# Thermal Ageing of Vinylester Neutron Shielding Used in Transport/Storage Casks

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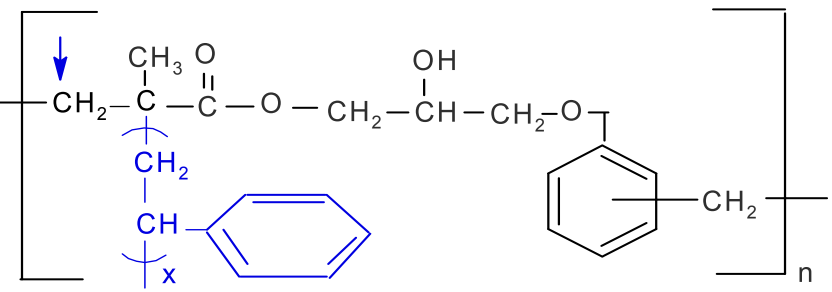
# Background

∗TN Vyal-B composite

**Thermosetting matrix (vinylester) + Mineral fillers**



**Alumina trihydrate (ATH)**

$Al_2O_3,3H_2O$

**zinc borate (ZB)**

$2ZnO, 3B_2O_3, 3.5H_2O$

**highly hydrogenated (hydrogen atoms slow down neutrons), temperature resistant**

**Contains hydrogen, flame retardant**

**Contains boron atoms for neutron capture, and flame retardant**

Service life of the casks: 3 kinds of ageing

**Thermo-oxidation**, radiochemical ageing and hydrolytic ageing

# Background

**Accelerated ageing**:

- 120°C & 140°C: $O_2$ pressure $2\times10^5$ Pa
- 160°C, $O_2$ pressure $2\times10^4$ Pa and $2\times10^5$ Pa

► **FTIR Spectroscopy**: C-H consumption at 2930 $cm^{-1}$ and C=O build-up at 1727 $cm^{-1}$

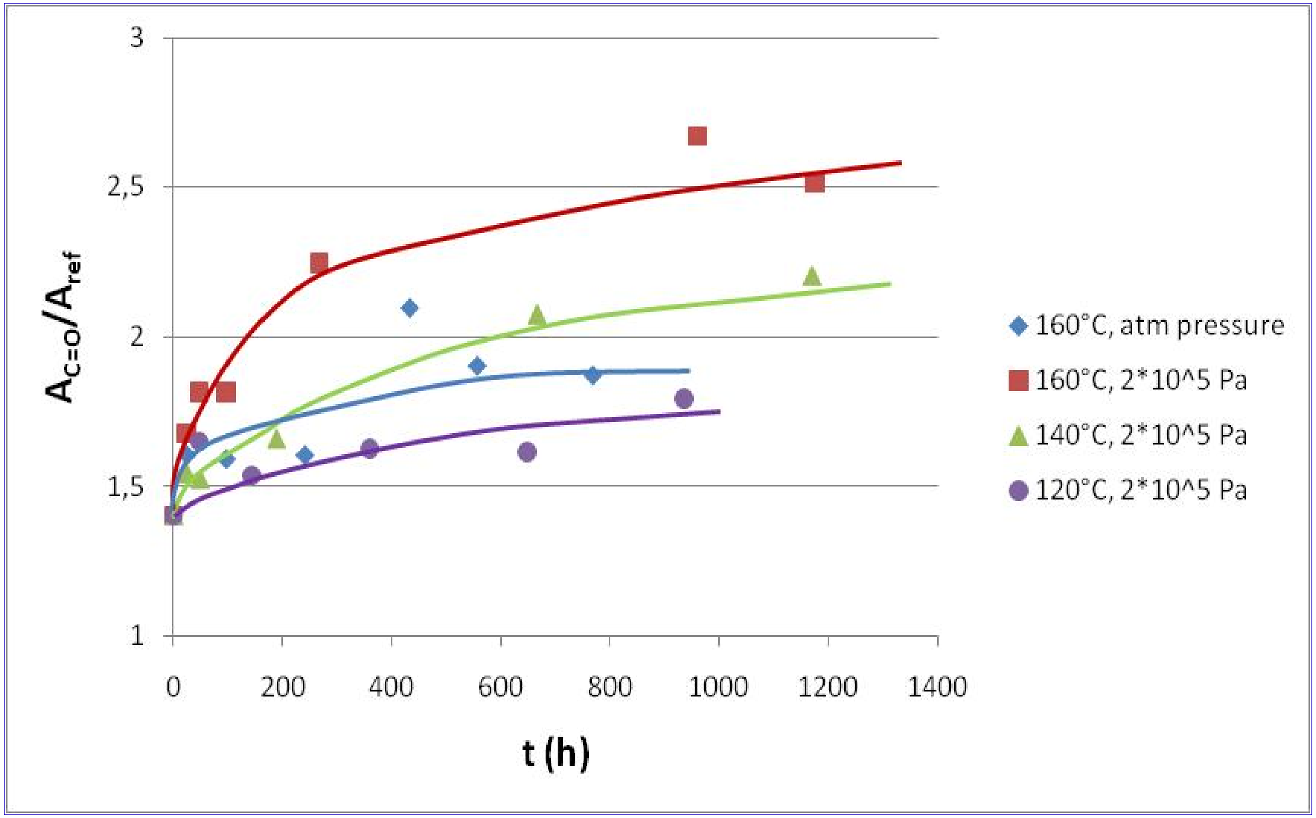
► **Gravimetric analysis:** experimental results and modelling

