



HAL
open science

Effect of physical and chemical ageing on barrier properties of epoxy coating

Blandine Queennec, Zhibo Duan, Romain Delannoy, Nicolas Gay, Matthieu Briffaut, Vincent Tognetti, Nicolas Delpouve, Laurent Delbreilh, Laure Bredif, Alexis Duthoit, et al.

► To cite this version:

Blandine Queennec, Zhibo Duan, Romain Delannoy, Nicolas Gay, Matthieu Briffaut, et al.. Effect of physical and chemical ageing on barrier properties of epoxy coating. *Construction and Building Materials*, 2023, 409, pp.133908. 10.1016/j.conbuildmat.2023.133908 . hal-04272058

HAL Id: hal-04272058

<https://hal.science/hal-04272058>

Submitted on 8 Dec 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

EFFECT OF PHYSICAL AND CHEMICAL AGEING ON BARRIER PROPERTIES OF EPOXY COATING

Blandine Quelennec¹, Zhibo Duan², Romain Delannoy³, Nicolas Gay², Matthieu Briffaut², Vincent Tognetti⁴, Nicolas Delpouve¹, Laurent Delbreilh¹, Emmanuel Richaud^{3*}

1. UNIROUEN Normandie, INSA Rouen, CNRS, Groupe de Physique des Matériaux, 76800, St Etienne du Rouvray, France

2. Univ. Lille, CNRS, Centrale Lille, FRE 2016 – LaMcube – Laboratoire de mécanique multiphysique et multiéchelle, F-59000 Lille, France

3. Laboratoire PIMM, Arts et Metiers Institute of Technology, CNRS, Cnam, HESAM Université, 151 boulevard de l'Hopital, 75013 Paris, France

4. Normandy Univ., COBRA UMR 6014 & FR 3038, Université de Rouen, INSA Rouen, CNRS, 1 rue Tesnière, 76821 Mont St Aignan Cedex, France

Corresponding author : emmanuel.richaud@ensam.eu

ABSTRACT

This work describes the change of gas permeability of epoxy coatings thermally aged at different temperatures from 50 to 200°C in order to address their barrier properties for protecting concrete in civil engineering industry. Argon permeability characterization tests were carried out on samples either coated on concrete or aged as free standing films. With the increase of time and aging temperature, epoxy becomes more and more permeable and its barrier properties are lost. For better understanding those results, possible ageing mechanisms were investigated. Plasticizer loss was studied by gravimetric analysis and by differential scanning calorimetry. It seems to induce only moderate consequences on barrier and mechanical properties. Reversely, thermal oxidation was shown to severely damage the barrier and mechanical properties due to the existence of chain scissions. Last, structural relaxation ageing is shown to play a negligible role on the investigated time scale but its consequences at longer time remain to be fully understood.

KEYWORDS

Epoxy, ageing, permeability, oxidation, structural relaxation

INTRODUCTION

Epoxy resins are widely used in the civil engineering sector. It is a material easy to process and apply. Epoxy resins can be used as a coating and repair resins. Numerous studies have been carried out to quantify the longevity of these materials [1,2,3]. However, these epoxy resins are subject to severe

environmental constraints: temperature, UV and physical ageing and possibly presence of rainwater (which is not addressed in this paper), all those constraints being at the origin of epoxy failure [4,5,6,7]. Given the high complexity of those superimposed ageing mechanisms, it is important to distinguish the critical mechanisms occurring in service conditions.

Epoxy resins are subjected to qualifications tests to check they meet the requirements of practitioners. They usually consist in ageing at 70 or 80°C monitored by mechanical tests with durations up to 200 days [8]. They are however only few evidences that such tests reflect that properties of epoxy resins will last enough. The effect of physical and chemical ageing on mechanical properties was already addressed in the literature [9] but their effect on epoxy permeability properties remains barely known. These properties are of key interest since epoxies are aimed at protecting concrete from carbonation reactions for example. In other words, a decrease in permeability may induce severe consequence with degradation of concrete.

The permeability values are well documented for many semi crystalline polymers being for example used as food packaging [10] and some structure relationships involved in predicting permeability are also available [11]. They are much more scarcely documented in the case of epoxies [12,13]. At last, the effect of ageing on permeability was scarcely addressed, to the best of our knowledge. According to Gardette et al. [14], the permeability of a PET film is improved after photo-oxidation, possibly because of a crosslinking mechanism or maybe crystallization induced by aging. The case of epoxies is thus interesting for several reasons: epoxies are amorphous polymers which mainly undergo chain scission during their chemical ageing [15].

The aim of this present work consists in investigating the effect of ageing mechanisms being at the origin of failure (either in terms of mechanical or barrier properties) during epoxy use namely (i) the physical ageing by structural relaxation, (ii) the loss of plasticizers (plasticizers being used to allow curing the resin in its entirety at room temperature) and (iii) the thermal oxidation. For that purpose, epoxy coatings were aged at several temperatures and argon permeability tests were carried out on samples. Argon was preferred to CO₂ because it is an inert gas (with no possible reaction with epoxy and subsequent diffusion reaction coupling phenomena) and is closer to an ideal gas which simplifies the exploitation of experimental measures of permeability. Its lower molecular size [16] makes a finer probe of barrier properties of epoxy since, basically, CO₂ will diffuse slower than Argon. In the same time, physicochemical characterization will be performed so as to investigate the occurrence of each sort of ageing and its consequences on permeability properties.

EXPERIMENTAL

1. Materials and curing conditions

Epoxy resin was obtained by mixing a prepolymer of DGEBA type together with a hardener mixture containing triethylene tetramine mixed with a cycloaliphatic diamine hardener. This industrial epoxy system contains also contains benzylic alcohol used as a plasticizer to improve the processing and the curing [17] in practical conditions typically encountered in Public Works field.

