

TOWARDS A NON-EMPIRICAL KINETIC MODELING OF THICKNESS STRUCTURAL CHANGES DURING PETI-330 THERMAL AGEING

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Abstract

The thermal ageing of a neat PETI-330 matrix has been studied between 250 and 380°C under different oxygen partial pressures ranging between 0 and 100% of the atmospheric pressure, by using complementary analytical techniques: high resolution mass spectrometry, thermogravimetry, densitometry, optical microscopy and nano-indentation. In this temperature range, two degradation processes compete: thermolysis and thermal oxidation, leading to a real-time detectable emission of three main organic volatile compounds (benzene, toluene and benzaldehyde). However, thermal oxidation is, by far, the main degradation process, leading to strong mass losses, density increase, and Young's modulus increase in a superficial layer of about 45 and 100 µm thickness respectively at temperatures below and above the glass transition temperature. A radical chain oxidation mechanism, giving an exhaustive description of the chemical changes occurring in the PETI-330 network during its thermal ageing at high temperatures (typically for $T > 250^{\circ}\text{C}$), is proposed. The non-empirical kinetic model derived from this scheme, coupling oxygen diffusion and its chemical consumption, predicts satisfyingly the distribution of oxidation products in the sample thickness and its evolution against time of exposure.

1 Introduction

There is a lack of composite materials dedicated to aeronautic and space applications between 250 and 700°C in Europe. Since the early 1970s, in US, a first family of highly aromatic thermosetting polyimides, named "Polymerisation of Monomer Reactants" (PMR), has been synthesized in order to tentatively fill this gap [1]. But, the dangerousness of one of its constitutive monomers, the 4,4'-methylene dianiline (MDA), was a major obstacle for its commercialisation. Today, a second family of highly aromatic thermosetting polyimides, named "Phenyl Ethynyl Terminated Imide" (PETI), appears as a serious candidate for the production of low cost composite structures displaying high mechanical properties up to about 300°C [2]. But, these latter will be used by airline companies only if their long-term durability is clearly demonstrated.

The present communication is devoted to the analytical and kinetic study of the thermal ageing of a fully crosslinked PETI-330 network between 250 and 380°C under different oxygen partial pressures ranging between 0 and 100% of the atmospheric pressure.

2 Materials and testing methods

2.1 Materials

The PETI-330 powder was supplied by UBE Industries. It is a linear oligoimide of low molar mass ($2500 \text{ g}\cdot\text{mol}^{-1}$) obtained by the alternating copolymerization of three monomers: 2,3,3',4'-biphenyl tetracarboxylic dianhydride (α -BPDA), 4-phenylethynylphthalic anhydride (4-PEPA) and 4,4'-oxydianiline (ODA). Its chemical structure is presented in Figure 1.

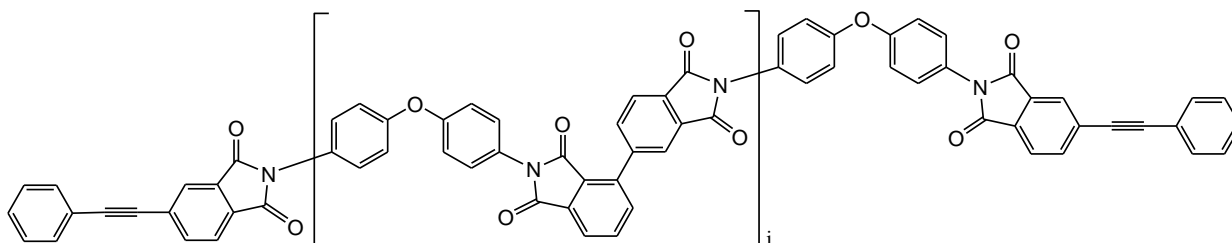


Figure 1. Chemical structure of PETI-330 oligoimide.

This oligoimide is terminated by reactive phenyl ethynyl chain-ends, where the intermolecular then intramolecular additions, between 300 and 350°C , would lead respectively to polydienic sequences [3] and, then, aliphatic polycyclic structures [4].

