

**NEUTRON SHIELDING MATERIALS LONG TERM PERFORMANCE: A NEW  
APPROACH FOR MODELING THERMO-OXIDATIVE AGING**

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**ABSTRACT**

Polymeric matrix composites (PMC) are widely used in radioactive material transportation and storage casks. The PMC neutron shielding ability relies on the concentration in hydrogen atoms (to decelerate neutrons) and neutron-absorbing atoms such as boron. However, throughout the service life of the casks and due to severe environments (high temperature for instance), the concentration of hydrogen atoms might fall, and consequently, decrease PMC shielding capability. Therefore, their long term behavior must be accurately predicted. In this regard, Arrhenius law-based models are commonly applied. First, accelerated aging tests (at various temperatures and oxygen pressure) are carried out. Then, without rigorous explanations, short-term experimental data are extrapolated to long periods. To overcome obvious limitations of these models, TN International has launched a multi-year R&D program in order to elucidate the oxidation processes and develop a non-empirical methodology. The “diffusion-limited” character of oxidation reported in several studies is well known. Basically, thin films exposed to oxidative environments become fully oxidized. However, thick samples present a heterogeneous process: a superficial layer is oxidized, whereas the core is not affected. Therefore, in our new numerical model, oxidation kinetics is coupled with oxygen diffusion. It simulates more confidently PMC weight losses (which are then converted into a loss of hydrogen atoms) and oxidation profiles. In this paper, our new model is briefly described, followed by a comparison of simulated and experimental data.

Key words: Neutron shielding, Polymeric composite, Accelerated aging, Oxidation, Numerical model

## 1. BACKGROUND

On the occasion of the last PATRAM Symposium in 2010, we reported our views on how aging mechanisms of polymeric matrix composites (PMC) should be confidently modeled.[1] In fact, before extrapolating accelerated experimental data, accelerated experiments must be planned, aging mechanisms understood, lifetime criteria chosen and predicted.

However, in 2010, we recalled controversies surrounding empirical models such as Arrhenius while predicting PMC lifetime. Since then, as no significant changes have been made by nuclear transportation and storage actors, our criticism has remained intact.

In using these models in our industry, accelerated aging tests are carried out at higher temperatures, often above glass temperature ( $T_g$ ) for glassy polymers or above melting point ( $T_m$ ) for semi-crystalline. Ignoring a series of chemical reactions that yield properties changes, experimental data are simply extrapolated to lower temperatures and protracted durations. This is too risky for reasons pointed out by Gillen, et al. [2]

All criticism put aside, it is worth mentioning that it may work for specific polymers, however. Sometimes, it is conducive to “pure” polymers, especially when the range of temperatures explored is slight and includes service temperature so that there is no need to extrapolate to lower or higher temperatures. In this case, Arrhenius “works” because the activation energy ( $E_a$ ) does not vary too much.

This said, one might keep in mind that most commercial polymers are full of additives, stabilizers, antioxidants, fillers, among others. These additives are usually incorporated into polymer matrices to enhance a given application or function or even durability. The incorporation of additives leads to new properties and, undeniably, to outstanding innovation features. On the other hand, it complicates technical understanding of their long-term behavior. During their service lifetime, stabilizers might diffuse erratically, blooming at the surface of the material and unfortunately leading to non-Arrhenius behavior. [3] In addition, polymer-filler interfaces very often yield additional stability issues and must be checked and correlated to polymer durability.

In the nuclear industry, especially in transport or/and storage casks, neutron shielding materials (NSM) have commonly been integrated for decades. Therefore, robust and accurate simulations are more than crucial in predicting their long-term in-service performance. Even though modeling oxidative aging is not an easy task, at least, its “Diffusion-Limited Oxidation or DLO” character could be considered. Furthermore, chemical mechanisms need to be checked carefully and oxygen diffusion integrated in our numerical models.

This paper focuses on this new approach and completes our preliminary results published during the last PATRAM [1]. First, a kinetic model involving “three steps” of chemical reactions (initiation, propagation and termination) and oxygen permeation parameters are successfully established. The results including weight losses, H depletion over aging time and temperature, as well as oxidation distribution in sample thicknesses will be shown.

## 2. EXPERIMENT

### Material

The investigated polymer material is a TN International neutron shielding material (NSM), *TN Vyal B<sup>TM</sup>*. It is essentially composed of a vinyl ester matrix and mineral fillers. Its outstanding properties have been extensively communicated [1,4,5].

