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# Life time prediction of polymer used as thermal insulation in offshore oil production conditions: Ageing on real structure and reliability of prediction

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## Abstract:

Polymers are widely used for passive thermal insulation coatings on steel pipe in offshore oil and gas production. In this industry, structures used in deep sea have to be reliable as they are in service for more than 20 years in a very severe environment: sea water, hydrostatic pressure, temperature. One of the main questions is how to test and predict the lifetime of such structures in the laboratory. This study presents one approach that has been developed to characterize and predict the degradation of polyurethanes used as thermal insulation materials.

Based on results obtained during accelerated ageing of the PU in sea water, a prediction of degradation through the thickness has been set up taking into account the temperature profile in the coating, water absorption and hydrolysis. Validity of this model has been investigated by comparing predictions with experimental data obtained on a real structure that has been aged for more than a year with an internal temperature up to 125°C in water under hydrostatic pressure. Using this prediction, the effect of different parameters (such as coating thickness, internal and external temperature) on the degradation level of a structure has been examined.

**Keywords :** Polyurethane ; Life time prediction ; Hydrolysis ; Offshore ; Thermal insulation; Durability

## Introduction

This paper describes a method to make life time predictions of polymer coating used as thermal insulation on steel pipe in offshore oil extraction. Some papers have been published on the durability of polymers for such applications [1] [2] [3] [4] [5] but often there is no prediction of the long term behaviour, and no ageing on real structures to check prediction reliability.

In a previous paper, the degradation of polyurethane in sea water at high temperature was presented [6]. Using ageing in natural sea water at different temperatures from 70°C to 120°C both water diffusion and hydrolysis kinetics have been characterized. Based on these data, a degradation model of this polyurethane in sea water has now been set up. Using this model it is possible to make life time predictions of a real structure in service conditions taking into account three coupled phenomena:

- temperature profile in the coating,
- water diffusion from the sea water into the polymer coating,
- hydrolysis of the PU.

### *Temperature profile*

The temperature profile in the coating considered here is limited to the steady state. Under these conditions, the temperature profile in the polymer coating can be calculated based on equation 1 using the pipe dimensions and internal and external temperatures [7].

$$T(r) = Ti - (Ti - Te) * \frac{\ln(ri/re)}{\ln(re/ri)} \quad \text{(Eq 1)}$$

where T(r) is the temperature in the coating at a radius r, $r_i$ is the external radius of steel pipe, $r_e$ is the external radius of coating, $T_i$ is internal temperature and $T_e$ is external temperature.

Water content in the coating is calculated considering both water absorption in the polymer and water consumption by the hydrolysis process [8] [9] [10]. From experimental data it appears that water diffusion in this PU can be modelled using Fickian behavior (equation 2) coupled with an Arrhenius equation (equation 3) in order to take into account the temperature effect. At the same time, when hydrolysis occurs, chemical reaction leads to consumption of water present in the material. This consumption is calculated at different temperatures and over time based on a degradation model that has been set up (equations 4 and 5 below).

### *Water diffusion in the polymer*

A Fickian equation that can be used to describe water absorption in PU is as follows:

$$\frac{dC}{dt} = D.\frac{d^2C}{dx^2} \quad \text{(Eq 2)}$$

where D is the water diffusion coefficient (m²/s), C is the water concentration (mol.$L^{-1}$), t is time (s) and x in the position in the sample thickness (m).

In order to take into account the temperature dependence of water diffusion kinetics, an Arrhenius equation is used:

$$D = Do.\exp(-\frac{Ea}{RT}) \quad \text{(Eq 3)}$$

with Do the pre-exponential factor equal to 1.15.10-5 m²/s, Ea activation energy equal to 34.5KJ/mol, R gas perfect constant and T temperature in K.

*Hydrolysis of polyurethane*

The water content profile through the coating thickness is needed to assess urethane hydrolysis kinetics and so evaluate the extent of the degradation over time at different positions. The kinetics of urethane hydrolysis are defined by:

$$d[U]/dt = -k(T).C.[U] \quad \text{(Eq 5)}$$

where [U] is the concentration of urethane linkage in the polymer, t is time, C is the water concentration and k is a hydrolysis kinetics parameter that depends on temperature.

Based on equations 4 and 5, it is possible to assess actual water content in the coating at any time and any position using the following reaction/diffusion equation:

$$\frac{dC}{dt} = D.\frac{d^2C}{dx^2} - k.C.[U] \quad \text{(Eq 6)}$$

This equation has been used many times when degradation is limited by the diffusion of a reactant from the external environment into polymers, especially for oxidation [11] [12] [13].