PETI-330 films and plates (of 150 - $200 \mu\text{m}$ and 2 mm thick respectively) were obtained by press moulding at 320°C during 4 hours. Then, the samples were post-cured at 350°C during 16 hours under primary vacuum in order to reach the maximum crosslinking density while preventing any polymer pre-oxidation before thermal ageing. All the samples were characterized by Fourier transform infrared spectroscopy (FTIR), in a transmission mode, and differential scanning calorimetry (DSC), at a $20^\circ\text{C}\cdot\text{min}^{-1}$ heating rate in nitrogen, prior to testing. The residual triple bonds concentration is about $10^{-4} \text{ mol}\cdot\text{L}^{-1}$, and the maximal glass transition temperature T_g is about 360°C .

2.2 Ageing conditions and test methods

All the samples were stored in the dry atmosphere of a desiccator prior to testing.

The effect of the oxygen partial pressure on the oxidation kinetics was determined by high resolution mass spectrometry (HR-MS, Alyxan BTrap analyser, the principle of this method was presented recently in reference [5]) and thermogravimetry (TGA, TA Instruments Q50 Apparatus) both equipped with a gas diluter (GasMix from AlyTech). The gas diluter was used for elaborating a precisely controlled oxygen atmosphere by mixing two pure gases: nitrogen and oxygen, at atmospheric pressure. In both cases, PETI-330 films were subjected to isothermal exposures at 280 , 300 , 320 , 340 , 360 and 380°C under an oxygen partial pressure ranging between 0 and 100% of the atmospheric pressure in the apparatus cavity, and the signal (concentration of organic volatile compounds for HR-MS, weight changes for TGA) was recorded continuously versus exposure time for each couple (temperature and oxygen partial pressure) of ageing conditions. Complementary investigations under oxygen partial pressures higher than 1 bar were performed at 250°C . But, in this case, the PETI-330 films were exposed in an autoclave and were intermittently removed to be weighted manually. The coupling between oxygen diffusion and its chemical consumption was investigated by 2D imaging techniques. PETI-330 films and plates were subjected to isothermal exposure at 320 , 340 , 360 and 380°C in air-circulating ovens and were removed intermittently to be examined by optical microscopy and nano-indentation after a careful polishing of cross-sections. Optical microscopy examinations were performed using interferential contrast in order to measure the thickness of oxidized surface layer (TOL). Nano-indentation measurements were performed with the indenter of an atomic force microscope (AFM, Veeco apparatus). The force-displacement curve collected during indentation provides indications both on material

mechanical and physical properties. The “indentation elastic modulus” (EIT) was calculated from the slope of the curve at F_{\max} using Equation 1:

$$EIT = \frac{\sqrt{\pi} \cdot \frac{dF}{dh}}{2\beta\sqrt{A_p}} \quad (1)$$

where β is a parameter depending on the indenter type ($\beta = 1.013$ for a Vickers indenter) and A_p is the contact area between the indenter and the sample, projected on a plane perpendicular to the indenter axis ($A_p = 1/2(h \times b)$, h and b being the height and the base of the projected equilateral triangle).

3 Results and discussion

3.1 Elucidation of thermal ageing mechanisms

After thermal ageing of PETI-330 films in both neutral and oxidizing atmospheres, no change in the residual concentration of triple bonds was detected by FTIR. It was thus assumed that, in the temperature range under study, post-crosslinking reactions are negligible.

The gravimetric curves of films obtained at 380°C between 0 and 100% of the atmospheric pressure are reported in Figure 2. In neutral atmosphere, a small but significant weight loss is observed (e.g. about 2.45 % after 110 hours at 380°C), indicating the existence of a slow thermal decomposition of the PETI-330 network. The accelerator effect of the oxygen partial pressure on the oxidation kinetics is clearly highlighted. As an example, under 1 bar of pure oxygen, a strong weight loss is observed (e.g. about 60 % after 20 hours at 380°C), indicating the existence of a rapid thermal oxidation of the PETI-330 network (Figure 2).