$$\frac{\Delta m}{m_0}(\%) = \frac{m_t - m_0}{m_0}\times 100$$

► **Mechanical analysis** (three-point flexural test) in accordance with NF T51-001: **Flexural modulus (E)** and **ultimate stress ($\sigma_R$)**

$$E = \frac{D^3}{4\times b\times h^3}\times\frac{F}{\gamma} \qquad \sigma = \frac{3\times F\times D}{4\times b\times h^2}$$

# FTIR Spectroscopy

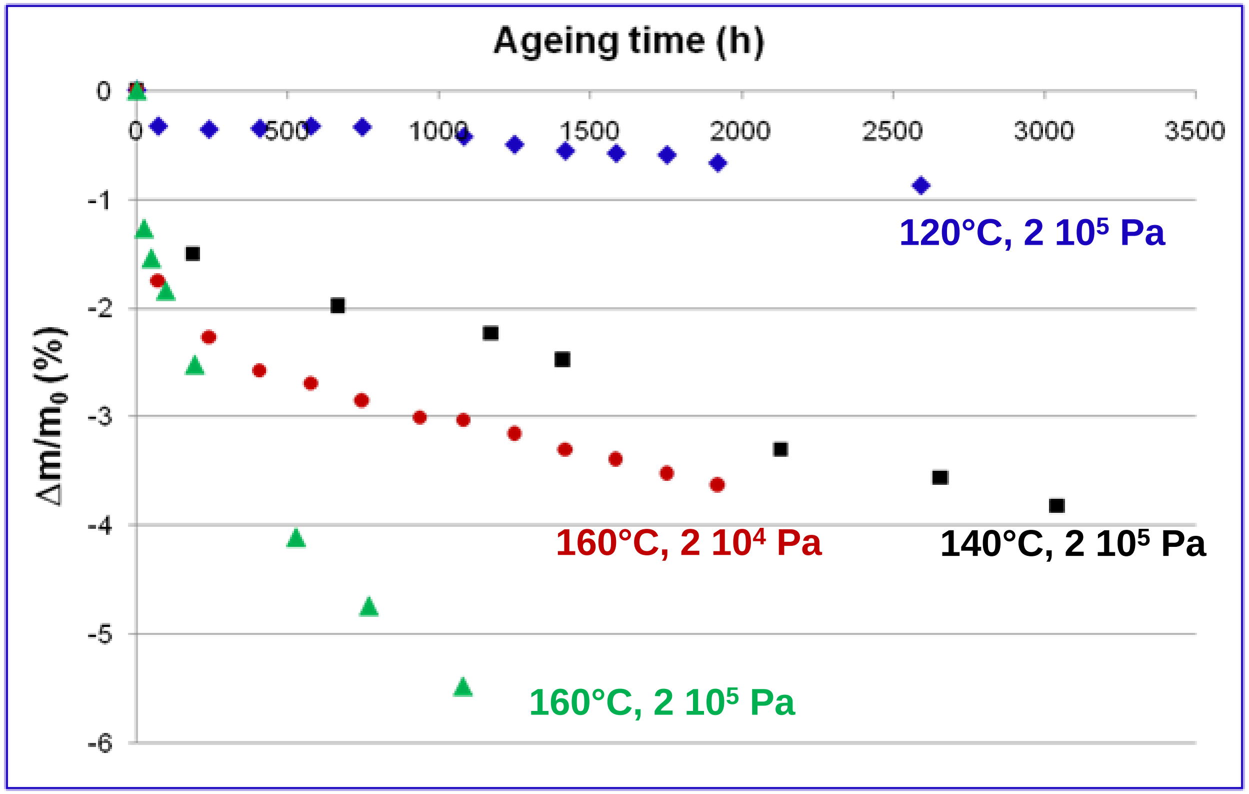



Ref: aromatic C=C stretching abs(1494 $cm^{-1}$)

$O_2$ pressure accelerates carbonyl group build-up:

at 140°C and 160°C, $P_{O2}$ $2\times10^5$ Pa, [C=O] > values obtained at 160°C under atmospheric pressure.