Based on the approach described above, it is possible to evaluate water content and also degradation level as a function of time and position in the polyurethane coating. However, one of the remaining questions is the reliability of this prediction when applied to a real structure. This paper aims to evaluate the reliability of the model by comparing predicted degradation and experimental degradation measured on a real coated pipe. Therefore, a specific ageing device has been set up to perform ageing of coated pipe under service conditions, i.e. high temperature inside and low temperature outside and hydrostatic pressure loading, for more than a year. This test was performed in the framework of an industrial collaborative program named TIDEEP 2.

## Ageing on a real structure

### *Description of the Structure*

The structure used in this study was a steel pipe with an internal diameter of 10 inches (254mm) and 2m long, coated with 63mm thick PU insulation material. The material used for the coating is a polyether-based polyurethane widely used for passive thermal insulation made by reacting polyether polyol with MDI using 1,4-butanediol as chain extender. Figure 1 shows the structure before ageing.

### *Ageing tank and conditions*

Ageing of the structure was performed in natural water under hydrostatic pressure in a pressure vessel for more than a year (Figure 2). In order to simulate the effect of hot oil, the pipe was internally heated by a heating blanket This blanket was placed directly in contact with the inner surface of the tube and covered the whole internal surface of the tube (ref Bassompierre Scientax 3500W 760*1185 mm). Both internal and external temperature (i.e. water) were controlled and measured throughout the ageing period.
During the first phase of ageing (105 days), internal temperature was fixed at 85°C and then, during the second phase (279 days), this temperature was raised to 125°C (table 1). More details on the ageing protocol can be found in [14].
Ageing conditions and duration are summarized in table 1.

## Characterization after ageing

In order to characterize degradation in the coating at the end of the ageing period, a slice of the pipe has been sampled. Tensile measurements have been performed on 200 micron thick films taken from different positions in the PU coating, as shown in Figure 3.
Specimen geometry was 3 x 10mm². Tensile measurements were performed at 10mm/min using an Instron machine with a 50N load cell.

## Results

### *Characterization of the coating after degradation*

Figure 4 shows the tensile behavior of 200 micron thick films extracted from the coating at different positions. Because samples are not dumbbell shaped, ultimate properties such as elongation and stress at break cannot be considered, thus we will focus on tensile behavior up to 100% elongation.

In the same way as what has been observed during accelerated ageing, degradation of PU leads to a decrease of material stiffness. Moreover, it appears that the closer to the hot pipe the more degraded is the polyurethane due to the temperature profile through the coating thickness. In order to compare experimental results with predictions from the model, a damage factor has been defined as the ratio between remaining urethane bonds and initial urethane bonds in the material, i.e. :

$$\alpha = ([Uo]-[U])/[Uo] \quad (Eq\ 7)$$

This means that when PU is not degraded $\alpha$ is equal to 0 whereas when the material is fully hydrolyzed $\alpha$ is equal to 1. Both remaining and initial urethane concentration are calculated from tensile results in the same way as for accelerated ageing [6]. The alpha value as a function of the position through coating thickness is plotted in figure 5.

Polyurethane degradation occurs mainly close to the hot steel pipe (left side in Figure 5). A clear gradient through coating thickness is observed due to limitation of polyurethane hydrolysis by diffusion of water from the cold side to the hot side. Sample close to water at low temperature (right side in Figure 5) is similar to unaged material. Prediction of this behavior will be considered in the next section.

*Reliability of the prediction*

Using multiphysics sofware (Comsol™), a prediction of the degradation in the coating under the same conditions as experiments has been performed. Modelling parameters are reported in table 2.

External temperature at the coating surface was measured around 12°C with an internal temperature of 120°C. Differences between water temperature (5°C) and actual external temperature is due to water convection at the coating surface.

In the same way as for experimental results and in order to evaluate the reliability of the prediction, the damage factor $\alpha$ has been considered as a degradation marker; figure 6 shows predicted $\alpha$ value as a function of position in the coating for several ageing times. A degradation profile through the coating thickness is observed. In fact, degradation occurs mainly close to the hot pipe (left side in figure 6) but this degradation is limited by water diffusion from the external side of the coating (right side in figure 6).