## Procedures

To understand properties changes, a series of experimental characterizations have been carried out on both “unaged” and “aged” samples. These analyses include glass temperature evolution (using DSC and DMA), mechanical tests, weight changes by gravimetric analysis, morphological changes by optical or scanning electron microscopy, and structural changes with IR, among others. In this paper, only gravimetric analysis and oxidation profile determination will be evaluated.

- **Gravimetric analysis**

Gravimetric analysis was performed periodically over aging time using the balance with a relative accuracy of  $10^{-4}$ . Weight changes were calculated as follows:

$$\frac{\Delta m}{m_0} (\%) = \frac{m_t - m_0}{m_0} \times 100 \quad \text{With } m_0, \text{ and } m_t \text{ corresponding to initial weight and weight at aging time } t, \text{ respectively.}$$

- **Oxidation profiles**

Thicknesses of oxidized layers (TOL) were monitored using a comparative analysis of optical microscopy and IR cartography with  $\mu$ ATR imaging. The former is based on color gradients in “aged” samples while the latter provides precise concentrations of oxidation products in the oxidized layer.

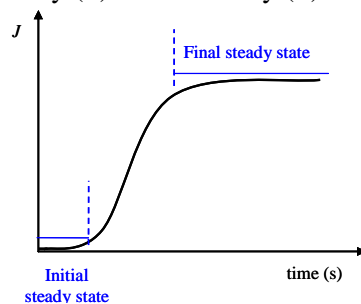
- **O<sub>2</sub> permeation**

As mentioned earlier, oxidation is a diffusion-limited phenomenon. In other words, over aging time heterogeneities can be observed. Therefore, in modeling, oxygen permeation properties in the material must be taken into account. Thus, oxygen permeability (P) and diffusion (D) coefficients were determined experimentally. Tests were performed on an Oxygen Permeation Analyzer with thin films (<615 $\mu$ m). Films were basically clamped in a compartment composed of two half chambers.

After an initial purging step, permeation followed 3 phases:

- Phase 1: O<sub>2</sub> is introduced in the upper half of the chamber, then dissolves in the film*
- Phase 2: O<sub>2</sub> diffuses through the film to the lower half of the chamber*
- Phase 3: O<sub>2</sub> dissolves in the lower half of the chamber. It is directed to the detector by a carrier of pure gas (nitrogen).*

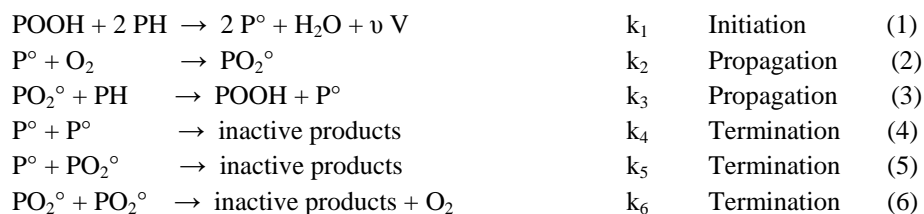
Mathematical calculations were done and curves similar to figure 2 were derived and plotted. Then, diffusivity (D), permeability (P) and solubility (S) were calculated.



**Fig. 1: Example of O<sub>2</sub> Permeation curve**

- **Modeling**

A non-empirical kinetic model was derived from the standard oxidation scheme proposed by Bolland and Gee in the early 1940s [6]. Our model theoretical fundamentals were detailed in a paper published elsewhere [2]. Hence, below, only the mechanistic scheme is indicated.



From this scheme, a system of differential equations is set up to express each concentration species over aging time. The differential equations are coupled with the Fick 2<sup>nd</sup> law,  $\frac{\partial [\text{O}_2]}{\partial t} = D \frac{\partial^2 [\text{O}_2]}{\partial z^2}$ , where D is O<sub>2</sub> diffusion, [O<sub>2</sub>] O<sub>2</sub> concentration in depth x.

Then, a numerical resolution by the Runge-Kutta (Ode23tb of Matlab) finite difference method was then applied.