# Gravimetric analysis



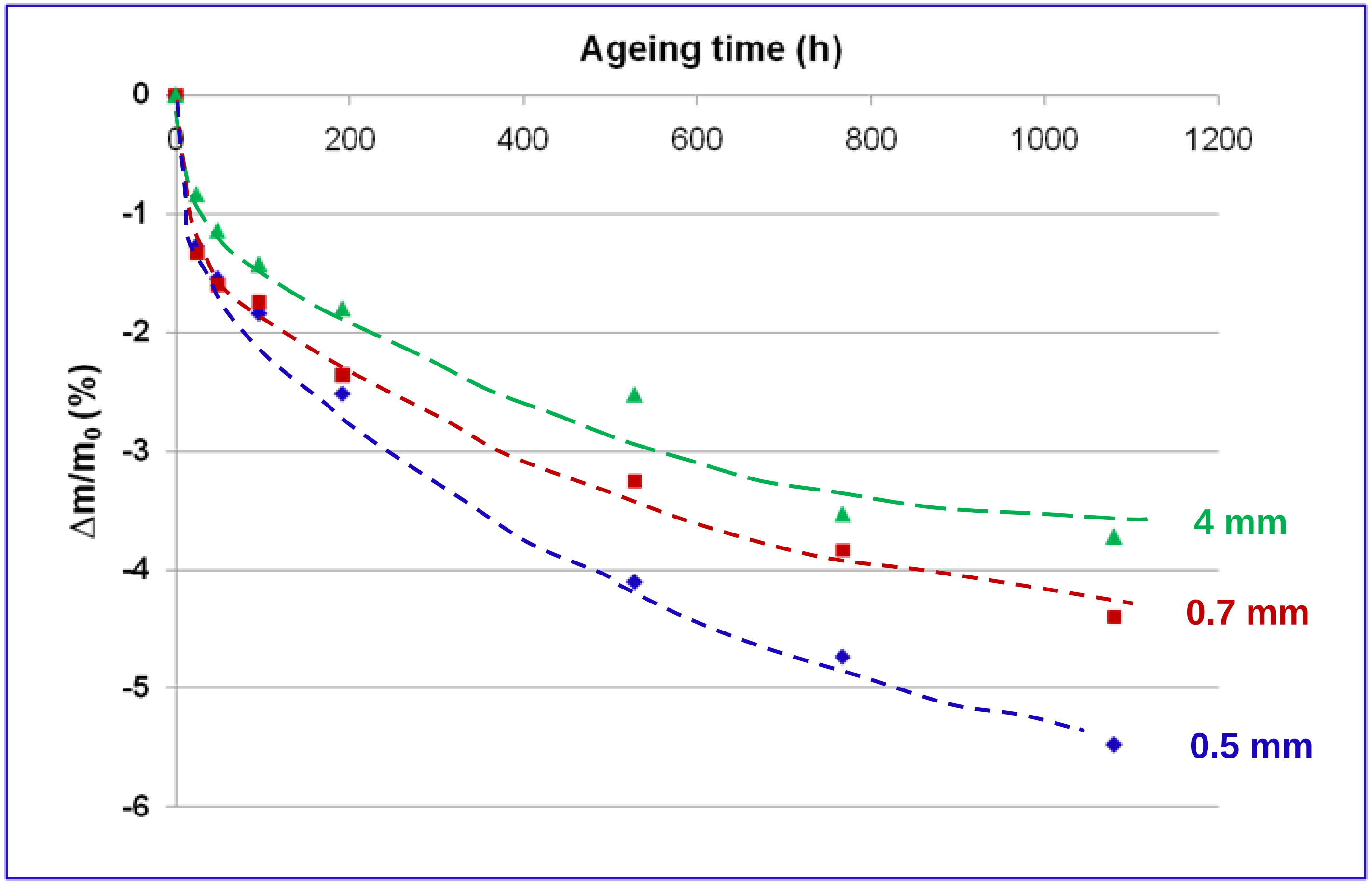

Specimen size
25*0.5mm

► Temperature and $O_2$ pressure accelerate sample weight loss

► t < 48h: higher weight loss rates, mostly extraction (volatility) of low molecular weight species and residual unreacted components (accelerator, styrene...)

► t > 48h: progressive weight loss rates, this second phase of weight loss is due only to the thermo-oxidative process