In order to evaluate the reliability of this prediction a comparison between predicted results and experimental data after 384 days of ageing is plotted in figure 7. It is clear that good correlation is observed between experimental and predicted degradation levels (i.e. $\alpha$ values) and position in the coating thickness. Thus, this model can be used to predict coating behavior under service conditions.

*Lifetime prediction of a structure in service conditions based on this model*

This section is devoted to lifetime prediction of polyurethane coating in service conditions for 20 years duration. Here, an 80mm thick coating has been considered with an internal temperature of 80°C and an external temperature of 5°C (all other parameters are the same as in table 2). Figure 8 shows a profile of the degradation factor through the coating for different ageing durations up to 20 years.

If we consider alpha = 0.5 as an end of life criterion, which is completely arbitrary (this point will be discussed later with respect to limitation of the model), after 20 years about 1cm of the coating is useless, that is to say about 12 %. Using this prediction it is possible to evaluate the effect of different parameters on degradation level in the coating. In the following sections the effects of internal temperature, external temperature and coating thickness on degradation will be investigated.

### *Internal temperature*

Changes in temperature inside the steel pipe affect both kinetic reactions and water diffusion; the effect of internal temperature on the degraded thickness (i.e. thickness where $\alpha$ is higher than 0.5) in the coating after 20 years is plotted in Figure 9.

An increase in the internal temperature in the pipe leads to a large increase in the degraded thickness of the coating after 20 years of service due to faster water diffusion from the external layer and an increase in hydrolysis kinetics.

### *External temperature*

In deep sea exploitation, external water temperature is usually about 5°C, but for some specific shallow water fields the water temperature can be up to 25°C. The influence of external temperature on degradation level in the coating is plotted in figure 10. Furthermore, due to natural convection of water a thermal boundary layer appears at the coating surface. Because of this boundary layer there is a temperature profile between the surface of the coating and external sea water, leading to a real surface temperature which is higher than the actual water temperature.

Because degradation in the coating is limited by water diffusion from external water to the hottest part of the topcoat, an increase in the external temperature leads to an increase in the degradation level. In fact, the external part of the coating can be considered as a barrier material that delays the entry of water into the hot part of the polymer, so if the external temperature is raised the barrier properties decrease.

### *Coating thickness*

Coating thickness for this application is usually chosen based on thermal properties of the structure, nevertheless, when coating durability is an issue it is possible to overcome it by using a thicker coating. Figure 11 shows the evolution of degraded thickness normalized by coating thickness after 20 years with an internal temperature of 80°C and an external temperature at 5°C for different coating thicknesses.

One way to delay water diffusion to the hot part of the coating (i.e. close to the steel pipe) is, therefore, to increase the thickness of the coating on the pipe. Although this solution is costly, it remains an option to improve durability.

### *Limitation of this modeling approach*

In this section, the limitations of the modeling approach will be discussed. There are three major points to be considered: thermal degradation of the PU, limitation of the modeling for a high level of hydrolysis and end life criteria.

Firstly, this prediction does not take into account any thermal degradation of PU, but polyurethane could undergo depolymerization at elevated temperature [15] [16] [17]. The main difference between thermal degradation and hydrolysis is that the hydrolysis reaction requires the presence of water whereas thermal degradation only needs heat. During accelerated ageing of the pipe, the time without water in the hot part of the coating is short whereas under service conditions this time could be much longer and so thermal degradation could be more important. This will lead to an underestimation by the model of the actual degradation in service.

Also, even although it has not been observed during ageing of this material, hydrolysis can be an auto-accelerated process [18] [19] due to the effect of degradation products on the reaction kinetics. This means that the prediction might not be accurate when degradation is well advanced.

Finally, the prediction is made using a damage factor based on a physical parameter, i.e. cross link density in the material, and an arbitrary change in this value. Nevertheless, there is considerable discussion over end-of-life criteria. For this industry, the main issues are when the thermal insulation of the coating decreases, when the coating disbonds from the steel pipe or when cracks occur. The link between these properties and the damage factor is not obvious and needs further investigation.

## Conclusions

Based on results obtained during a previous study on polyurethane ageing in sea water at high temperature, a life time prediction of the degradation of a real coated pipe structure has been made by coupling thermal gradient, water absorption and hydrolysis kinetics. The accuracy of this prediction has been checked by comparison between modeling results and experimental data obtained from a test on a real length of coated pipe that has been aged for more than a year, with an internal temperature up to 125°C in water under hydrostatic pressure. The model has then been employed to examine the influence of several factors on degradation level, including coating thickness, internal and external temperature and could be used to define new accelerated ageing tests but also to limit number of ageing tests on structures that are very costly.