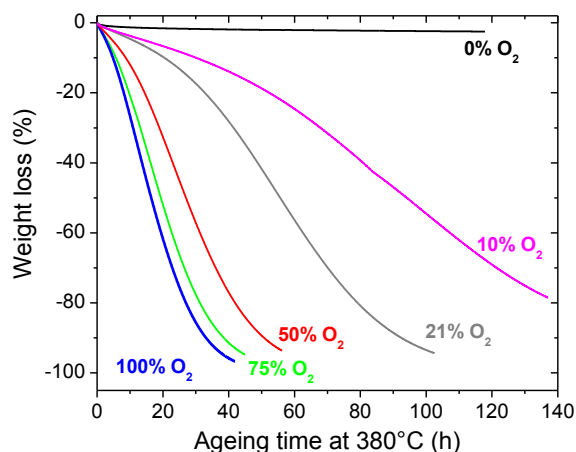


Figure 2. Weight changes of PETI-330 films of about 180 μm thickness at 380°C under oxygen partial pressures ranging between 0 and 100% of the atmospheric pressure.

However, the critical pressure beyond which the oxygen is in excess is greater than 100% of the atmospheric pressure. So, ageing under oxygen partial pressures higher than 1 bar (up to 50 bars) in an autoclave at 250°C have been performed (at 380°C these measurements are unfortunately inaccessible). The films were intermittently removed from the autoclave to be weighted manually. Example of weight losses obtained at 250°C under different oxygen pressures are reported in Figure 3 (left). The maximum weight loss rate has been plotted versus oxygen partial pressure in Figure 3 (right). It appears clearly that oxygen excess is reached above a critical oxygen pressure of about 30 bars.

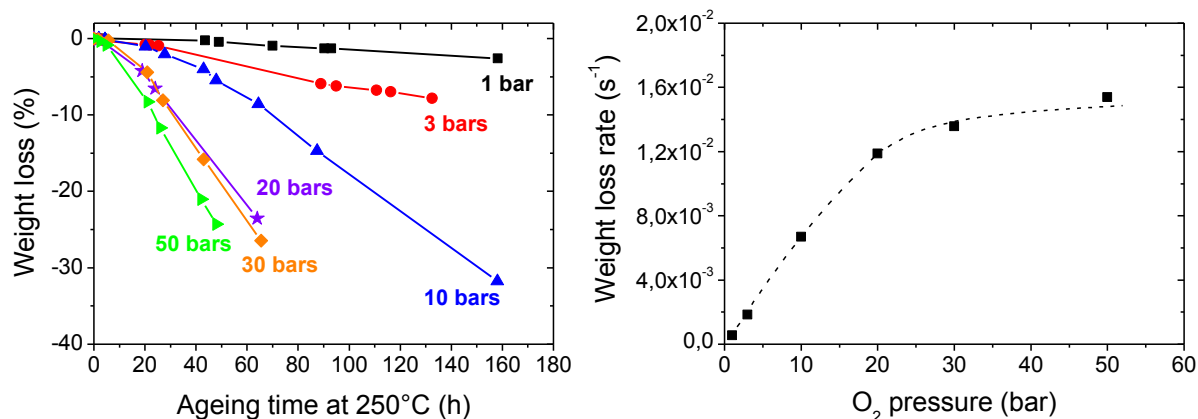


Figure 3. Weight losses of PETI-330 films of about 180 μm thickness at 250°C under oxygen partial pressure ranging between 1 and 50 bars (left). Maximum weight loss rate versus oxygen partial pressure (right).

At 380°C under nitrogen, two main organic volatile compounds (OVCs) formed in a relatively close concentration, have been detected in real-time analysis by HR-MS: benzene and toluene. At 380°C in air ($P_{\text{O}_2} = 0.21$ bar), a third main OVC, formed in almost the same concentration than benzene and toluene, has been detected in real-time by HR-MS: benzaldehyde. The aliphatic polycyclic structures of the ideal PETI-330 network are essentially composed of tetra-substituted carbon atoms. The corresponding C–C covalent bonds are characterized by relatively low dissociation energy, typically 300 $\text{kJ}\cdot\text{mol}^{-1}$, against more than 330 $\text{kJ}\cdot\text{mol}^{-1}$ for all the other aliphatic C–C bonds. The thermal decomposition of these bonds, plus the rapid rearrangement by β scission of the resulting thermally unstable radicals (tertiary alkyl and alkoxy radicals), have been thus considered as the main sources of the detected OVCs.