Several kinds of samples were studied as described in Table 1 and Figure 1. They were obtained by blending the two-part components (epoxy prepolymer + amine hardener) and casting it so as to obtain the desired shape.

Table 1. Description of samples under study.

samples	manufacturing	Test	picture
cylindric blocks about 1 cm thick	casting of 2 parts components in aluminium cups	microscopic observations for oxidized layer value	SI
20-25 μm films	microtomed from blocks	FTIR, structural relaxation ageing, plasticizer loss by TGA and gravimetry	6-12
H4 dogbones samples	casted in Teflon mould	tensile test	5
0.5-1.5 mm thick disk	Casted into a Teflon mold and stored 12h at 21 °C	Thermal monitored ageing by permeability measurements and plasticizer loss	3, 6
concrete coated with epoxy (epoxy thickness about 300-500 μm)	casting in wood mould. Concrete with a ratio W/C: 0.5. Brush application for epoxy coating	Ageing at temperatures lower than 100°C monitored by permeability measurements	4

The curing was checked by DSC (Q10 apparatus – TA Instruments) at 10°C.min⁻¹ for free standing films given in Figure 1). Curves were acquired to ensure no residual curing exothermal peak was observed at the end of this process (Fig. 1). Glass transition of the unaged samples was acquired both with DSC at 10 °C/min and DMA at 3 °C/min and 1 Hz, and will be part of a later discussion on plasticization. According to Figure 1, it can be concluded that samples are almost fully cured after 48 h at room temperature so that no post curing was added.

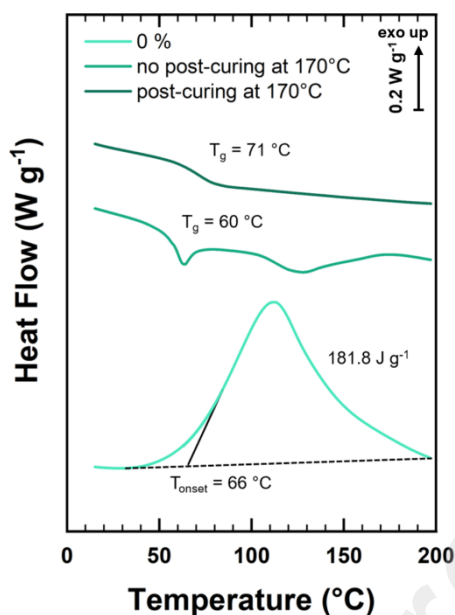


Figure 1. DSC thermograms (1st heating) of epoxy uncured resin and epoxy networks after several curing cycles (48 h at room temperature, 48 h at room temperature + 30 min at 170°C).

Since efficient for thin films, the same curing protocol was followed to manufacture thicker samples to control the diffusion-limited oxidation (DLO) phenomenon with ageing temperature and time. Large disks of about 10 mm thickness were cut in small bricks of about 5x5x10 mm³ and aged at thereafter described temperature and time conditions. Besides, thin samples of 20-25 μm were cut from blocks of epoxy resin (previously cured for 48 h at ambient temperature) using a Leica microtome with a SiC blade.

2. Ageing conditions

For the chemical ageing (namely thermal oxidation) study, samples were thermally aged at 80, 100, 120, 160 and 200°C in AP60 ventilated ovens (Systèmes Climatiques Service, France).

For plasticizer loss, two kinds of ageing were performed

- in situ ageing in TGA cell (described below on paragraph 3.5.)
- ageing in oven monitored by gravimetry

For the structural relaxation, the sample, about 10 mg encapsulated in a DSC pan, was heated up and held 1 min at 200°C to erase any previous thermal history. Then the sample was cooled down to the aging temperature T_{ag} , aged isothermally for aging times t_{ag} ranging from 0 to 6000 min under nitrogen atmosphere, and finally cooled down to 0°C. All ramps were performed at 10°C min⁻¹. For ageing times exceeding 6000 min, the sample was annealed at controlled temperature in a furnace.

3. Characterization methods

3.1. FTIR spectroscopy

FTIR spectroscopy in transmission mode was carried out using a Frontier spectrophotometer (PerkinElmer) by averaging 8 scans at resolution 4 cm^{-1} between 400 cm^{-1} and 4000 cm^{-1} . Absorbances were measured by subtracting baseline and defined as the maximum height of characteristic peaks.

3.2. Tensile tests on thin samples

Mechanical properties of epoxy-amine thin samples were followed by tensile tests using an Instron[®] 4301 machine on at least five samples per exposure condition. Atmosphere temperature was regulated at 23°C , and testing was carried out with a crosshead speed of 1 mm/min .

3.3. Microscopic observation of oxidized layers

After ageing, the brick samples were set in 40 mm diameter cylindrical moulds, then soluble acrylic resin provided by MX-MET was poured onto them to obtain large cylinders of about 2 cm thickness easier to further process. Samples were polished using MecaTech 334 automatic polishing machine with abrasive papers of grades up to 1200. Optical changes of the sample through ageing were visually assessed using a LEICA M80 microscope. Pictures were taken at $\times 2.5$ magnification with the same light intensity to properly discern colour changes.

3.4. Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed with the Perkin Elmer[®] DSC 8500 at $10^{\circ}\text{C min}^{-1}$ from 0 to 200°C . Nitrogen was used as a sweeping gas at a flow rate of 20 ml/min . The temperature calibration was performed using indium and benzophenone as reference standards for melting temperatures. The calibration of energy was done using the enthalpy of fusion of indium.

3.5. ThermoGravimetric Analysis (TGA)

20 mg samples placed in a platinum pan were continuously heated at a $10^{\circ}\text{C min}^{-1}$ rate under a pure nitrogen flow (20 ml min^{-1}). Measurements were performed using a Q50 apparatus (TA Instruments) driven by QSeries Explorer. Data were processed using TA Analysis software.