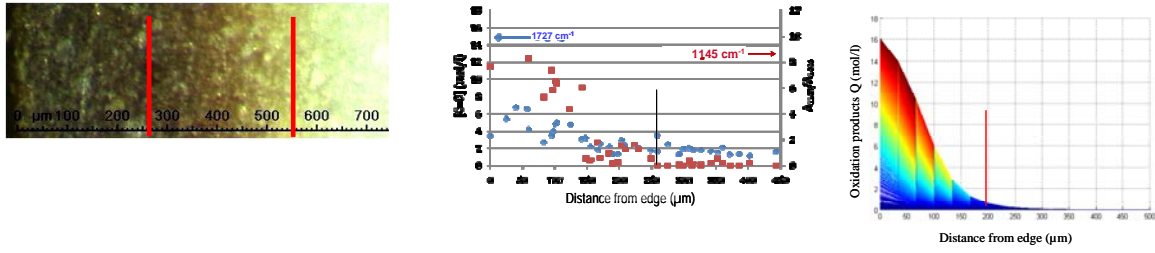
## RESULTS AND DISCUSSION

### TOL measurements

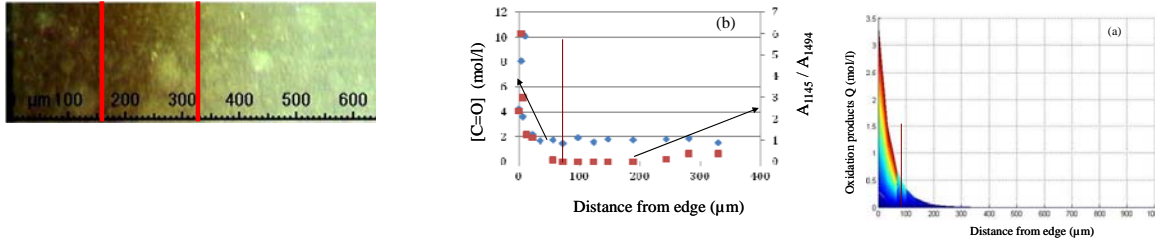
Thicknesses of oxidized layers (TOL) were determined on 2000 micrometer-thick samples exposed to various aging conditions. Some examples of TOL are given in figure 2. By optical microscopy, samples exposed to 160°C displayed 3 parts that are easily distinguishable: “brown” and “yellow” parts corresponding to the TOL are successively observed, whereas a third core is unaffected as the original color (before exposure) remains the same.

As can be seen, TOLs grow faster with increased partial O<sub>2</sub> pressure. Additionally, oxidation products are more concentrated in the “brown” part as revealed by μATR curves (figure 2). At lower temperatures (120°C), however, different behavior is observed. In fact, a “brown” part was not observed. The TOL is only “yellow” indicating a “moderate” degradation. This argument is confirmed by μATR results where the concentrations are a little bit erratic and too low.

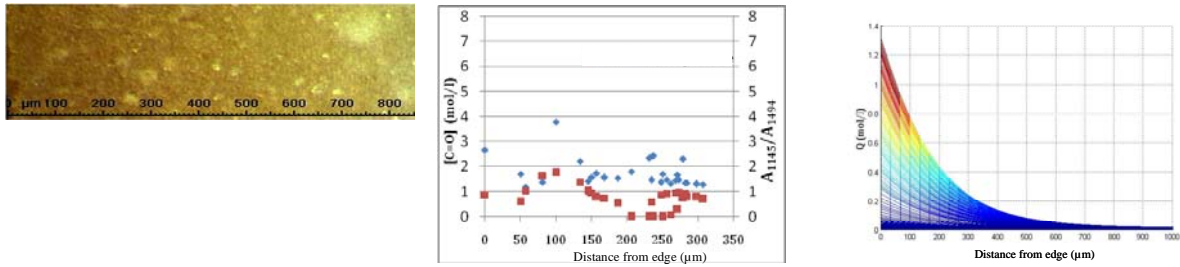
Finally, as shown in figure 2, TOLs experimentally determined by μATR accord with the simulation.