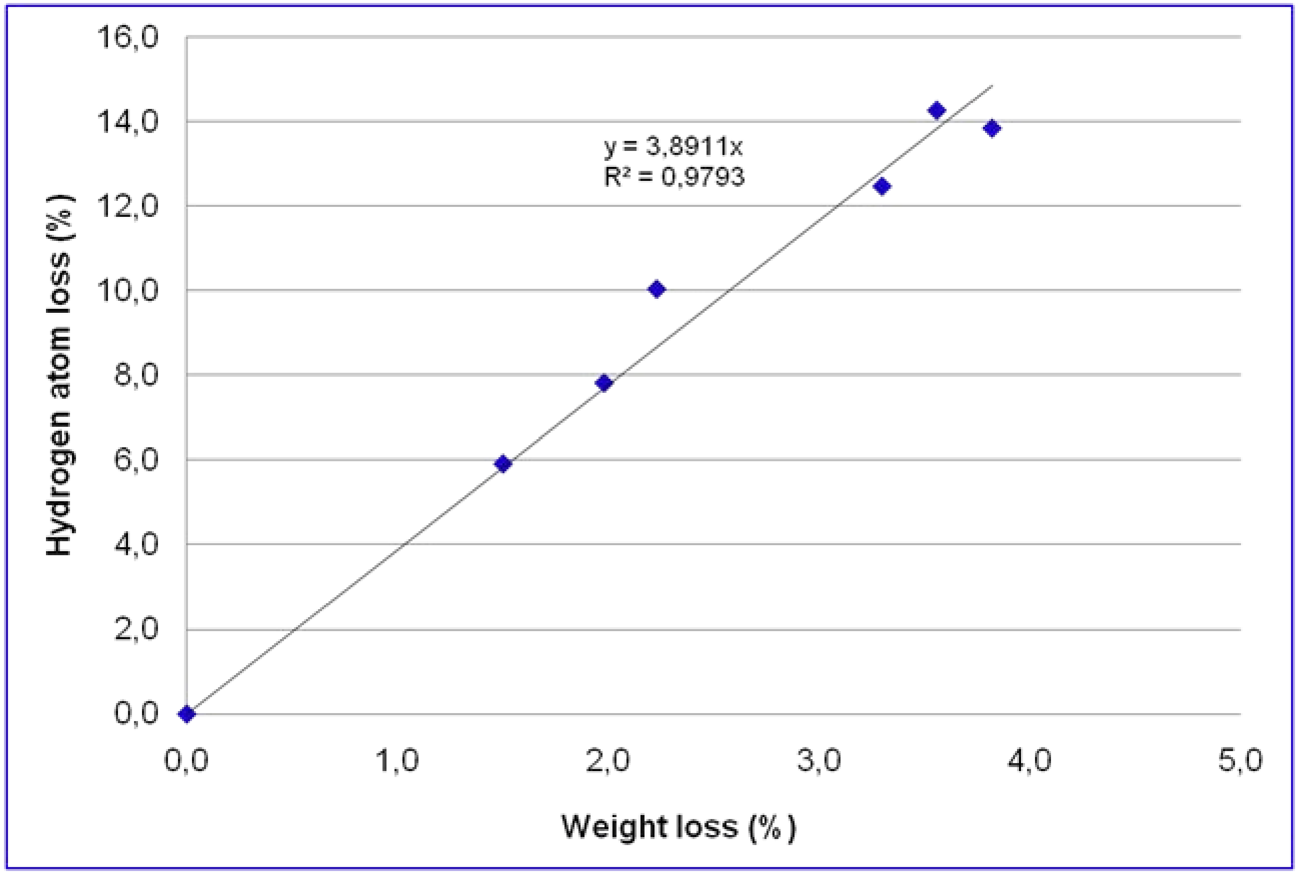
# Gravimetric analysis




160°C, 2*10^5 Pa

**Effect of specimen thicknesses**

# Gravimetric analysis




140°C/ 2 bars

Specimen 25*0.5 mm

**Evolution of hydrogen atom loss with overall weight loss**

# Kinetic Modelling

| | | | | |
|---|---|---|---|---|
| $POOH + 2\,PH$ | $\rightarrow$ | $2\,P^\circ + H_2O + \upsilon\,V$ | $k_1$ | (1) Initiation |
| $P^\circ + O_2$ | $\rightarrow$ | $PO_2^\circ$ | $k_2$ | (2) Propagation |
| $PO_2^\circ + PH$ | $\rightarrow$ | $POOH + P^\circ$ | $k_3$ | (3) Propagation |
| $P^\circ + P^\circ$ | $\rightarrow$ | inactive products | $k_4$ | (4) Termination |
| $P^\circ + PO_2^\circ$ | $\rightarrow$ | inactive products | $k_5$ | (5) Termination |
| $PO_2^\circ + PO_2^\circ$ | $\rightarrow$ | inactive products + $O_2$ | $k_6$ | (6) Termination |

# Kinetic Modelling

**Resulting set of differential equations :**

$$\frac{d[P°]}{dt} = 2k_1[POOH] - k_2[O_2][P°] + k_3[PH][PO_2°] - 2k_4[P°]^2 - k_5[P°][PO_2°] \qquad (I)$$

$$\frac{d[PO_2°]}{dt} = k_2[O_2][P°] - k_3[PH][PO_2°] - k_5[P°][PO_2°] - 2k_6[PO_2°]^2 \qquad (II)$$

$$\frac{d[POOH]}{dt} = -k_1[POOH] + k_3[PH][PO_2°] \qquad (III)$$

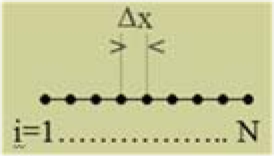
$$\frac{d[PH]}{dt} = -k_3[PH][PO_2°] - 2k_1[POOH] \qquad (IV)$$

$$\frac{d[O_2]}{dt} = \underbrace{-k_2[O_2][P°] + k_6[PO_2°]^2}_{O_2 \text{ consumption rate}} + \underbrace{D\frac{\partial^2[O_2]}{\partial z^2}}_{O_2 \text{ diffusion}} \qquad (V)$$