3.6. Plasticizer loss

Plasticizer loss was monitored for 1 mm plates (initial mass close to $2\text{-}3\text{ g}$). Those latter were regularly weighted after ageing using a Mettler Toledo XS105 Dual range balance.

3.7. Permeability

The permeability tests were carried out on steady flow test method in a hydrostatic cell under confining pressure (see Figure 2). During the permeability measurement, the hydrostatic stress on the material was maintained with confining pressures (P_c) of 3 MPa being applied with a Gilson pump. The gas (Argon) injection pressure (P_i) was set to 1.5 MPa using a gas injection device. At first, the gas was injected in R_1 from a big gas tank, the valve C_1 was closed when P_i reached 1.5 MPa, and valve C_2 , C_3 , C_4 and C_5 remained open. When the gas flow was steady, we close valve C_5 and record an increase ΔP_0 in comparison with P_0 (atmospheric pressure) within a Δt by connecting a Keller Barometer and a computer, which allows the flow rate Q_0 at downstream to be calculated. Using Darcy's law, the gas permeability K_g can be computed as:

$$K_g = \frac{\mu Q_0}{A} \frac{2LP_0}{(P_i^2 - P_o^2)} \quad (1)$$

where μ is the viscosity of argon ($2.2 \cdot 10^{-5}$ Pa·s), L is the length and A is the cross-sectional area of the sample.

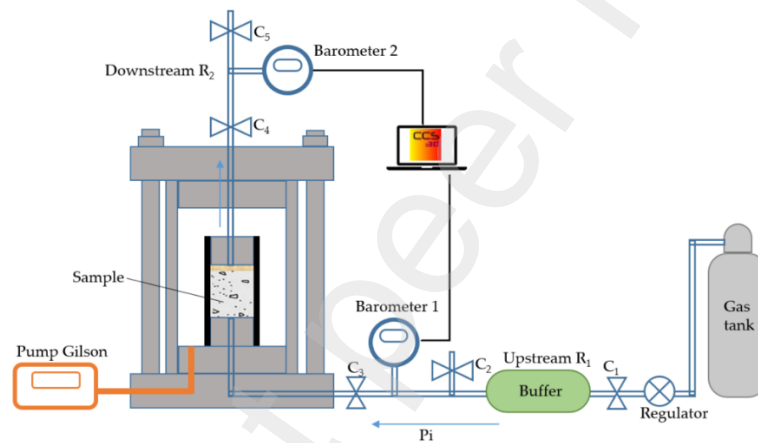


Figure 2. Schematic diagram of steady flow test device.

RESULTS

1. Barrier properties of epoxy coated concrete

Figure 3 depicts typical changes of permeability of epoxy disks after thermal ageing at 100 °C. The value of single epoxy foil is close to 10^{-22} m² [18]. During ageing, it is clear that barrier properties are severely damaged.

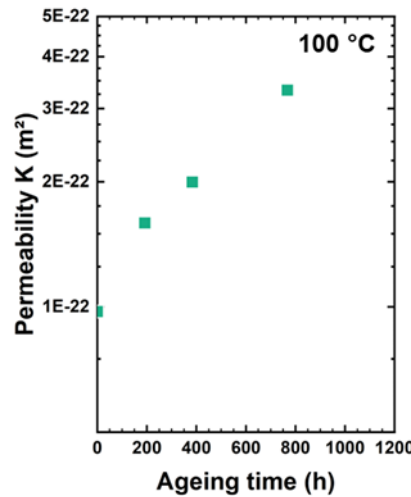


Figure 3. Changes of permeability versus time for epoxy resin after ageing at 100°C.

Those experiments were completed by ageing concrete coated with epoxies assemblies at 50 ,80 and 100°C (pictures are given in supplementary informations-1). Characteristic values can be commented as follows:

- for unaged samples, values of permeability of concrete coated epoxies are observed to be close to 10^{-20} m². This value is consistent with the mixture law:

$$\frac{x_A + x_B}{P} = \frac{x_A}{P_A} + \frac{x_B}{P_B} \quad (2)$$

Where x_A and x_B are the thicknesses of A and B layers (being on the order of 0.05 m for concrete, and 0.0005 m for epoxy) and P_A and P_B their respective permeability being on the order of 10^{-17} m² for concrete (2.59×10^{-17} m² for the concrete used in this work) [19,20] meanwhile the permeability of epoxy is about 10^{-22} m² (see the value for unaged sample in Figure 3). Using Eq. 2, one sees that for unaged sample, the permeability of concrete + epoxy is 10^{-20} m², which is exactly the value observed in Figure 4 for unaged sample.

Here also, during ageing, the value of the permeability increases. For ageing at 100°C, the final value of permeability of epoxy + concrete becomes on the order of the value for pure concrete. The permeability of coatings aged at 80°C is multiplied by almost 10 after 70 days meanwhile at 50°C it does not significantly change after more than 30 days.

After ageing at 100°C, epoxy coating was removed and permeability was measured to assess the changes in concrete. Obtained values ranged between 4.69×10^{-17} m² and 6.49×10^{-17} m². Using those values in Eq. 2 with 10^{-22} m² for epoxy layer, the obtained result is about 10^{-20} m², as for unaged epoxy coated concrete. In other words, it is impossible to describe the changes observed in Figure 5. It means that degradation of the barrier properties observed in Figure 5 is induced by the epoxy layer itself, consistently with observations given in Figure 4. Therefore, we dedicate the following paragraphs to the analysis of the epoxy behavior.