This assumption has been successfully checked by studying the thermal ageing of a linear commercial polyimide (Upilex-R) having the same chemical structure than the PETI-330 oligoimide, but not being terminated by reactive phenyl ethynyl chain-ends. Indeed, in the temperature range under study, no weight loss and no OVC emission were detected both in neutral and oxidizing atmospheres, confirming that the only weak points of the PETI-330 network are the tetra-substituted carbons of aliphatic polycyclic structures.

Complementary experiments have been conducted by densitometry on PETI-330 films at 380°C in air. The results are presented in Figure 4 (left). Density increases gradually (up to 10.5%) and reaches a final plateau after 24 hours at 380°C in air. According to Equation 2, the increase in density combined with weight losses would induce significant volume shrinkage in the superficial oxidize layer:

$$\frac{\Delta V}{V_0} = \frac{\Delta m}{m_0} - \frac{\Delta \rho}{\rho_0} \quad (2)$$

However, this shrinkage is hindered by the fact that the oxidized layer sticks strongly to the sample core. Considering that, in a first approach, the PETI-330 matrix behaves as an elastic material with an Young's modulus of 3.3 GPa, the order of magnitude of the resulting tensile stress, which develops at the sample edge, can be assessed by combining the Hooke's law and Equation 2:

$$\sigma = E_0 \epsilon = \frac{E_0}{3} \frac{\Delta V}{V_0} \quad (3)$$

This stress reaches the value of the stress at break of the virgin material (i.e. 32 MPa) after about 5 hours in air at 380°C (Figure 4, right). At this time, it is expected that oxidation leads to spontaneous cracking, which is effectively observed by optical microscopy (see below).

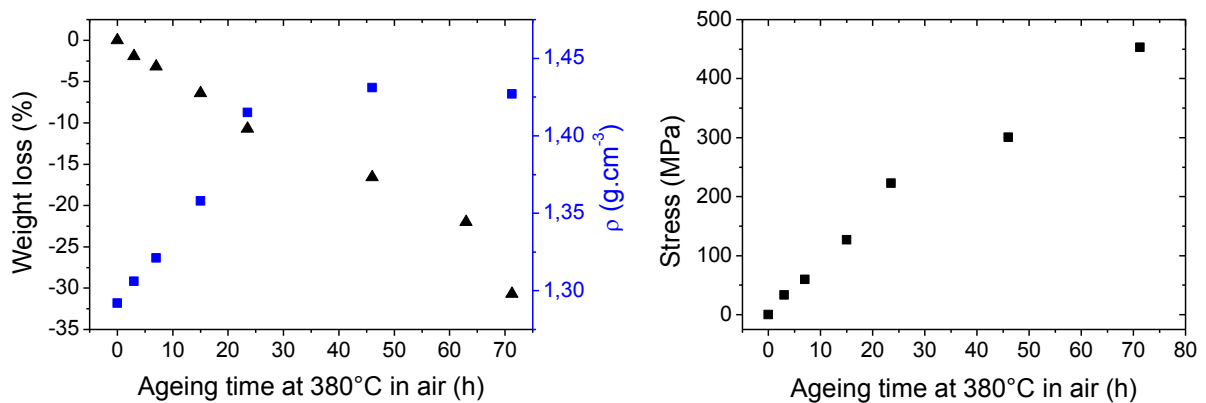


Figure 4. Increase in the density of PETI-330 films (left) and resulting tensile stress at the sample edge of PETI-330 plates (right) versus ageing time in air at 380°C.

