it is essential to evaluate their long term behaviour in sea water if structural integrity of offshore structures is to be guaranteed. Accelerated test procedures are frequently required, and this paper will present three examples showing how the durability of polymers, in the form of fibres, matrix resins in fibre reinforced composites for structural elements, and thermal insulation coatings of flow-lines, have been evaluated for offshore use. The influence of the ageing medium, temperature, and hydrostatic pressure will be discussed first, then an example of the application of ageing test results to predict long term behavior of the thermal insulation coating of a flowline will be presented.*

Résumé — **Durabilité des polymères pour application pétrolière offshore** — Les polymères et composites sont largement utilisés pour les applications en mer et particulièrement dans le domaine de l'industrie pétrolière. La fiabilisation des structures utilisées pour ces applications nécessite la prise en considération du comportement à long terme des matériaux. L'évaluation de la durabilité des polymères et composites en milieu marin exige la mise en place de vieillissements accélérés spécifiques. La nature de ces vieillissements ainsi que les paramètres influant tels que la nature de l'eau, la température ou la pression hydrostatique seront discutés dans cet article à travers trois exemples. Le premier sera dédié au comportement à long terme de fibres polymériques utilisées principalement pour l'amarrage, le second traitera de la durabilité des composites. Enfin le dernier traitera de la prédiction du comportement à long terme de polyuréthane utilisé comme isolant thermique sur des pipes.

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INTRODUCTION

Offshore exploration and production are pushing deeper and deeper, with ultra-deep water applications targeting beyond 4 000 metres depth, and for production applications a service lifetime of 20 years or more is often required. Despite their attractive specific properties the deep sea use of polymers and composites offshore is still quite limited, so there is little in-service experience to validate design predictions. It is generally necessary therefore to employ accelerated tests, in order to check the long term durability of these materials. Ageing can be accelerated by increasing the severity of environmental conditions (temperature, humidity) or mechanical loading (applied stress, hydrostatic pressure) but in all cases it is essential to ensure that the acceleration does not introduce degradation mechanisms which will not be encountered under service conditions. This is not an easy task, and this paper illustrates this by providing some examples in which accelerated tests have been performed on polymers intended for a range of offshore applications.

There is a vast literature on the hygro-thermal ageing of polymers and the aim here is not to provide a review. The reader is referred to books by Verdu [1] and Weitsman [2], on polymers, and Martin [3] in the area of polymer composites.

Researchers at ENSAM [4-5] have been particularly active in this area and detailed phenomenological studies have been published on a number of polymers such as PA11, of direct interest to the offshore oil & gas industry for flow-line liners. Their approach involves acquiring a detailed understanding of the chemical degradation reactions and their kinetics, so that a predictive model can be set up. This allows subsequent changes in formulation or test conditions to be analysed without having to restart the ageing tests and can provide a very powerful tool for durability analysis. The only disadvantage of this approach is that it is very time-consuming so that for many applications a more pragmatic approach is required.

In this paper, three case studies will be described. First, the influence of ageing medium and temperature will be discussed, using the ageing of polymer fibres as an example; synthetic fibres are finding increasing offshore use, in the form of mooring and handling ropes and in umbilical line reinforcements, but there is still relatively little experience to allow lifetime predictions to be made with confidence. Examples from studies on polyamide and aramid fibres will be discussed. Then the influence of mechanical loading will be shown, for an epoxy resin and its glass fibre reinforced composite, aged under different hydrostatic pressures. Finally, a more detailed case study will be presented, concerning the prediction of the long term behaviour of a polyurethane flow-line coating under a combination of ageing conditions.

1 INFLUENCE OF AGEING MEDIUM AND TEMPERATURE

The first decision to be made when defining an accelerated test procedure is the choice of the ageing medium. Ideally natural sea water should be used, but this is rarely available so tap water, distilled water or artificial sea water are employed. These media do not have the same chemical activities so the choice may affect the results. Once the ageing medium has been defined the second parameter to be selected is the range of temperature to be applied, as this is generally the main accelerating factor available to the experimenter. Upper ageing temperature is often limited by polymer transitions so these must be clearly identified before embarking on a long testing programme.

In order to discuss these parameters a form of polymeric material will be studied which has increasing applications offshore; polymer fibres. Various types of fibre are employed today, from the hundreds of tons of nylon and polyester fibre used for mooring and station-keeping [6-7] to the large high performance fibre ropes used for deep sea installation [8-9]. For fibres such as aramids high ageing temperatures can be used, as these fibres are very stable at high temperature, but when we consider melt spun fibres such as nylon and polyester, which show poorer high temperature behaviour than the aramid fibres, the choice of ageing temperature becomes more complicated. For example, the nylon 6 fibres used in Single Point Moorings (SPM) show a dry glass transition temperature around 60°C. Water will tend to reduce this value further, so a maximum ageing temperature of 40°C has been applied.

One direct approach to studying the influence of water for this application is to immerse sections of large ropes, but these may take many months to reach an equilibrium state. Measuring the diffusion kinetics of water in fibres is more accessible, and can be very useful if modeling is to be performed, but is not straightforward, as water absorbed at the surface makes it difficult to obtain accurate weight changes. In order to get round this DVS (Dynamic Vapour Sorption), involving continuous accurate (μg) weight change measurements on a small length of fibre exposed to different relative humidity and temperature conditions appears attractive. Figure 1 shows an example of results for a nylon (PA6) sample. The sample was first dried *in-situ* at 40°C, until constant weight was achieved, (about 1% water by weight was removed), then temperature was maintained at 40°C and relative humidity increased in 20% steps up to 80%. At 80% RH the weight gain was around 4% by weight. The humidity was then reduced and it can be seen that weight gain was completely reversible.

Such measurements can provide the first data needed for modeling, and also help to indicate the amount of water to expect when larger structures are being aged. The aim of studies on fibres is generally to establish whether long term exposure affects fibre mechanical properties. For this PA6 fibre, used in single point mooring lines, lengths of yarn were fully immersed in natural sea water at the Ifremer Brest laboratory at 40°C, and samples were removed periodically and tested on a tensile test machine. Stiffness values were measured first, by cycling around different mean load levels, then the samples were tested to failure. Figure 2 shows an example of results.