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| Phase | Max temp (°C) | Max pressure (bar) | Total duration (Days) |
|---|---|---|---|
| 1 | 85 | 100 | 105 |
| 2 | 125 | 200 | 279 |

Table 1 : Ageing conditions

| | |
|---|---|
| Internal diameter (mm) | 250 |
| Coating thickness (mm) | 63 |
| Internal temperature (°C) | 85 for 105 days and then 125°C for 279 days |
| Water diffusion coefficient (m²/s) | $D = 1.15.10^{-5} \exp(-34.5.10^{3}/RT)$ |
| Hydrolysis kinetics ($L.mol^{-1}.s^{-1}$) | $k = 8.9.10^{-5} \exp(-115.10^{3}/RT)$ |

Table 2 : Parameters used for the prediction

Figure 1 : Photo of the coated pipe before ageing

Figure 2 : Ifremer ageing tank

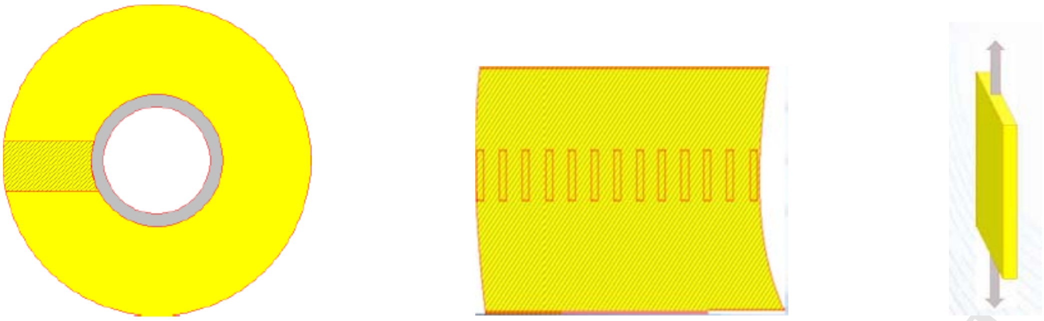

Figure 3 : Schematic representation of sampling in PU coating after more than one year of ageing

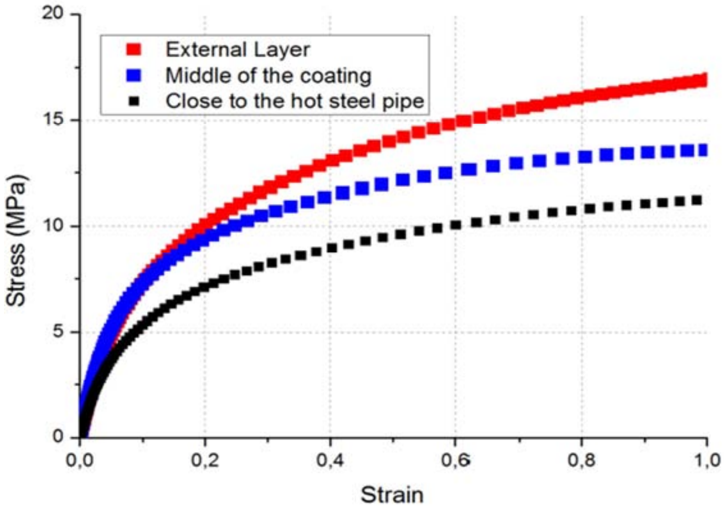

Figure 4 : Evolution of tensile behavior as a function of position in the PU coating (external layer is directly in contact with water)

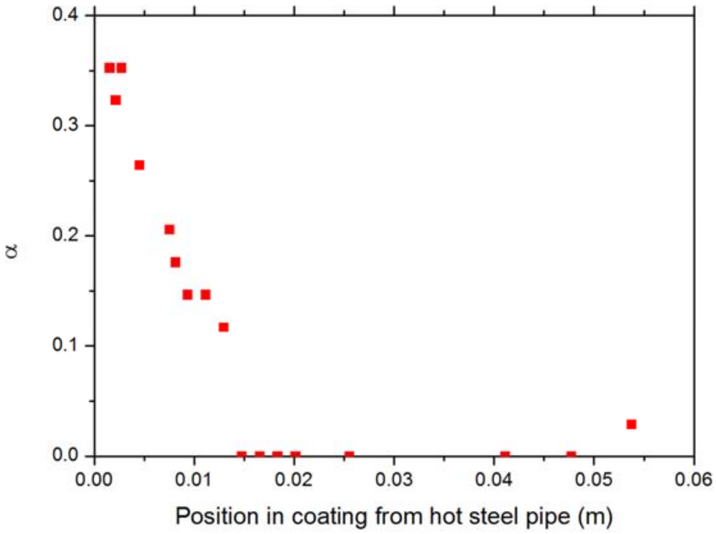

Figure 5 : Degradation profile measured after ageing in the coating used on top of steel pipe