**$O_2$ consumption rate** | **$O_2$ diffusion**

# Numerical resolution by the finite difference method of Runge-Kutta (Ode23tb of Matlab)

Discretisation of the sample into N knots equally spaced with a distance $\Delta x$




Lines i=1 and i=N correspond to both surfaces of the sample

- Initial conditions (t=0)

i =1,...,N

$$[P°]_i = [PO_2°]_i = 0,\ [POOH]_i = [POOH]_0 = 10^{-4}\ \text{mol/l},\ [PH]_i = [PH]_0 = 40\ \text{mol/l and } C_i = C_s$$

Then the system of differential equations can be rewritten as:

- For each time t > 0 and for i =1,...,N

$$\frac{d[P°]_i}{dt} = 2k_1[POOH]_i - k_2C_i[P°]_i + k_3[PH]_i[PO_2°]_i - 2k_4[P°]^2_i - k_5[P°]_i[PO_2°]_i$$

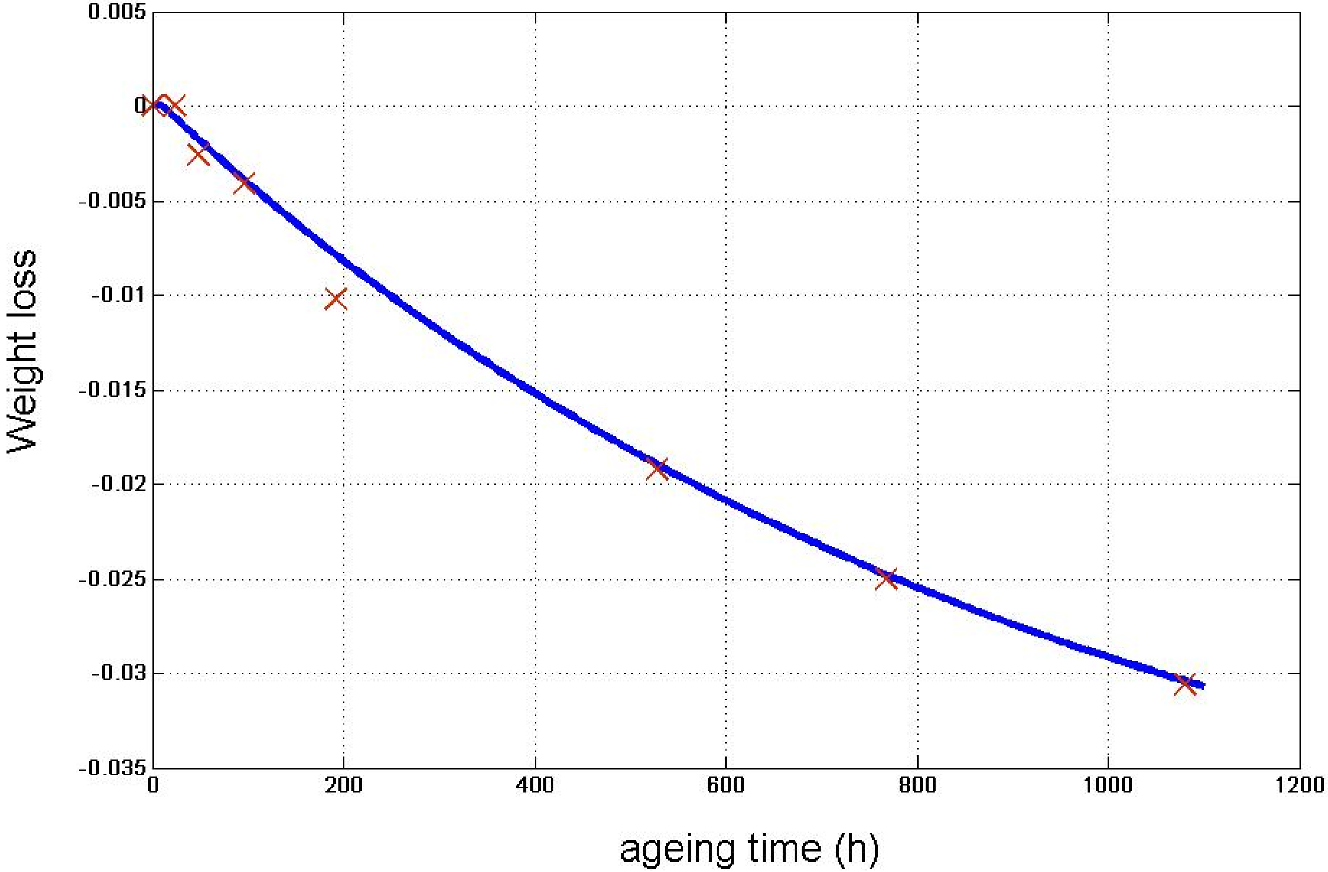
$$\frac{d[PO_2°]_i}{dt} = k_2C_i[P°]_i - k_3[PH]_i[PO_2°]_i - k_5[P°]_i[PO_2°]_i - 2k_6[PO_2°]^2_i$$