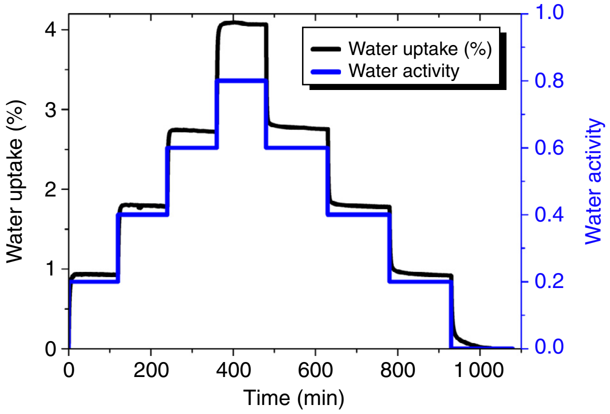


Figure 1

DVS example PA6 fibres, showing weight gain at increasing then decreasing humidity levels, 40°C.

Even after 10.5 months in water at 40°C, the yarn stiffness and strength values are unchanged. This is an interesting result, as it is generally accepted that wet strength of nylon ropes is about 10% lower than that of dry ropes. One might conclude that water affects the interactions between the elements (yarns, rope yarns, strands) in ropes, affecting their relative movements, more than the properties of the elements themselves. It is also interesting to compare this result to the effect of water on bulk PA6 properties. For the latter, a significant reversible effect of water is noted, revealed as a drop in Young's modulus after saturation as water plasticizes amorphous regions [10]. The lower sensitivity of fibre properties to water is the result of their more highly oriented microstructure, as detailed by Richards [11].

Another case where the long term behaviour of synthetic fibres is particularly critical is in the many umbilical control lines employed underwater. Here aramids are often used as the strength member, and these must resist both mechanical loads and the marine environment. A recent study focussed on the ageing of these materials and tests on single fibres were performed after different ageing periods under different conditions. Full details of testing can be found in [12-15]. Figure 3 shows the influence of ageing test temperature on tensile properties of *Twaron* 1 000 aramid yarns.

Tests in different environments also revealed the influence of water activity and pH, Table 1 [13].

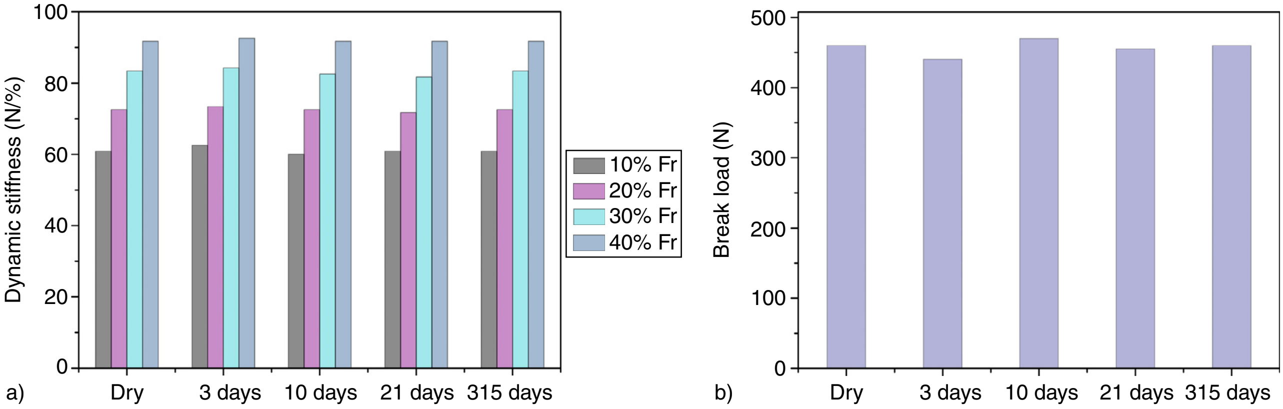


Figure 2

Influence of immersion on a) dynamic stiffness of PA6 yarns at different mean load levels, 10% amplitude, shown as % average dry break load (Fr), and b) break load, after ageing for different periods in sea water at 40°C.

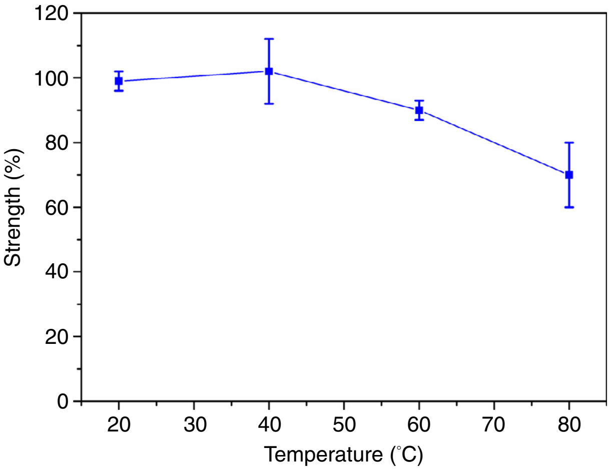


Figure 3

Tensile strength (tests performed at 20°C) of aramid fibres after 231 days seawater immersion at different water temperatures, as a percentage of unaged strength.

Figure 4

Test facility to age resin and composite samples under temperature and pressure. Control specimens in water on left, pressure vessel on right.