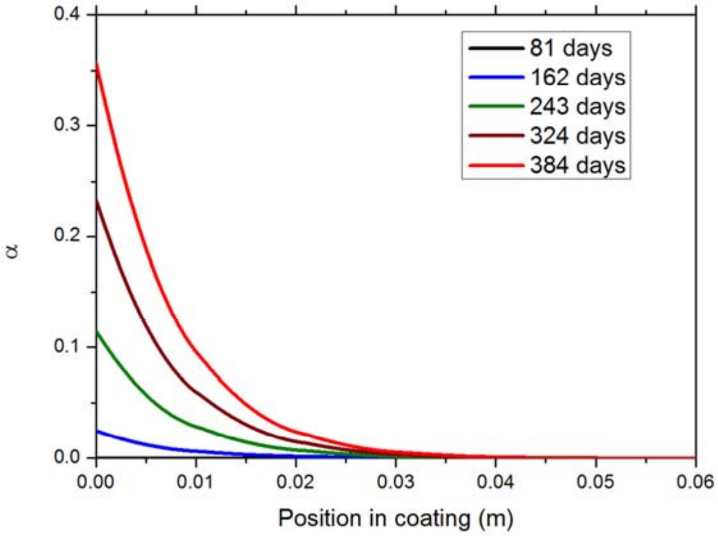

Figure 6 : Predicted degradation level through coating thickness for different ageing times (the hot steel pipe is on the left side, cold water is on the right)

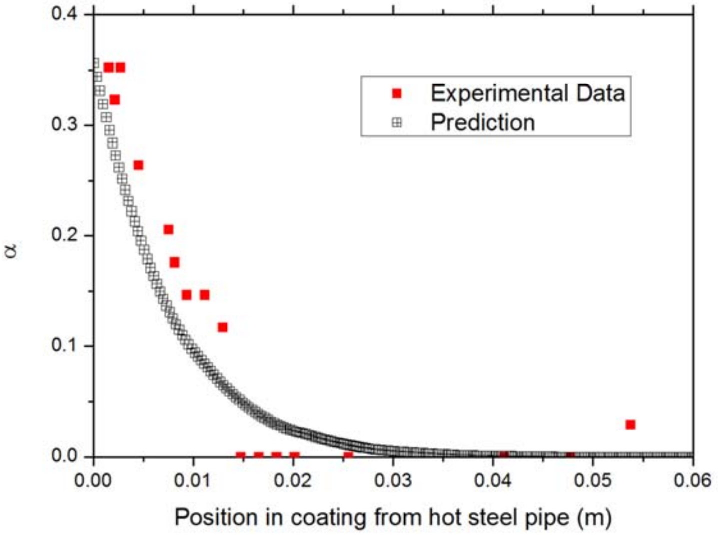

Figure 7 : Comparison between predicted degradation (line) and experimental data after 12 months of ageing

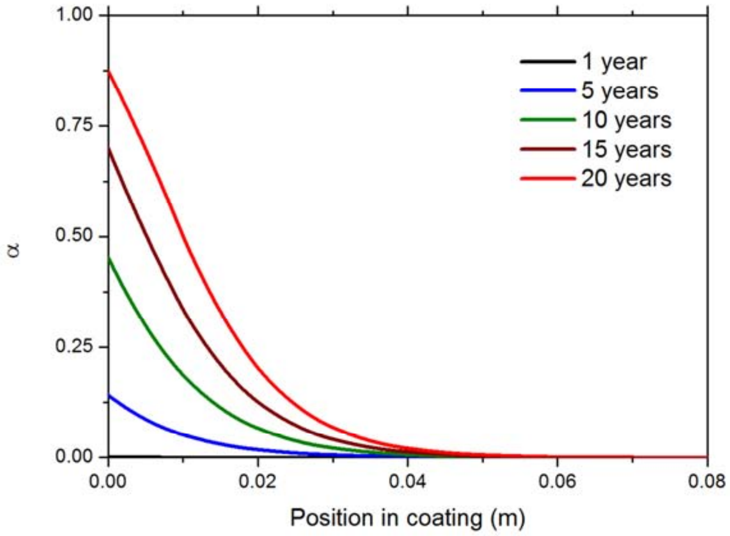

Figure 8 : Degradation profile through coating thickness (hot pipe is on the left side, cold water on the right)