$$\frac{d[POOH]_i}{dt} = -k_1[POOH]_i + k_3[PH]_i[PO_2°]_i$$

$$\frac{d[PH]_i}{dt} = -k_3[PH]_i[PO_2°]_i - 2k_1[POOH]_i$$

# Kinetic Modelling

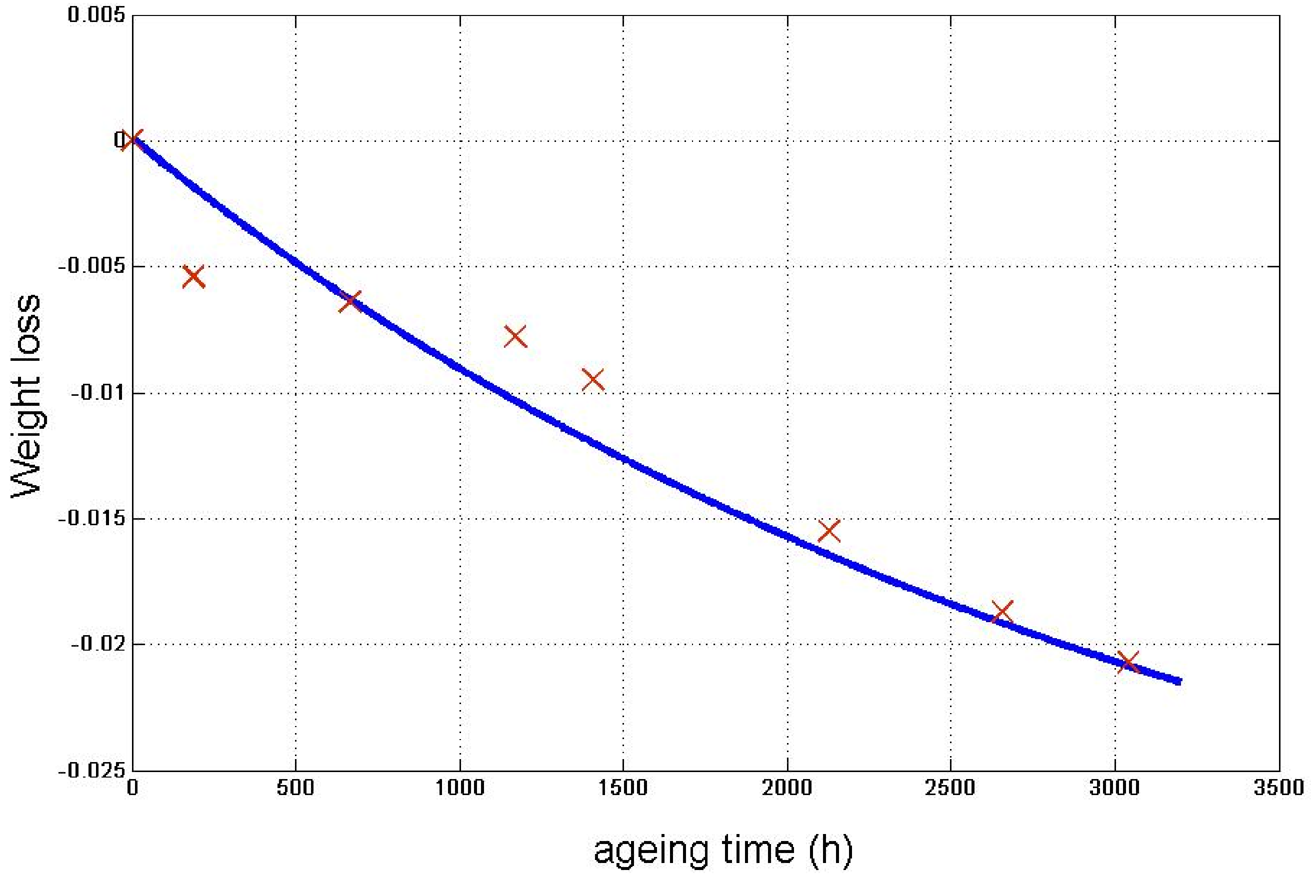
**160°C, $2\times10^5$ Pa of $O_2$ pressure**