3.2 Determination of the thickness of oxidized layer (TOL)

Thick PETI-330 plates were exposed in air during 60 hours at 280, 300, 320, 340, 360, 370 and 380°C. Polished cross-sections were examined by optical microscopy using an interferential contrast in order to distinguish the superficial oxidized layer. This latter appears rougher and brighter than the specimen core. An example of micrograph obtained after 60 hours at 380°C in air is given in Figure 5 (right). At temperature higher than the glass transition temperature ($T_g \approx 360^\circ\text{C}$) micro-cracks appear clearly at the sample edge. Experimental values of TOL are summarized in Figure 5. From 280°C to T_g , TOL is about 45 μm (Figure 5, left). However, above T_g , TOL increases suddenly to reach a value of about 100 μm . This discontinuity on either sides of T_g can be reasonably attributed to a jump of about one decade in the coefficient of oxygen diffusion between glassy and rubbery states, as already shown in the literature for many thermosetting polymers [6].

Moreover, as shown in Figure 5 (right), the length of micro-cracks resulting to spontaneous cracking (as predicted in 3.1) becomes significant, especially above T_g ($L_{\text{max}}=140 \mu\text{m}$ at 370°C). Below T_g , micro-cracks are just restricted in the outer surface of the superficial oxidized layer, whereas at temperatures above T_g , micro-cracks cross easily the skin/core boundary to reach the sample core, allowing oxygen to penetrate into deeper layers.

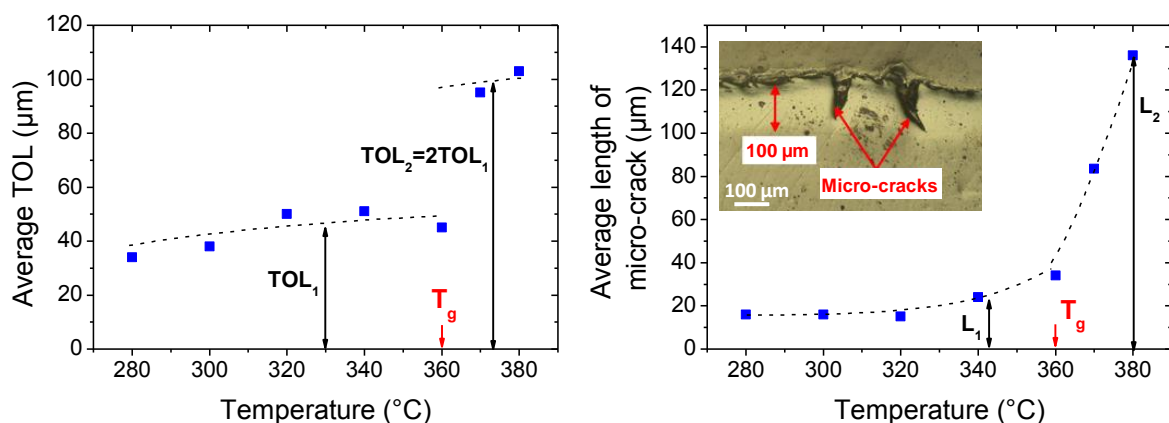


Figure 5. Average thickness of oxidized layer (left) and average length of micro-cracks (right) versus ageing temperature at the sample edge of PETI-330 plates after 60 hours in air.

In Figure 6, values of indentation elastic modulus (EIT) have been plotted as a function of distance from the sample edge after 60 hours of thermal ageing in air at 380°C. Each value corresponds to the average value of three measurement campaigns made far away from specimen corners. It appears clearly that there is an EIT profile at the sample edge. The EIT value at the sample surface is about 52% higher than the EIT value in the sample core. As for optical microscopy, an oxidized layer thickness value close to 100 µm is found.