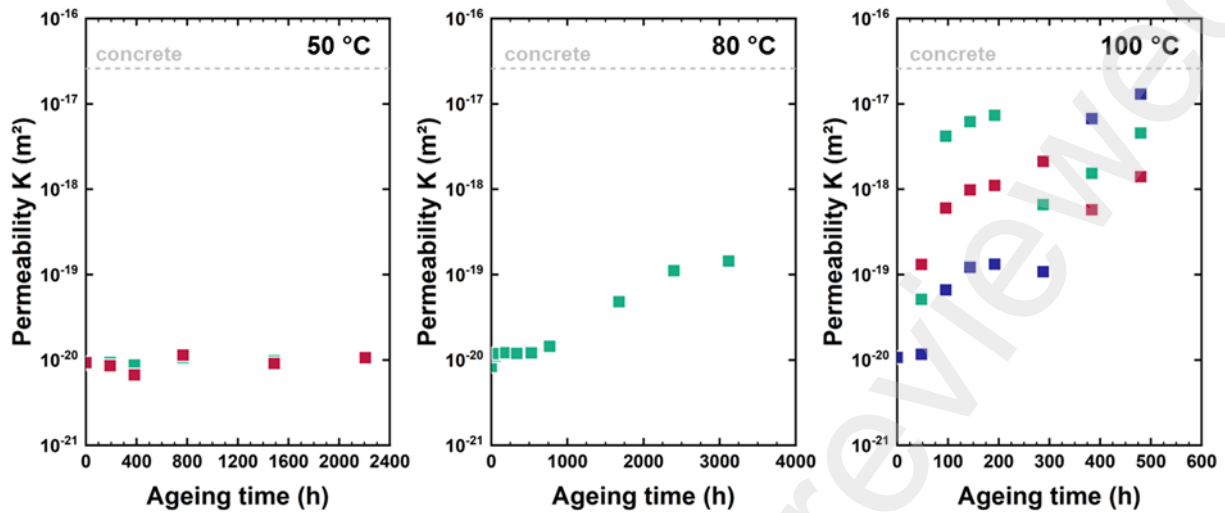
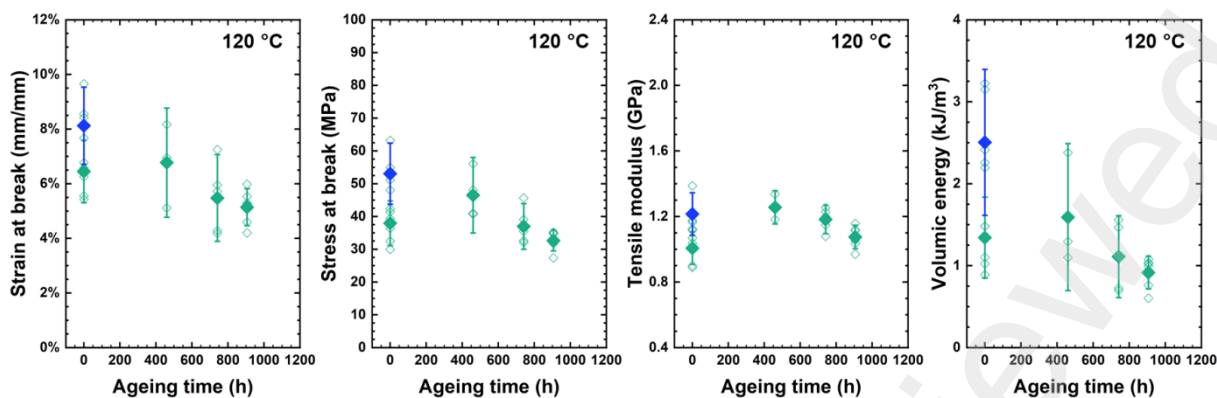


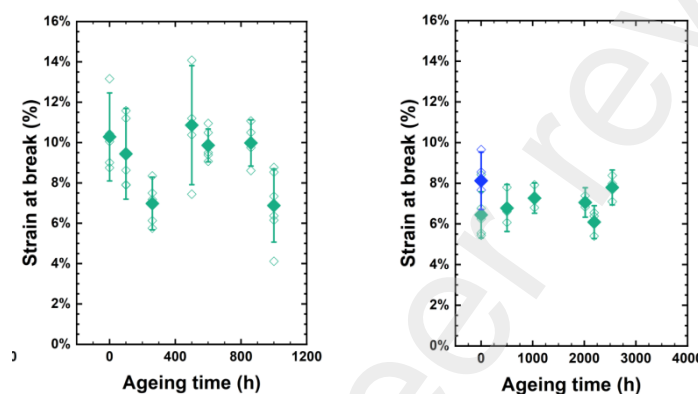
Figure 4. Changes of permeability of epoxy coated concrete after ageing at 100, 80 and 50°C.

2. Mechanical properties of aged epoxy

Stress strain curves were recorded for virgin and aged materials. Changes of mechanical properties were recorded for various ageing temperatures (80, 100 and 120). As depicted in Figure 5a for data at 120°C, thermal ageing induces (i) a slight increase in elastic modulus and (ii) a decrease in stress at break and in maximal (ultimate) strain associated to a decrease of the volumic energy (i.e. the area under stress strain curves). Ultimate strain is an excellent tracker of oxidation induced embrittlement. Its values are also presented in Figures 5c and 5b for 80 and 100°C ageing respectively. It is observed that, even when ageing time is sufficient to induce the loss of barrier properties, there is no strong change of the mechanical behavior.