**Experimental (x) and simulated (——) weight loss**

# Kinetic Modelling

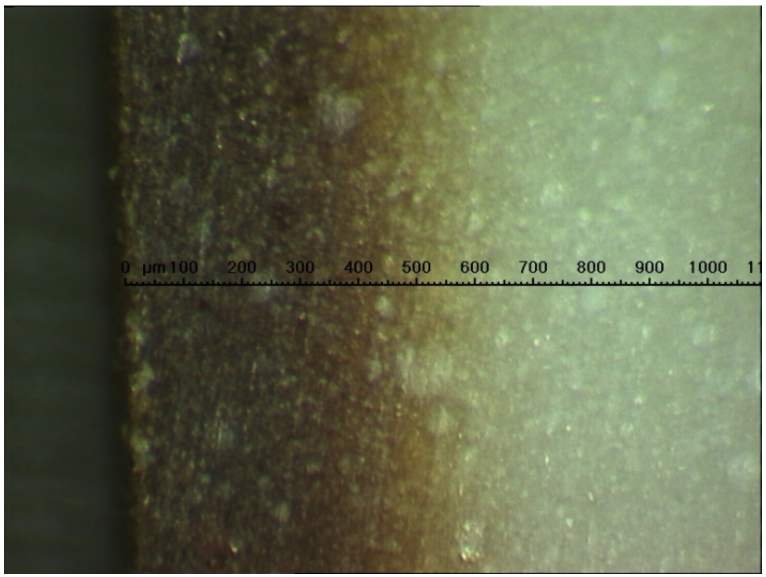
**140°C, $2\times10^5$ Pa of $O_2$ pressure**