TABLE 1

Residual tensile strength of *Twaron* 1 000 fibres after one and a half years' ageing at 80°C in different environments, mean (± one standard deviation) values

	Residual tensile strength (%)
As-received	100
Air	92 ± 12
Sea water	72 ± 10
Deionised water	58 ± 7
pH9	62 ± 20
pH11	20 ± 7

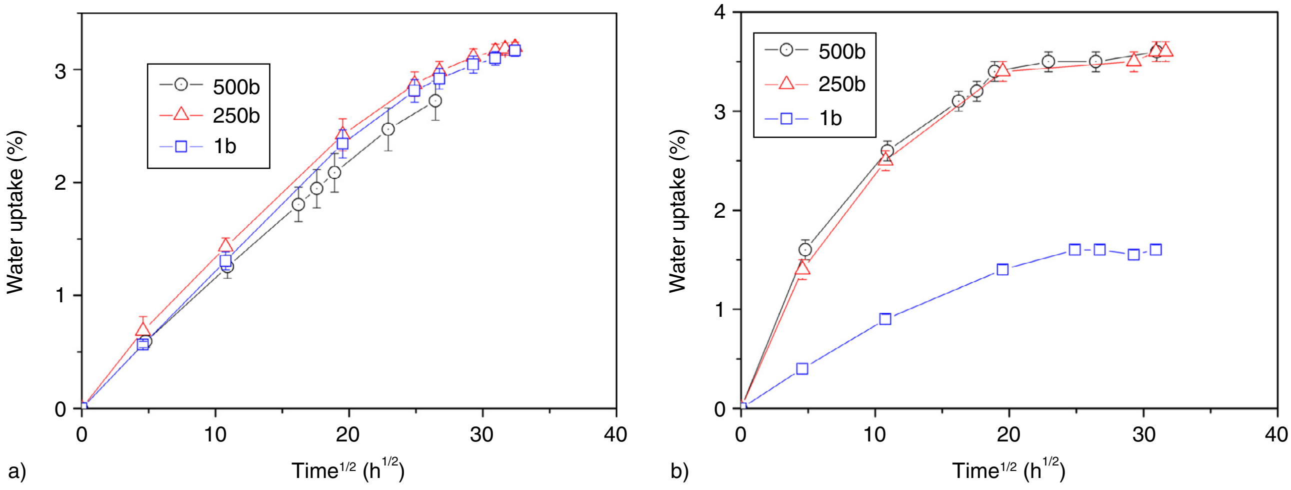
After one and half years at 80°C in air, the strength loss is close to 8%: thermo-oxidation is thus not a serious concern for this fibre. However, the degradation is significant in the presence of water. After one and half years at pH9 and in deionised water the degradation in tensile strength is similar, and is slightly lower under sea water exposure. It appears that the degradation is significantly higher at pH11 than for the other conditions, and this may be due to an additional degradation mechanism, degradation of the crystallites, at the higher pH [14]. Tensile modulus remained unchanged for all these conditions.

2 INFLUENCE OF HYDROSTATIC PRESSURE

Another parameter which may have a strong influence on ageing behavior is mechanical loading, so under certain conditions this may be used to accelerate ageing. For underwater applications the effect of hydrostatic pressure is particularly relevant, and several authors have examined this parameter. Extensive work in the 1970's on a wide range of polymers has shown that high pressures can significantly modify polymer properties [16-17].

Weight gain results are less abundant but some data exist. Pressure effects on composites were discussed by Fried [18] and he noted a difference between low and high void composites. In a study on flat composite panels, the effect of a 10 MPa pressure on water absorption was also examined and found to be very small [19]. Other authors have also noted rather small effects, with increases in moisture absorption [20-22], no effect [23] or decreases in absorption [24] being reported. However, some results from tests performed by the authors for specimens taken from filament wound cylinders [25] have shown strong pressure effects. The latter materials may be particularly susceptible to pressure effects as void contents tend to be quite high (several percent) in filament wound tubes. Voids influence directly the moisture pick-up [26].

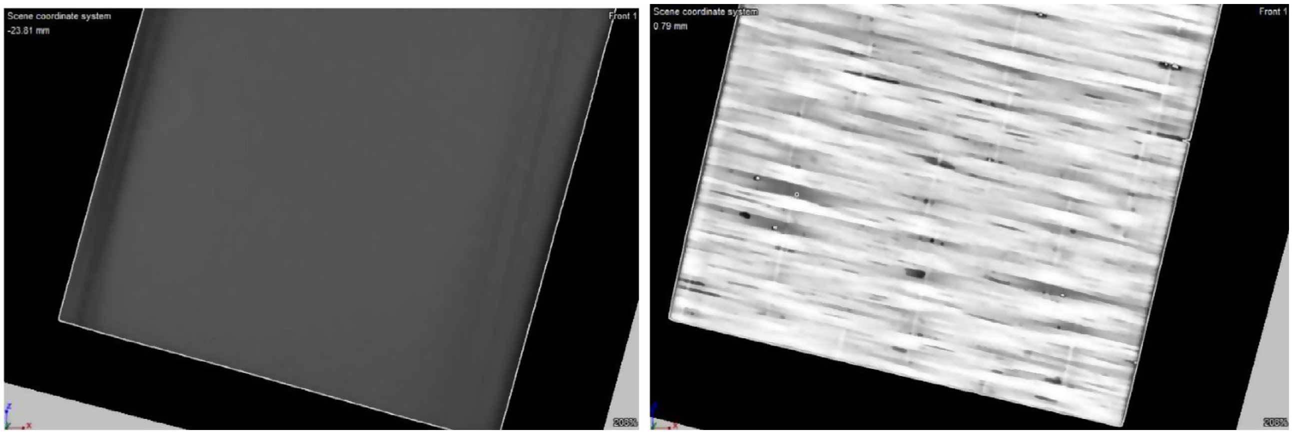
It is clear that water absorption results are inconclusive, in some cases an influence of pressure is observed, in others there is no effect. A test program was therefore launched to examine this parameter in more detail. Pressure vessels were manufactured and placed in ovens in order to be able to immerse specimens at different pressures and control the temperature, Figure 4.



a) b)

Figure 5

Weight gains, a) epoxy resin, b) glass fibre reinforced epoxy.



a) b)

Figure 6

X-ray micro-tomography images, a) epoxy resin, b) glass reinforced epoxy composite.