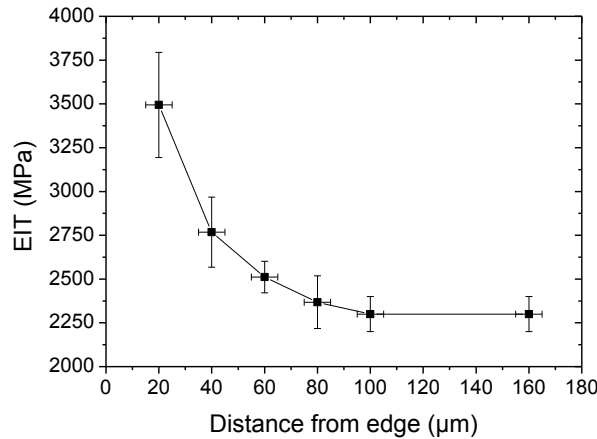


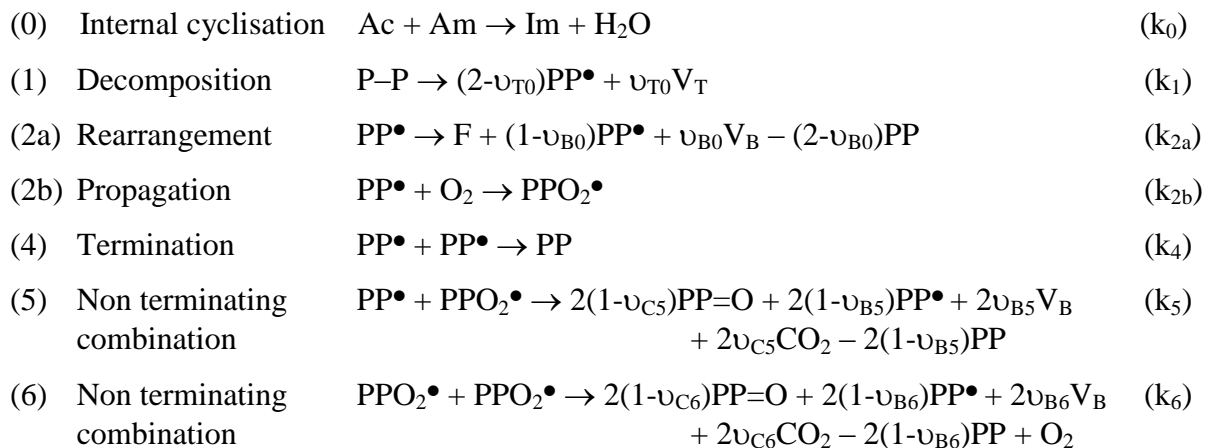
Figure 6. Indentation elastic modulus versus distance from the edge (average values from 20 points) in a PETI-330 plate after 60 hours in air at 380°C.

In fact, EIT is not a true Young's modulus, but a local measurement (at the nanometer scale) of the material stiffness. Thus, the obtained values must be considered with caution. However, these values have been compared to values of storage modulus and Young's modulus measured at room conditions by dynamic mechanical analyses (DMA) and tensile testing respectively: $E_0^* = 3.1$ GPa by DMA, and $E_0 = 3.3$ GPa by tensile testing. Thus, the value of EIT determined by nano-indentation ($2.3 \pm 0,1$ GPa) seems to be quite realistic.

3.3 Kinetic model of mass changes

Starting from this base of results, a general mechanistic scheme has been proposed for describing the general trends of the thermal ageing kinetics of PETI-330 network at high temperature (typically for $T > 250^\circ\text{C}$) at the previous ECCM-14 conference [7].

It is composed of eight elementary reactions. The first one corresponds to the internal cyclization of acid and amide residual groups leading to the formation of water, the two following reactions are relative to thermolysis, and the five last ones are relative to thermal oxidation.





PP designates a weak C–C bond, F a double bond, and PP=O a ketone group; V_{T} , V_{B} and V_{BZ} designate respectively toluene, benzene and benzaldehyde compounds, and ν_{T} , ν_{B} , ν_{BZ} and ν_{C} are the respective yields of toluene, benzene, benzaldehyde and carbon monoxide or dioxide in the considered elementary reactions.