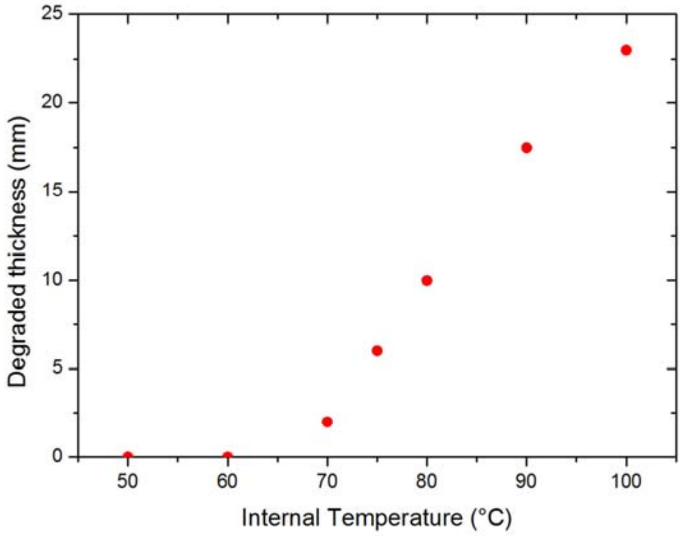

Figure 9: Effect of internal temperature on degraded thickness in the coating

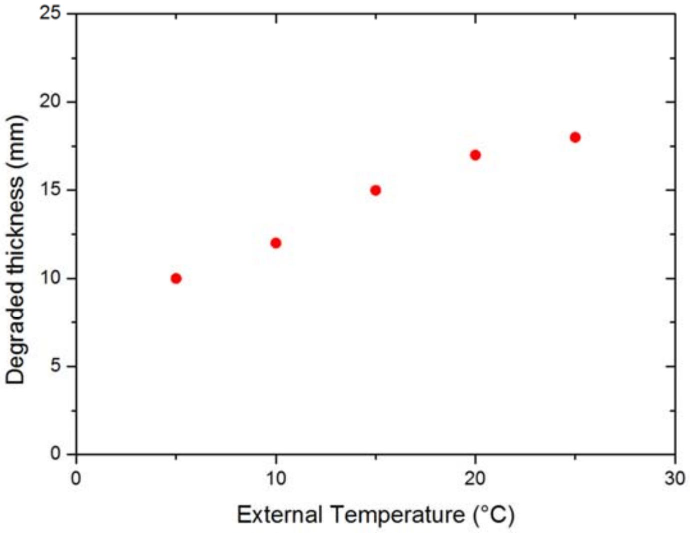

Figure 10 : Influence of external temperature on the degradation level in a 80mm thick coating

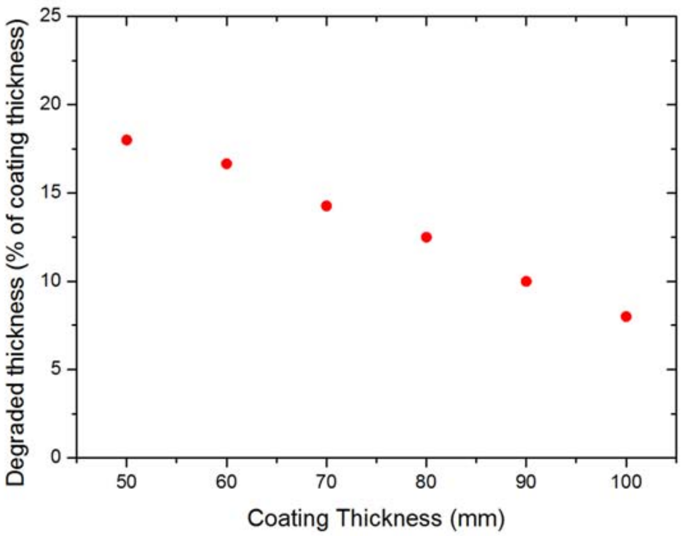

Figure 11 : Effect of coating thickness on degradation level in coating