First a series of 4 mm thick cast epoxy resin samples of dimensions 50 × 50 mm^2 was prepared. These were dried then 5 were immersed in tap water without pressure and 5 others were placed in the pressure vessels at 250 or 500 bar. All were held at 60°C in the oven. Figure 5a shows the weight gains measured periodically. For this resin, an amide cured epoxy with a Tg of 80°C, there is no influence of pressure even at 500 bar, suggesting that any effects of free volume changes and are not significant.

A second series of specimens was then prepared using the same epoxy resin to impregnate unidirectional glass fibres. The same procedure was followed and Figure 5b shows the result. At 60°C without pressure the weight gain is what would be expected based on the resin results and the fibre fraction (around 50%). At higher pressure however, significantly higher weight gains are recorded. After drying however the weight returns to its initial value.

In order to investigate this, samples of both resin and composite were examined by X-ray micro-tomography. Figure 6 shows examples of images, which indicate significantly higher levels of porosity in the composite. The hydrostatic pressure may force additional water into these cavities, though the fibre/matrix interface may also accommodate some additional water.

These results show the difficulty in using hydrostatic pressure as an accelerating factor. For a polymer (with no porosity) there is no effect, while for a composite (with voids) a pressure of 250 or 500 bar will result in the same weight gain increase compared to a test without pressure. Thus while investigation of pressure effects remains important for deep sea applications of composites, this parameter will not be easy to employ to accelerate ageing tests.

3 PREDICTION OF DEGRADATION OF A STRUCTURE DURING AGEING: THERMAL INSULATION COATING

One of the key points for offshore oil and gas production is flow assurance. Under particular conditions of pressure and temperature, solid gas hydrates can appear in the oil situated inside the pipe leading to a total interruption of the production. In order to avoid gas hydrate formation, it is essential to limit the cooling of extracted hot oil during transport in the flowlines from the Christmas trees (at 2 000 metres depth for example) to the production structure (at the surface). Passive thermal insulation coatings are usually employed to limit thermal exchange between hot oil inside the steel pipe and the cold sea water outside (4°C), Figure 7 is a schematic representation of a flow line under service conditions. Due to their excellent thermal properties, polymers are widely used for this application, especially PolyPropylene (PP) and PolyUrethane (PU). Furthermore, to improve the thermal properties of the coating, glass bubbles can be included in these polymers to form so-called “syntactic foams”. From a material point of view this application is complex, the polymers are exposed to severe conditions (high temperature, sea water contact, high hydrostatic pressure) for long periods (up to 40 years). Thus it is important to study the polymer durability under these conditions using appropriate ageing tests. This section will discuss the influence of different parameters during accelerated ageing tests on a polyurethane coating polymer.

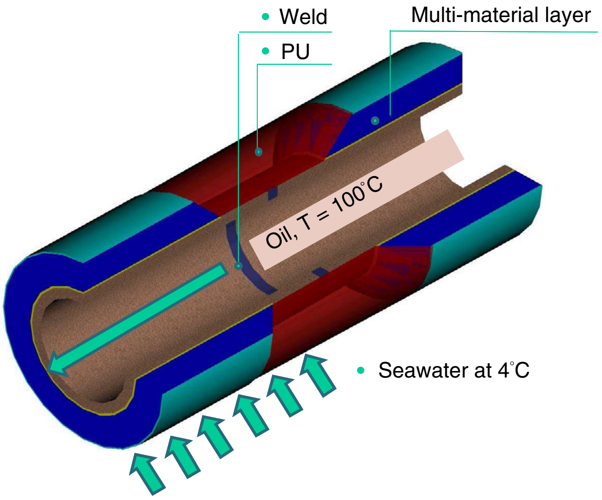


Figure 7

Schematic representation of a flow line under service conditions [27].

3.1 Water Diffusion

For this application, water diffusion in the thermal insulation coating is very important, as in the presence of water the thermal insulation properties of polymers decrease significantly [28]. The prediction of the water content in a coating as a function of time and field characteristics (such as temperature, depth) is therefore essential. Furthermore, if the polymer undergoes degradation in the presence of water, this reaction will be dependent on the water diffusion profile.

3.1.1 Water Diffusion Characterization

As discussed in the preceding sections, the easiest way to characterize water diffusion is by measuring weight changes. Using an appropriate protocol, it is possible to assess water diffusion characteristics by regularly measuring the weight gain of a polymer when immersed in water. In this section, we will discuss the effect of different experimental parameters on water diffusion.

Sample Thickness and Shape

In terms of characterization, the easiest way is to work in one-dimensional diffusion *i.e.* with a semi-infinite plate, in order to minimize water diffusion by the edges. This results in typical coupon dimensions of 50 × 50 mm^2 provided the thickness is less than 5 mm. It is also interesting to study mass evolution using samples with two different thicknesses, in order to check the validity of Fickian behaviour. Figure 8 shows an example for PU coating samples, which validates this approach as the two weight gain curves superpose.

Temperature

Water temperature has a strong effect on the diffusion kinetics of this material, Figure 9, whereas the water content at saturation does not change much (due to the small evolution of the solubility with temperature). On account of the temperature gradients in a flow-line coating during service it is necessary to assess water diffusion at different temperatures, to be able to predict water content in the coating as a function of time.

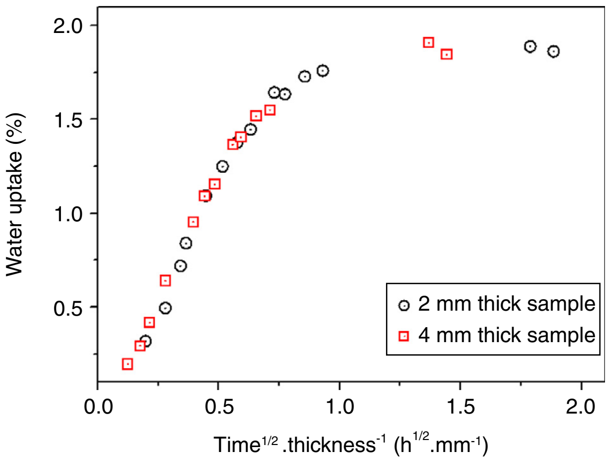


Figure 8

Weight evolution of solid PU samples of two thicknesses (2 mm and 4 mm) immersed in sea water at 80°C.