(a)



(b)

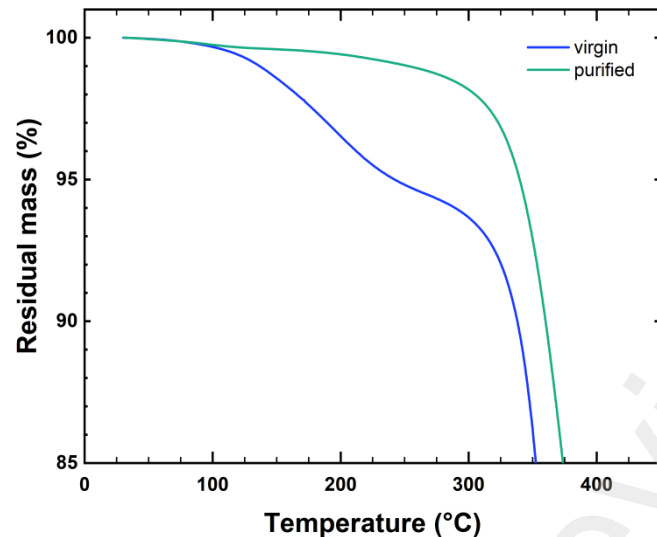
(c)

Figure 5. Changes of mechanical properties for epoxy resin thermally aged at 120°C (a), changes of elongation at break for ageing at 100 (b) and 80°C (c). Blue symbol corresponds to unplasticized resin (see Figure 7) and green ones to plasticized epoxy before and after ageing;

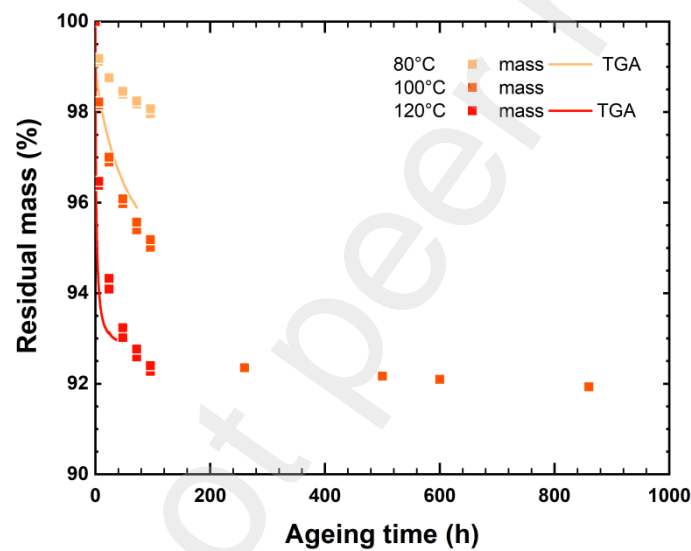
Since the embrittlement (linked to cracking) can be excluded as a reason for the loss of barrier properties, several other processes associated with ageing will be investigated in the following of this paper, allowing to determine which ones are critical for barrier properties.

3. Plasticizer loss

Anisothermal TGA measurements of virgin (formulated with plasticizer) epoxy resin are presented in Figure 6. A first mass loss is detected at temperatures around 100°C. It corresponds to the plasticizer loss (about 6% of the total mass). The residual mass stabilizes at temperatures around 250°C but decreases abruptly at higher temperatures due to the decomposition of epoxy network [21]. A similar experiment was conducted on a sample that was purified from its plasticizers (by an isothermally treatment at 160°C under vacuum prior to TGA experiment). This second experiment only shows the decomposition of the epoxy network at 350°C, and confirms that the first mass loss for “virgin epoxy resin” (at 200°C) phenomenon was ascribed to the loss of a plasticizer.



(a)



(b)

Figure 6. Thermogravimetric analysis of virgin (plasticized) and purified epoxy resin (a) and plasticizer loss during isothermal ageing of plates under air monitored by gravimetry or TGA (b).

It was previously shown that the loss of plasticizer has a minor effect on mechanical properties on free standing unaged samples [22]. It is however possible that plasticizer loss may affect the resistance in the case of aged samples. That is the reason why we investigated the kinetics of plasticizer loss either in situ using TGA cell (on 20 μm thin films) or from gravimetric measurements consecutive to ageing in oven (on 1.5 mm thick plates). Independently on the ageing temperature, the plasticizer loss occurs faster in TGA for thin films, since it is not controlled by diffusion.

For aging at 120 $^{\circ}\text{C}$, the plasticizer loss in thin films is almost total after $t < 10\text{h}$ leading the sample mass to reach a plateau, estimated about 6% of the total mass, in consistency with anisothermal TGA measurements. This duration is slightly longer for thick samples i.e., about 2 days (Figure 6) with a slightly lower plateau. At 100 $^{\circ}\text{C}$, in the case of thick plates, the residual mass reaches a plateau at about 200h. Thus, the residual mass does not evolve from 200 to 1000h ageing. Regarding mechanical

properties, the ultimate strain at break was constant for this aging duration. Regarding barrier properties, the permeability continued increasing from 200 to 600h aging whereas the plasticizer loss is considered total after 200h aging. In other terms, there is no obvious correlation between the plasticizer exudation and the loss of macroscopic properties at this aging temperature. We hence concluded that plasticizer loss cannot be considered as a possible reason for loss of barrier properties in the following.

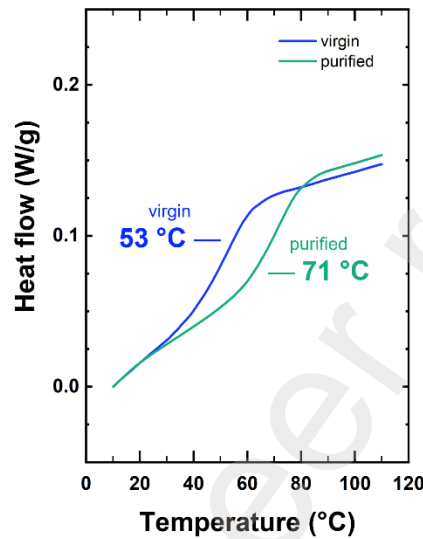


Figure 7. Effect of plasticizer loss on glass transition.