This scheme was validated by HR-MS (checking of OVCs) and was used to simulate the experimental data obtained on thin PETI-330 films between 280 and 380°C under neutral and pure oxygen atmospheres [7]. The first and very fast phenomenon (corresponding to the initial slope on TGA curves) is relative to the internal cyclisation of polyimides chains. This reaction appears to terminate when the temperature is higher than T_{g} . The second phenomenon, mainly responsible for the autoretarded character of TGA curves, is relative to the decomposition of the P-P bonds leading to the formation of the OVCs detected by HR-MS. Kinetics constants were determined from TGA curves using the kinetic model as an inverse method.

Experimental TOL values can be now used to determine the coefficient of oxygen diffusion. TOL have been measured on either sides of T_{g} (Figure 5). Examples of calculated thickness profiles of oxygen and oxidation products for a thick PETI-330 plate aged in air at 380°C are shown in Figure 7. To simulate the TOL in the rubbery state it was necessary to increase the value of the coefficient of oxygen diffusion determined in the glassy state ($D_{\text{O}_2} = 5 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ when $T \leq T_{\text{g}}$) by a factor 24 ($D_{\text{O}_2} = 1.2 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ at 380°C). Of course, these values must be taken with caution. It would be better to measure them directly from permeation measurements rather than using the kinetic model as an inverse method.

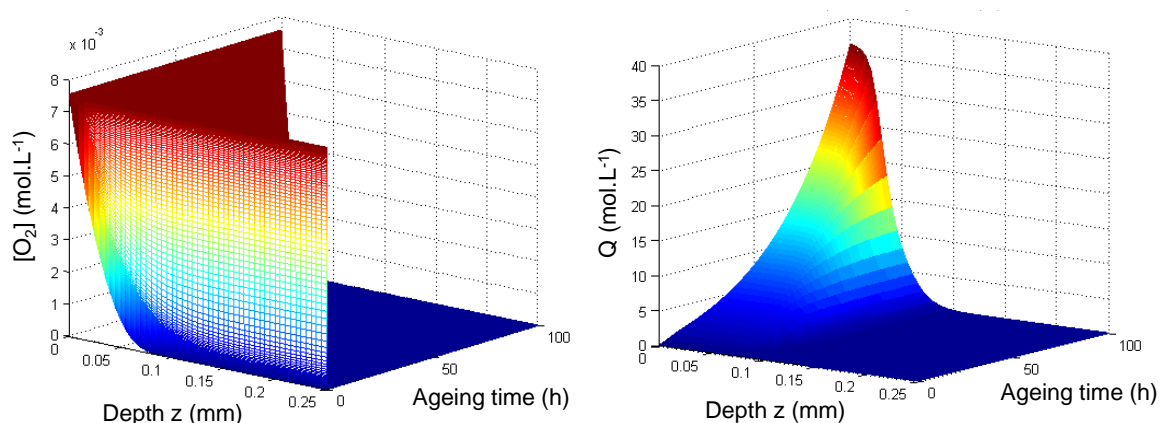


Figure 7. Calculation of thickness profiles of oxygen (left) and oxidation products (right) and their evolution against exposure time for PETI-330 plates in air at 380°C.

4 Conclusion

A non-empirical kinetic model has been elaborated to simulate the thermal ageing of PETI-330 network at high temperature (typically for $T > 250^\circ\text{C}$). This model has been derived from a realistic mechanistic scheme established from the real-time detection by HR-MS of three main OVCs: benzene, toluene and benzaldehyde.

The model validity was checked for PETI-330 thin films in a wide range of temperature at different oxygen partial pressures. Moreover, by coupling the oxygen diffusion and its chemical consumption by a non-empirical way, in particular by introducing directly the Fick's second law into the system of differential equations, the oxidation gradients in thick polymer plates (typically of few mm thick) has been predicted.

The model could be improved, in particular by optimizing the values of its kinetic parameters (rate constants, volatile fragments yields, coefficient of oxygen diffusion and solubility) and

eliminating the last empirical steps for predicting the consequences of oxidation on physical and mechanical properties. At this stage, it appears clearly that gas permeation measurements are essential to validate the values used for the coefficient of oxygen diffusion at high temperature (typically for $T > 250^{\circ}\text{C}$), as well in glassy than in rubbery state.

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