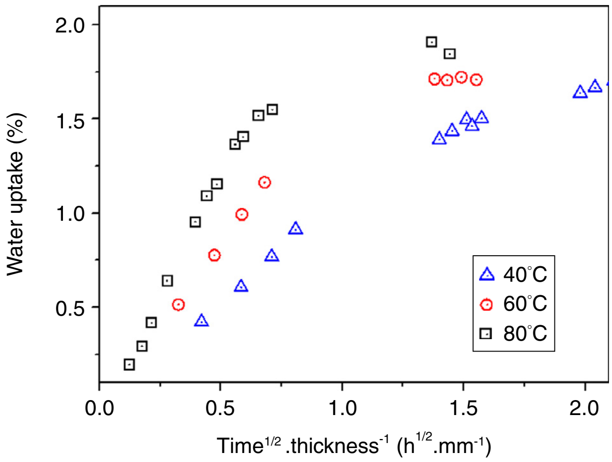


Figure 9

Influence of sea water temperature on water diffusion in PU coating polymer.

Pressure

The influence of pressure on water diffusion depends on the nature and composition of the polymer. For bulk polymers with no fillers, there may be a modification of free volume which leads to a slight modification of the water absorption. However for a polymer containing glass microspheres, hydrostatic pressure can significantly modify water absorption in the material due to collapse of these bubbles [29]. Figure 10 shows water uptake in a PU with glass bubbles in sea water at 40°C with and without hydrostatic pressure, for tests lasting over a year. Without pressure, water uptake is Fickian with a maximum weight gain of 4%, whereas with hydrostatic pressure (300 bar) water uptake increases continuously due to progressive collapse of the glass bubbles.

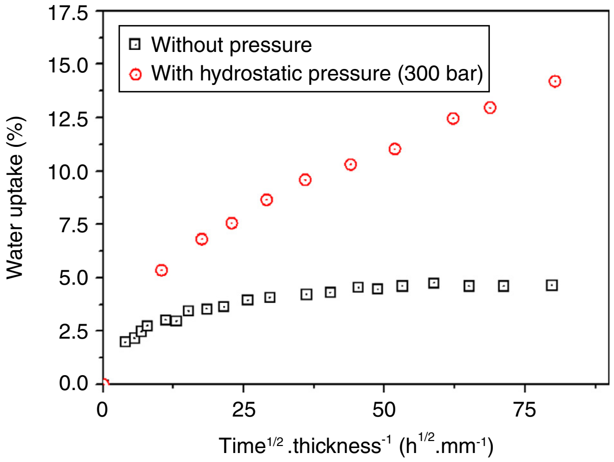


Figure 10

Influence of hydrostatic pressure on water uptake in PU with glass microspheres.

3.1.2 Water Diffusion Modeling

From Experimental Data

Because water absorption of a polymer depends on its nature and formulation there are many different behaviours, and hence many different models have been proposed [30-31]. Nevertheless, we have seen above that in the case of a PU coating Fickian modeling can be used, thus we will focus on the use of this model which can be presented as:

$$\frac{dC}{dt} = D.\frac{d^2C}{dx^2}$$

where C is water concentration, t is time (s), x is position in the sample (m) and D is the water diffusion coefficient (m^2/s).

From experimental data, it is possible to evaluate water diffusion coefficients and their evolution with temperature (Fig. 11). Water diffusion coefficients often show Arrhenius behaviour, and can then be written in the form:

$$D = D_o.exp\left(-\frac{E_a}{RT}\right)$$

where D is the water coefficient (m^2/s), D_o the pre-exponential factor (m^2/s), E_a the activation energy (J/mol),

R the perfect gas constant (m^2.Kg/(s^2.K.mol)) and T the temperature (K). These data will be useful to evaluate the water diffusion in the polymer coating in service.

Water Diffusion in a Polymer Coating During Service

Once sea water diffusion behaviour is known at different temperatures it is possible to predict the water content in the insulation coating as a function of time during service using numerical modeling. For example, we can consider a flow line with an internal temperature of 100°C immersed in sea water at 4°C and covered by an 80 mm thick PU coating. In this case, the temperature gradient during service can be modeled (*Fig. 12*) and thus water content and thermal properties can be predicted as a function of time and position (*Fig. 13*).

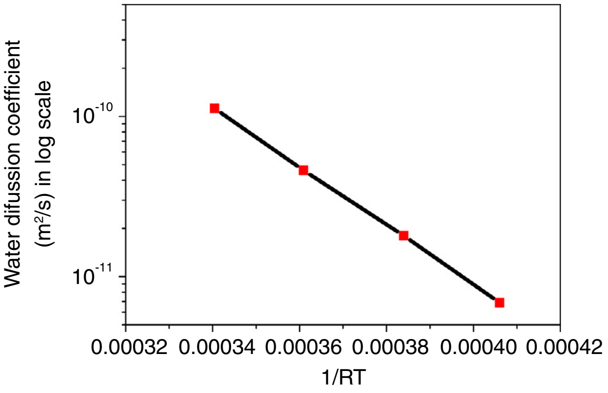


Figure 11

Evolution of the water diffusion coefficient with temperature.

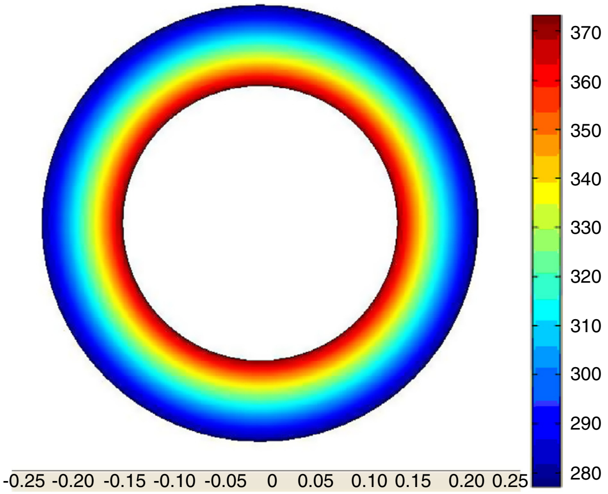


Figure 12

Temperature (K) profile in polymer coating in service.