Interestingly, when the plasticizer has been totally removed from the material, the glass transition increase has modified the state of the material at the aging temperature of 80 °C (Figure 7). Indeed, it moved from the rubbery state to the glass transition domain. Thus, after the plasticizer loss, the structural relaxation ageing could not be ignored.

4. Study of structural relaxation ageing

Structural relaxation is detected through the DSC overshoot at the glass transition (Figure 8), from which the ageing advancement can be estimated. The enthalpy of recovery associated to the physical ageing of the sample was calculated by integrating the difference between the scans of an aged sample and a sample with a nil aging time:

$$\Delta H(T_{ag}, t_{ag}) = \int_{T_1}^{T_2} [C_{p_{aged}}(T) - C_{p_{non-aged}}(T)] dT \quad (3)$$

Where T_{ag} is the ageing temperature, t_{ag} is the ageing time, $C_{p_{aged}}(T)$ and $C_{p_{non-aged}}(T)$ are the heat flows of the aged and non-aged samples, respectively, which are normalized to both sample mass and heating rate in order to be expressed in units equivalent to specific heat capacity. T_1 and T_2 are temperatures arbitrary chosen, beyond the start and ending of the glass transition respectively, and for which the curves of aged and unaged epoxy are perfectly superimposed.

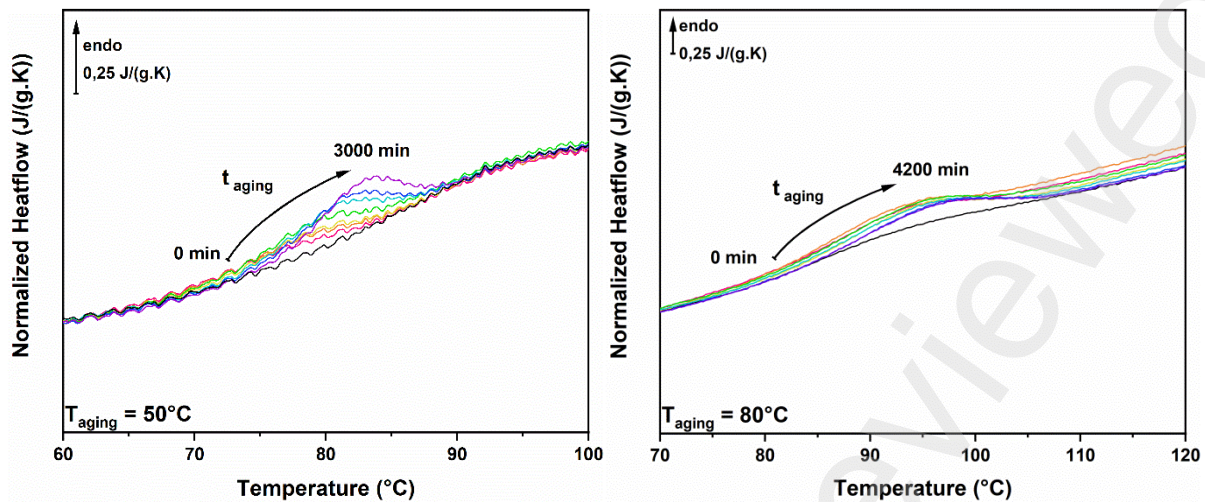


Figure 8. DSC traces of epoxy resin aged at 50 and 80°C with appearance of enthalpy overshoot.

The data confirm the existence of this ageing mode below the glass transition ($T_{ag} = 50^\circ\text{C}$), but also in the glass transition vicinity ($T_{ag} = 80^\circ\text{C}$). Indeed, as previously reported, the relaxation dynamics are heterogeneous enough to allow the structural relaxation of the glassy fraction in a sample which is not completely vitrified [23]. On the other hand, at 120 °C and 160 °C, the sample is in the liquid state and does not undergo the structural relaxation ageing. Structural relaxation was investigated for several durations up to 1000 h (Figure 9). The enthalpy overshoot value increases and calls for the following comments:

- at 80C, ΔH tends towards an asymptotic value which would be characteristic to an equilibrium state.
- At 50°C, ΔH increases but remains well below the theoretical asymptotic value given by

$$\Delta H_\infty = \Delta C_p \times (T_g - T_{ag}) \quad (4)$$

Where ΔC_p is the heat capacity jump when crossing the glass transition.

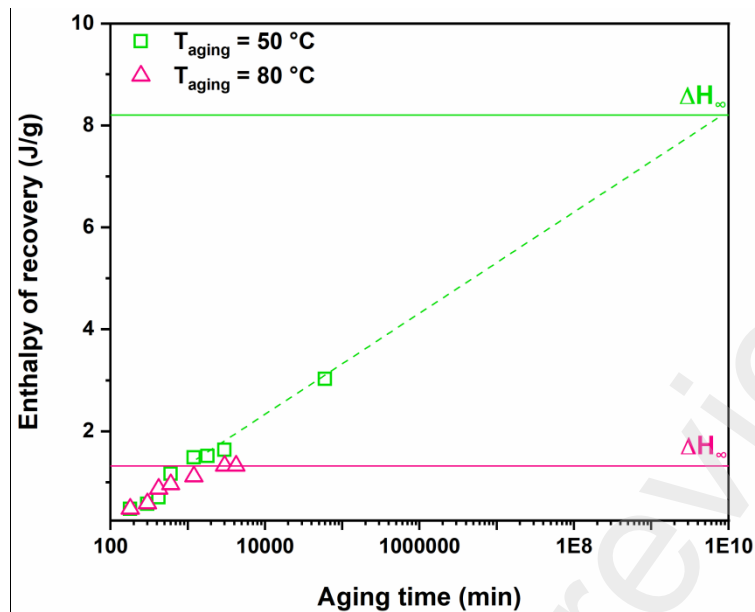


Figure 9. Enthalpy of recovery versus ageing time for epoxy resin.