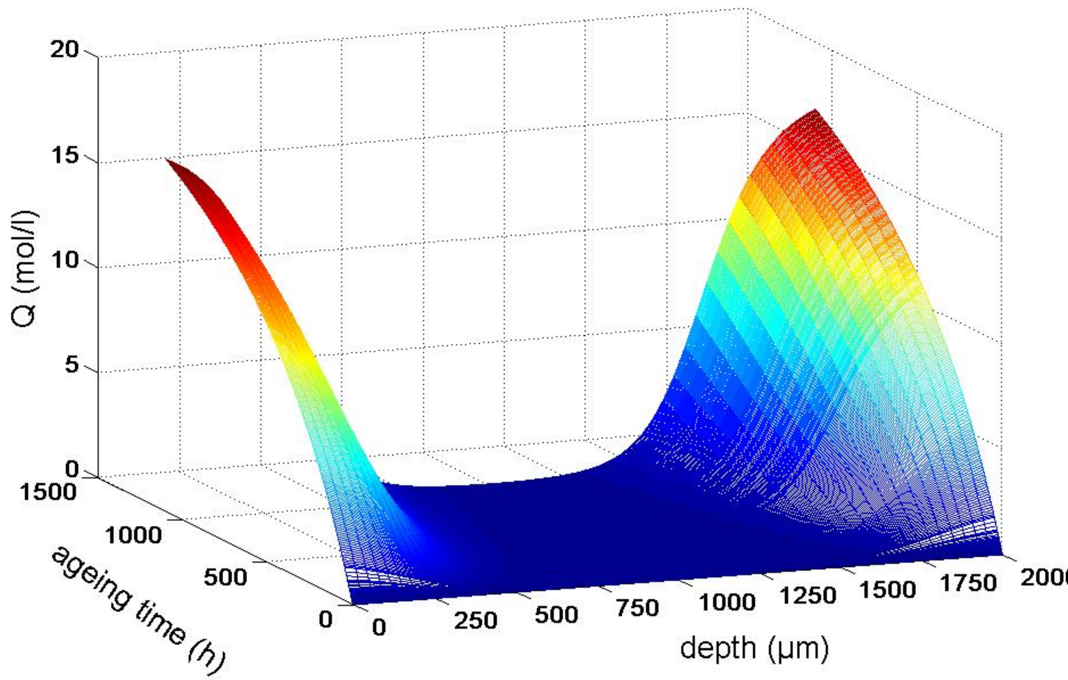



**Experimental (x) and calculated ( —— ) weight loss**

# Oxidised layer thickness for composite

**Profile of oxidation products Q=f(x,t) 160°C, $O_2$ pressure 2 $10^5$ Pa**

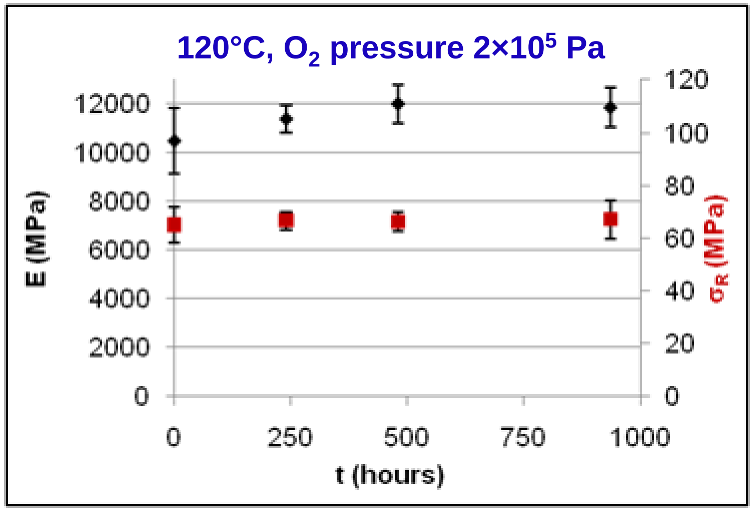


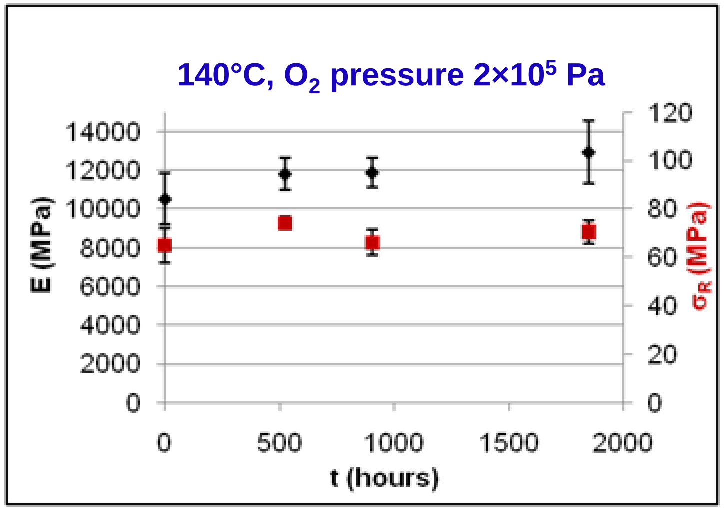



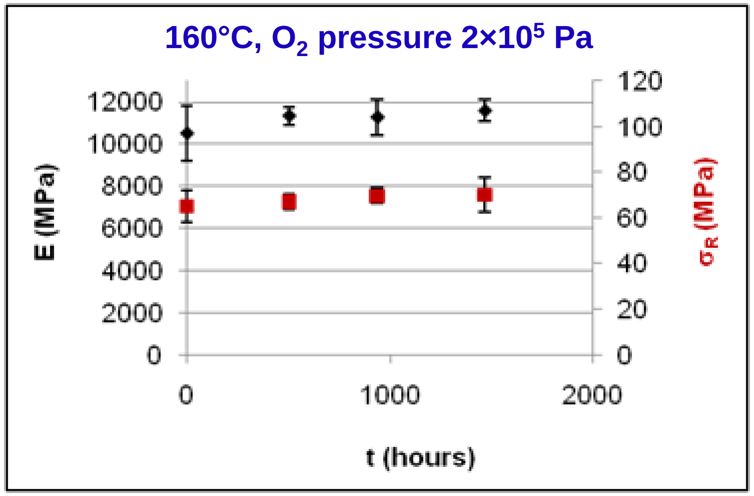

**Specimen 40*25*2 $mm^3$ aged for 1200h**

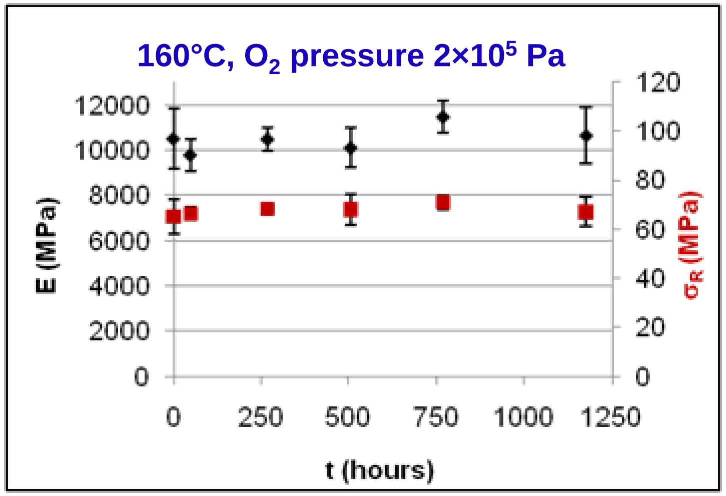
LOGISTICS

# Mechanical properties




**No significant changes of E and $\sigma_R$**

**→ from a mechanical point of view, the material's thermal stability is confirmed**

# Main conclusions and expectations

- Increasing T and $P_{O2}$ accelerate the thermo-oxidative ageing
- Oxidation is a superficial phenomenon
- t<48h: % weight loss mainly due to extraction of low molecular weight species
- After extraction, % weight loss due to thermo-oxidation
- Good match between experimental and simulated data

  for 160°C, $O_2$ pressure $2\times10^5$ Pa
- The next step of our study:
  - numeric modelling of overall weight losses for all studied ageing conditions
  - numeric modelling of hydrogen atoms depletion with ageing time
  - numeric modelling of oxidation products present on superficial oxidised layer