160°C under  $2 \cdot 10^5 \text{ Pa O}_2$ : (left) Optical; (middle)  $\mu\text{ATR}$ ; (right) model



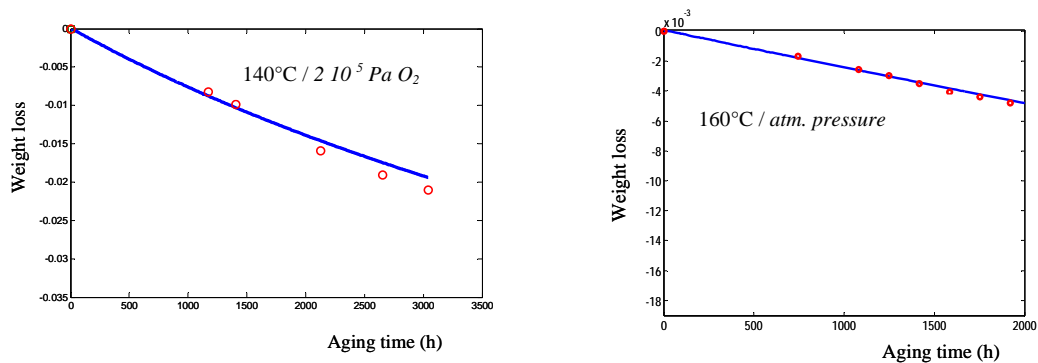
160°C under atmospheric pressure : (left) Optical; (middle)  $\mu\text{ATR}$ ; (right) model



120°C under  $2 \cdot 10^5 \text{ Pa O}_2$ : (left) Optical; (middle)  $\mu\text{ATR}$ ; (right) model  
**Fig. 2: Example of experimental TOL obtained on TN Vyal B<sup>TM</sup> samples exposed to various aging conditions for around 1000 hours:**  
 (a) Optical microscopy; (b)  $\mu\text{ATR}$  and (C) MatLab simulation

### Weight loss

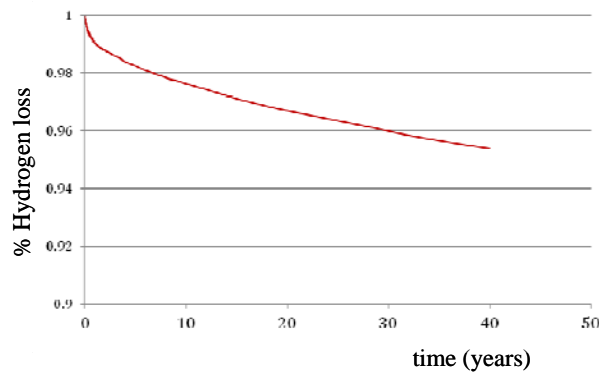
Experimental weight losses for samples exposed to different aging environments were compared with the simulation. Two examples are presented in figure 3, where the similitude between them can be observed.



**Fig. 3: Gravimetric curve of TN Vyal B<sup>TM</sup> with a thickness of 700μm**  
**Comparison with calculated data: (a) 140°C /  $2 \cdot 10^5 \text{ Pa O}_2$ , 160°C / atmospheric pressure**  
**Experiment (●), Model (—)**

### Service life prediction

Based on the results shown above and our model's solid theoretical hypotheses, confident predictions of weight variation can be made at any aging condition and aging time. These weight losses can then be converted into H loss. Figure 4 shows the evolution of H concentration in a sample in service for 40 years at 160°C under atmospheric pressure. H loss is roughly equal to 4.6%. Since in real service conditions, storage for instance, temperatures continuously decrease and neutron shielding is much thicker than 10 mm, H loss is less than 4.6%.



**Fig. 4: Prediction of H content of a TN Vyal B™ sample exposed to 160°C under atmospheric pressure for 40 years  
Sample's thickness considered = 10 mm**

### CONCLUSIONS

Oxidative degradation of polymeric-based neutron shielding materials (NSM) has been proven to be superficial. To predict our NSM long-term properties, relevant experimental characterizations have been performed and a robust kinetic model was successfully applied. Some conclusions can be stated:

- To successfully monitor experimental thickness of oxidized layer (TOL), two complementary techniques (Optical microscopy and  $\mu$ ATR) have been used. Optical microscopy showed a color gradient in the oxidized layer itself in the “aged” samples. Color shifted from “very rough brown” at the edge to “yellow” while the core was not affected.  $\mu$ ATR profiles confirmed the existence of a large concentration of oxidation product at the edge. The concentration decreased progressively through the entire TOL.
- TOL values are associated with weight loss. In other words, higher weight losses were observed for wider and “more browned” TOLs.
- To our knowledge, it is the first time in the nuclear transport/storage industry, that a kinetic model has been applied. This new approach allows a great understanding of neutron shielding long-term performance.
- The interesting results obtained on TN Vyal B™ confirmed the robustness of our model. Therefore, TN International is maintaining its efforts to implement this new approach to other neutron shieldings.

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