At 80 °C, the structural relaxation ageing can be considered as a quick process, initiated after about 100 min and over after 2000 min. It is worth reminding that these durations are not representative of real conditions because the structural relaxation is only possible after the plasticizer loss is complete. This means that the time needed to expulse the plasticizer which is very long at 80 °C on thick samples has to be added to the duration of the relaxation process. In other terms, the occurrence of the structural relaxation may coincide with the loss of the barrier properties.

Nevertheless, some arguments seem to contradict this idea. By comparing the data of the enthalpy of recovery recorded after ageing at 50 °C and 80 °C, the energy excess minimized within the experimental time is of the same order, following the same kinetic profile, whereas the loss of barrier properties is only observed when the ageing is performed at 80 °C. Moreover, the structural relaxation aging consists in a decrease of the specific volume, leading to a densification of the material, which is much more expected to decrease the permeability. A crack generation caused by the embrittlement of the system is still possible, as the mechanical properties are clearly impacted by the relaxation, but we can assume that such cracks would have led to a more brutal loss of the barrier properties. Finally, at 80 °C the minimization of energy is of weak amplitude contrary to what could happen at 50 °C where ΔH_{∞} is higher.

It would have been of high interest to investigate in more details the impact of structural relaxation at 50 °C. However, as shown in Figure 9, this leads to inaccessible experimental times to fully cover the process. Besides, even if this set of data recorded for early times suggests a linear dependence of δH with $\log(t_{ag})$, the possibility to transpose this dependence to the conditions of use, i.e., at lower temperatures, is far from ascertained. By decreasing temperature, the molecular mobility also decreases, so the kinetics of structural relaxation are slowed down. This last fact is illustrated by Figure 10 where δH is plotted versus T_{ag} for $t_{ag} = 300$ minutes. The curve displays a bell shape with a maximum. At low temperature, the glassy polymer is far from the equilibrium state. As a consequence, the major part of the relaxation is not covered, and the ageing features remain mostly unknown at low temperatures.

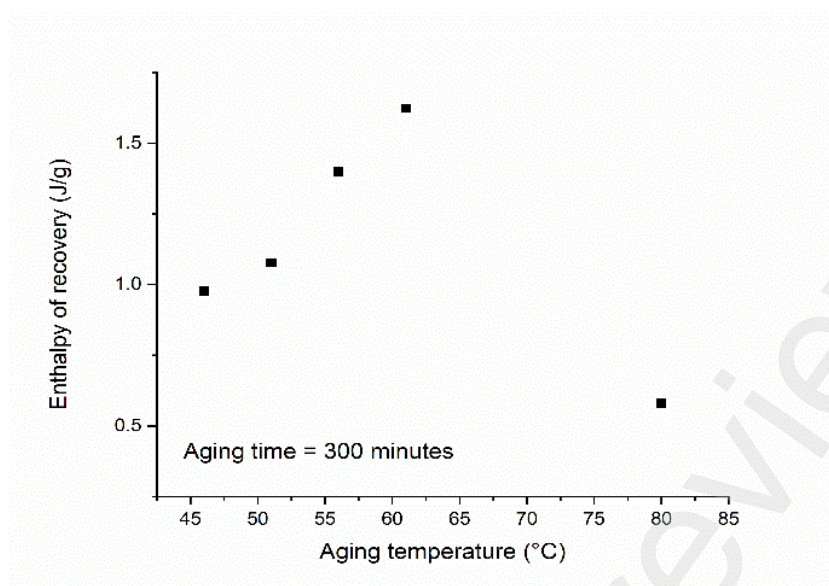


Figure 10. Enthalpy of recovery versus aging temperature for 300 minutes annealed samples.

5. Thermal oxidation

Since the physical structural consequences of aging, i.e., the free volume reducing, seem hardly compatible with a decrease of the barrier properties, chemical reactions have to be considered. During the ageing of thin films of epoxy resin, chemical changes can be classically observed by FTIR (Figure 11) with the appearance of new absorbances centered at 1740 and 1660 cm^{-1} . Their nature was recently reviewed in literature [24]. Amides are the main oxidation trackers and their appearance should come from the oxidation of methylene groups in α -position of nitrogen atoms.

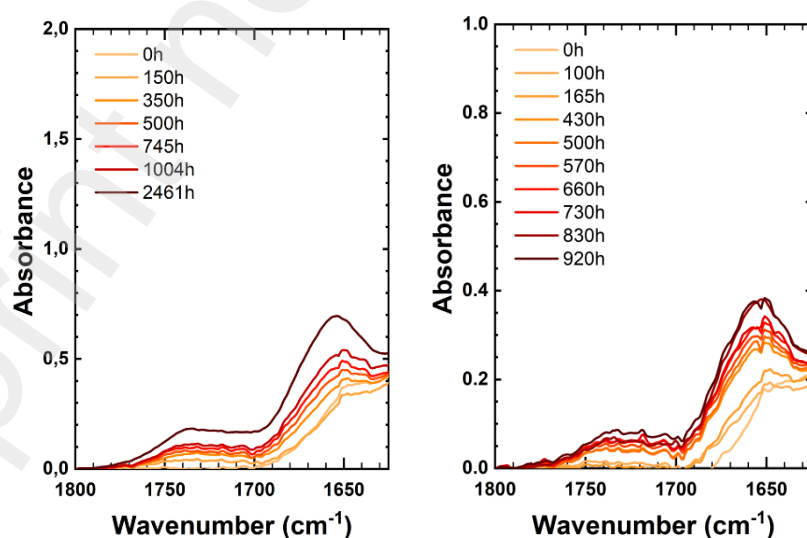


Figure 11. FTIR spectra for the carbonyl region for epoxy resin aged at 80 (a) and 100°C (b) under air.