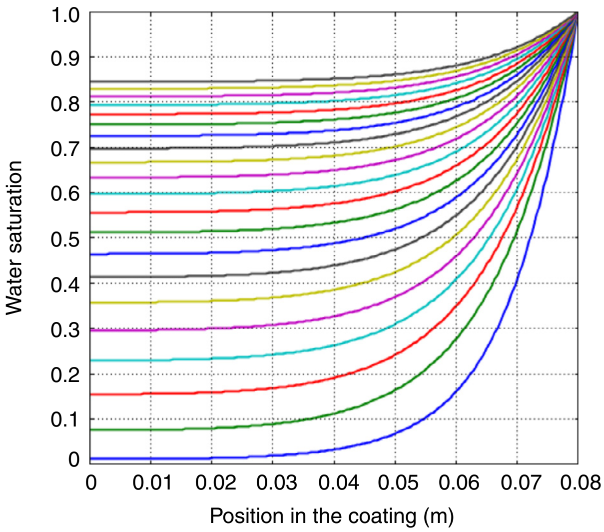


Figure 13

Evolution of the normalized water content as a function of time and position in the coating – the hot steel pipe is on the left side, at position 0 (one line for one year).

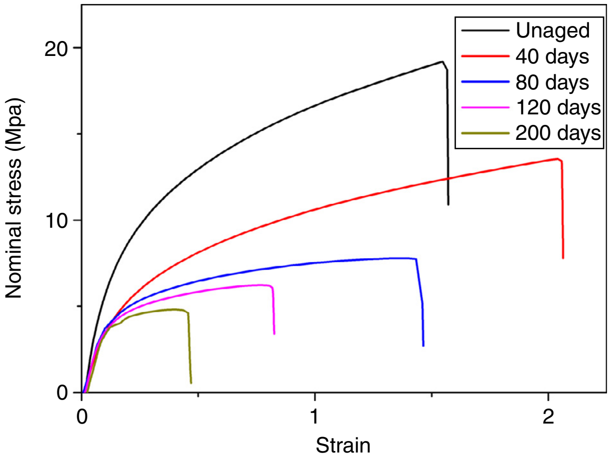


Figure 14

Evolution of tensile properties of PU during ageing.

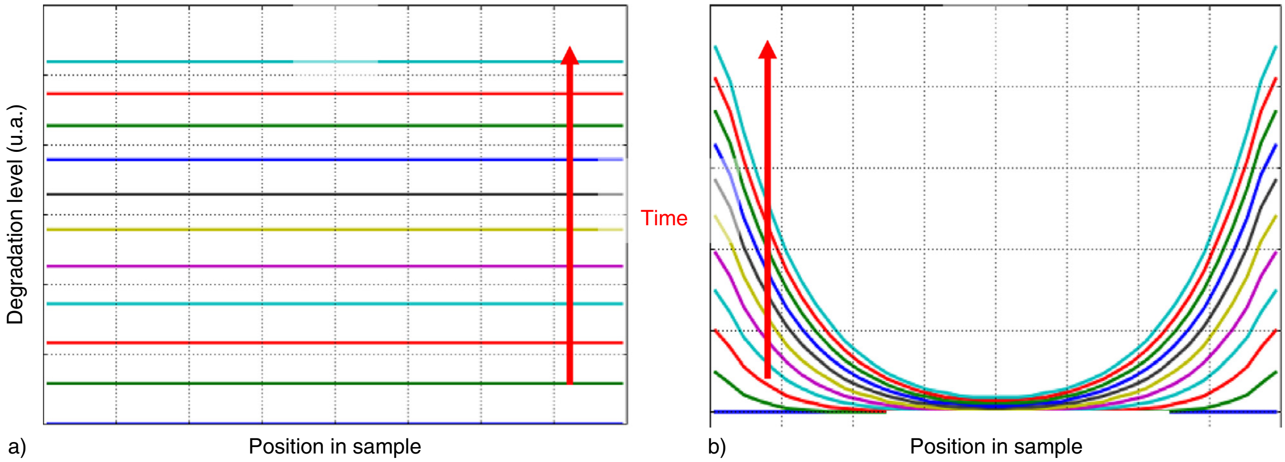


Figure 15

Degradation profiles through sample thickness showing competition between diffusion rate and reaction rate. a) Diffusion faster than reaction; b) reaction faster than diffusion (DLR).

3.2 Polymer Degradation in Sea Water

When a polymer is used in a marine environment, it absorbs water and may thus undergo reversible changes (plasticization) due to the presence of water within the polymer [32-33]. However, irreversible chemical reactions can also occur, due to reactions with water or oxygen [34-36]. Thus in addition to measuring the diffusion kinetics, it is necessary to establish how water affects the properties of the polymer and to characterize the degradation. Temperature is a useful accelerating factor and is widely used. Nevertheless it must be used carefully, especially for life time prediction.

3.2.1 Nature and Consequences of the Degradation

When temperature is used to accelerate polymer ageing, it is absolutely necessary to understand the chemical mechanisms involved in the degradation. At elevated temperature, the polymer degradation mechanisms can be changed, compared to what will occur at service temperature over a longer period. In the case of PU, the evolution of mechanical properties has been characterized at different temperatures in sea water from 110°C to 25°C for 18 months. Figure 14 shows the evolution of the tensile stress/strain curves during ageing for different periods at 100°C in sea water. In this case, loss in tensile properties is due to hydrolysis of the urethane bond [37-38].

Based on accelerated ageing and considering chemical reactions involved in the degradation, it is possible to propose a life time prediction. Nevertheless, to enhance reliability of this prediction it is necessary to take care of diffusion/reactions aspects.

3.2.2 Diffusion-Reaction Phenomena

If the reagent is not present in the polymer but only in the external environment, then the reaction will occur only if it diffuses into the material. This is the case for most degradation in a marine environment (*e.g.* hydrolysis and oxidation). In this case, it is important to examine the heterogeneity of the degradation within the sample. In fact if the diffusion of the reagent is faster than its reaction by degradation then the degradation level is constant through the sample thickness (*Fig. 15a*). On the contrary, if the reaction occurs faster than diffusion, the reagent does not have time to diffuse deeply into the sample and thus the degradation will be heterogeneous in the sample (*Fig. 15b*). For oxidation this phenomenon is known as a Diffusion Limited Oxidation (DLO) [39-40].

Limitation of the degradation in the polymer thickness due to diffusion of reactant can complicate the life time prediction. In fact, the two phenomena (reaction and diffusion) do not have the same evolution with temperature, thus an Arrhenius extrapolation cannot be used. For example, it has been shown that the mechanical behaviour of a polychloroprene used for 23 years as a flow line can not be correctly predicted using accelerated ageing and Arrhenius extrapolation (*Fig. 16*). To overcome this limitation it is necessary to describe each phenomena involved in the overall degradation and characterize its evolution with temperature.

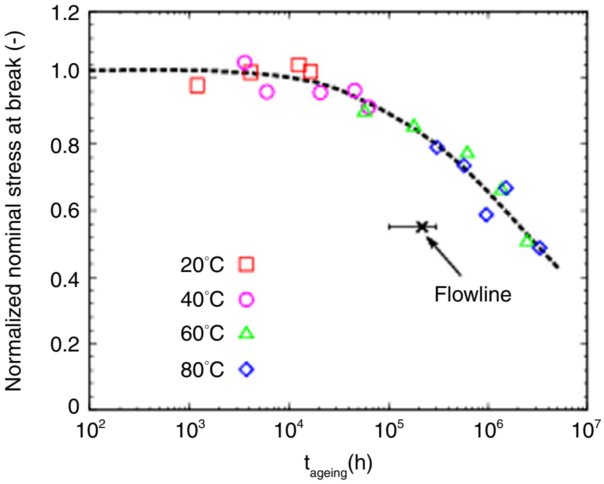


Figure 16

Comparison of stress at break predicted using Arrhenius extrapolation and experimental results on CR sample naturally aged during 23 years in service [41].

CONCLUSION

In this paper, a number of parameters affecting the ageing of polymers has been considered, in order to establish reliable and representative accelerated testing procedures for long term applications of these materials in offshore oil and gas applications. The influence of ageing temperature, medium and hydrostatic pressure has been examined using examples from previous studies, then the durability of a PU thermal insulation coating has been considered in detail. For the latter, a diffusion model has been determined which can be used to predict how the water profile within the insulation coating evolves with time under service conditions. This model can then be coupled with a mechanical model in order to establish the long term durability of such coatings. Further work is in progress to establish the kinetics of the reactions causing the changes in properties, in order to ensure that accelerated tests produce valid physical changes.

REFERENCES

1 Verdu J. (2012) *Oxidative ageing of polymers*, Wiley.

2 Weitsman Y. (2012) *Fluid Effects in Polymers and Polymeric Composites*, Springer.

3 Martin R. (2008) *Aging of Composites*, Woodhead Publishing.

4 Merdas I., Thominette F., Tcharkhtchi A., Verdu J. (2002) Factors governing water absorption by composite matrices, *Composites Science and Technology* **62**, 4, 487-492.

5 El Yagoubi J., Lubineau G., Roger F., Verdu J. (2012) A fully coupled diffusion-reaction scheme for moisture sorption–desorption in an anhydride-cured epoxy resin, *Polymer* **53**, 24, 5582-5595.

6 Hoppe L.F.E. (2003) Designing SPM hawsers to today's requirements, *OCEANS 2003 Proceedings*, San Diego, CA 22-26 Sept., **3**, 1353-1359.

7 Del Vecchio C.J.M. (1992) *Light weight materials for deep water moorings*, University of Reading.

8 Torben S. (2007) Fiber Rope Deployment System for Ultra Deep Water Installations, *2007 Offshore Technology Conference*, Houston, Texas, OTC, 30 April-3 May, OTC 18932.

9 Davies P., Reaud Y., Dussud L., Woerther P. (2011) Mechanical behaviour of HMPE and aramid fibre ropes for deep sea handling operations, *Ocean Engineering* **38**, 17-18, 2208-2214.

10 François M., Davis P., Grosjean F., Legerstee F. (2010) Modelling fiber rope load-elongation properties - Polyester and other fibers, *2010 Offshore Technology Conference*, Houston, Texas, 3-6 May, OTC 20468.

11 Richards A.F. (2005) Nylon fibres, in *Synthetic fibres*, McIntyre J. (ed), Woodhead Publishing.

12 Derombise G. (2009) *Comportement à long terme des fibres aramides en milieu neutres et alcalins*, École Nationale des Ponts et Chaussées, Paris.

13 Derombise G., Vouyovitch Van Schoors L., Davies P. (2009) Degradation of Technora aramid fibres in alkaline and neutral environments, *Polymer Degradation and Stability* **94**, 10, 1615-1620.

14 Derombise G., Chailleux E., Forest B., Riou L., Lacotte N., Van Schoors L.V., Davies P. (2011) Long-term mechanical behavior of aramid fibers in seawater, *Polymer Engineering and Science* **51**, 7, 1366-1375.

15 Derombise G., van Schoors L.V., Bourmaud A., Davies P. (2012) Morphological and physical evolutions of aramid fibers aged in a moderately alkaline environment, *Journal of Applied Polymer Science* **123**, 5, 3098-3105.

16 Radcliffe S. (1972) Effects of hydrostatic pressure on the deformation and fracture of polymers, in Deformation and Fracture of High polymers, in *Deformation and Fracture of High polymers*, Plenum Press.

17 Pae K.D., Bhateja S.K. (1975) The Effects of Hydrostatic Pressure on the Mechanical Behavior of Polymers, *Journal of Macromolecular Science, Part C* **13**, 1, 1-75.

18 Fried N. (1967) Degradation of composite materials, Proceedings of the *Fifth Symposium on Naval Structural Mechanics*, May, pp. 813-837

19 ASTM STP 1302 (1997) *Aging of composites in water*, pp. 73-96.

20 Tucker W.C., Lee S.-B., Rockett T. (1993) The Effects of Pressure on Water Transport in Polymers, *Journal of Composite Materials* **27**, 8, 756-763.

21 Tucker W.C., Brown R. (1989) Moisture Absorption of Graphite/Polymer Composites Under 2000 Feet of Seawater, *Journal of Composite Materials* **23**, 8, 787-797.

22 Pollard A., Baggott R., Wostenholm G.H., Yates B., George A.P. (1989) Influence of hydrostatic pressure on the moisture absorption of glass fibre-reinforced polyester, *Journal of Materials Science* **24**, 5, 1665-1669.

23 Bradley W.L., Chiou P.-L.B., Grant T.S. (1993) The effect of seawater on polymeric composite materials, *Proceedings of the First International Workshop*, Houston, Texas, 26-28 Oct, in *Composite Materials for Offshore Operations*, Wang S.S., Fitting D.W. (eds), NIST Special Publication, **887**, 193-202.

24 Avena A., Bunsell A.R. (1988) Effect of hydrostatic pressure on the water absorption of glass fibre-reinforced epoxy resin, *Composite* **19**, 5, 355-357.

25 Davies P., Choqueuse D., Mazéas F. (1997) Composites Underwater, *Proc Duracosys, 3rd International Conference Duracosys*, Blacksburg, Virginia, 14-17 Sept.

26 Harper B.D., Staab G.H., Chen R.S. (1987) A Note on the Effects of Voids Upon the Hygral and Mechanical Properties of AS4/3502 Graphite/Epoxy, *Journal of Composite Materials* **21**, 3, 280-289.

27 Le Gac P.-Y., Choqueuse D., Paris M., Recher G., Zimmer C., Melot D. (2013) Durability of polydicyclopentadiene under high temperature, high pressure and seawater (offshore oil production conditions), *Polymer Degradation and Stability* **98**, 3, 809-817.

28 Lefebvre X., Sauvant-Moynot V., Choqueuse D., Chauchot P. (2009) Durability of Syntactic Foams for Deep Offshore Insulation: Modelling of Water Uptake under Representative Ageing Conditions in Order to Predict the Evolution of Buoyancy and Thermal Conductivity, *Oil & Gas Science and Technology - Revue IFP* **64**, 2, 165-178.

29 Choqueuse D. (2012) Experimental study and analysis of the mechanical behaviour of syntactic foams used in deep sea, *PhD Thesis*, Université de Franche-Comté.

30 Frisch H.L. (1970) *Diffusion in polymers*, Crank J., Park G. S. (eds), Academic Press, London and New York, 1968; 452 pg, Journal of Applied Polymer Science **14**, 6, 1657-1657.

31 Park G.S. (1986) Polymer permeability, Comyn J. (ed.), Elsevier Applied Science Publishers, London, 1985, vii + 383, ISBN 0-85334-322-5, *British Polymer Journal*. **18**, 3, 209–210, DOI: 10.1002/pi.4980180315.

32 Xiao G.Z., Shanahan M.E.R. (1997) Water absorption and desorption in an epoxy resin with degradation, *Journal of Polymer Science Part B-Polymer Physics* **35**, 16, 2659-2670.

33 Gaudichet-Maurin E., Thominette F., Verdu J. (2008) Water sorption characteristics in moderately hydrophilic polymers, Part 1: Effect of polar groups concentration and temperature in water sorption in aromatic polysulfones, *Journal of Applied Polymer Science* **109**, 5, 3279-3285.

34 Xiao G.Z., Shanahan M.E.R. (1998) Irreversible effects of hygrothermal aging on DGEBA/DDA epoxy resin, *Journal of Applied Polymer Science* **69**, 2, 363-369.

35 Le Gac P.Y., Le Saux V., Paris M., Marco Y. (2012) Ageing mechanism and mechanical degradation behaviour of polychloroprene rubber in a marine environment: Comparison of accelerated ageing and long term exposure, *Polymer Degradation and Stability* **97**, 3, 288-296.

36 Jacques B., Werth M., Merdas I., Thominette F., Verdu J. (2002) Hydrolytic ageing of polyamide 11. 1. Hydrolysis kinetics in water, *Polymer* **43**, 24, 6439-6447.

37 Matuszak M.L., Frisch K.C., Reegen S.L. (1973) Hydrolysis of linear polyurethanes and model monocarbamates, *Journal of Polymer Science: Polymer Chemistry Edition* **11**, 7, 1683-1690.

38 Chapman T.M. (1989) Models for polyurethane hydrolysis under moderately acidic conditions: A comparative study of hydrolysis rates of urethanes, ureas, and amides, *Journal of Polymer Science Part A: Polymer Chemistry* **27**, 6, 1993-2005.

39 Celina M., Wise J., Ottesen D.K., Gillen K.T., Clough R.L. (1998) Oxidation profiles of thermally aged nitrile rubber, *Polymer Degradation and Stability* **60**, 2-3, 493-504.

40 Celina M., Wise J., Ottesen D.K., Gillen K.T., Clough R.L. (2000) Correlation of chemical and mechanical property changes during oxidative degradation of neoprene, *Polymer Degradation and Stability* **68**, 2, 171-184.

41 Le Saux V., Le Gac P.Y., Marco Y., Calloch S. (2014) Limits in the validity of Arrhenius predictions for field ageing of a silica filled polychloroprene in a marine environment, *Polymer Degradation and Stability*, **99**, 254-261.

Manuscript accepted in November 2013

Published online in June 2014

Cite this article as: P.-Y. Le Gac, P. Davies and D. Choqueuse (2015). Evaluation of Long Term Behaviour of Polymers for Offshore Oil and Gas Applications, *Oil Gas Sci. Technol* **70**, 2, 279-289.