Maximum absorbances of characteristic peaks between 1625 cm^{-1} and 1800 cm^{-1} were used to calculate concentrations of C=O carbonyl groups using the Beer-Lambert law:

$$A = \varepsilon \cdot l \cdot c \quad (5)$$

where A is the maximum absorbance measured, ε the molar attenuation coefficient at the considered wavelength (in $\text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), l the thickness of studied film samples (in cm), and c the concentration of chemical groups (in $\text{mol}\cdot\text{L}^{-1}$). Molar extinction coefficients for amides was assessed using values from previous studies: $574\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ at 1660 cm^{-1} [25]. It was previously shown that their appearance correlates well with progressive depletion of mechanical properties [21]. Kinetic curves for amide build up are thus given in Figure 12a for several ageing temperatures. The characteristic times for reaching various level of amide concentration are plotted in the Arrhenius diagram in Figure 12b. It clearly proves that at 50°C , there is almost no oxidation in the timescale investigated in Figure 4.

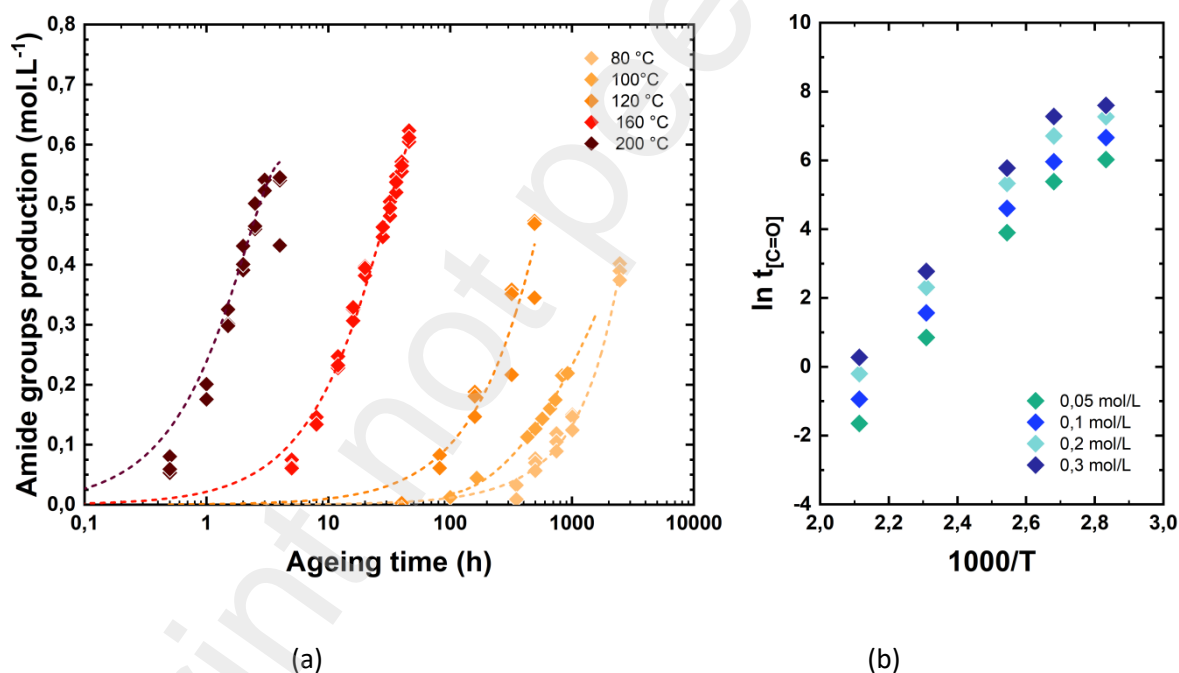


Figure 12. Changes in amide concentration for ageing at 200, 160, 120 and 80°C (a) and Arrhenius diagram of characteristic times for reaching concentrations in oxidation products, the values being given in caption (b).

DISCUSSION

Let us start by discussion on the possible phenomena responsible for the alteration of the epoxy coated concrete. At temperatures below 100°C, as observed from the absence of significant changes in permeability values (see Figure 5), concrete can be considered as stable and the changes in properties can be discussed either in terms of:

- Structural relaxation at glassy stage, i.e., below 50°C for plasticized resin and about 70°C for resin having lost its plasticizer.
- Plasticizer loss
- Thermal oxidation (at all temperatures).

Regarding the structural relaxation, we observe, that permeability properties are almost unchanged after more than 2000 h ageing at 50 °C (in conditions where plasticizer loss and oxidation are negligible in the timescale under investigation meanwhile Figures 8-10 show the existence of a significant structural relaxation process). It suggests that structural relaxation poorly influences the barrier properties. This result is not so surprising: physical ageing is usually associated with a reduction of free volume. It is already documented that free volume decreases with crosslink density [26] and that an increase of crosslink density induces a decrease of solubility and diffusivity [27].

It is however impossible to conclude that structural ageing will have no effect on barrier properties at higher conversion degrees than those observed in Figures 8-10, at which structural relaxation may induce the embrittlement of epoxy (the epoxy glass being far from equilibrium at 50 °C, the minimization of specific volume continues during its whole service life), and then a catastrophic failure of its barrier properties. Moreover, the “coupling” of structural relaxation and oxidation was never investigated to our knowledge. In other words, the consequences of the sum of both ageing remains to be investigated.

Another question is the possible responsibility of structural relaxation in the barrier property loss observed at 80 °C. As previously mentioned, relaxation at both 50 and 80 °C has led to similar enthalpy loss, while barrier properties have differently evolved within the considered experimental time. These results, combined with the expected increase of barrier properties under the free volume reducing, explain why we do not assume the structural relaxation to be the main component behind the permeability variations.

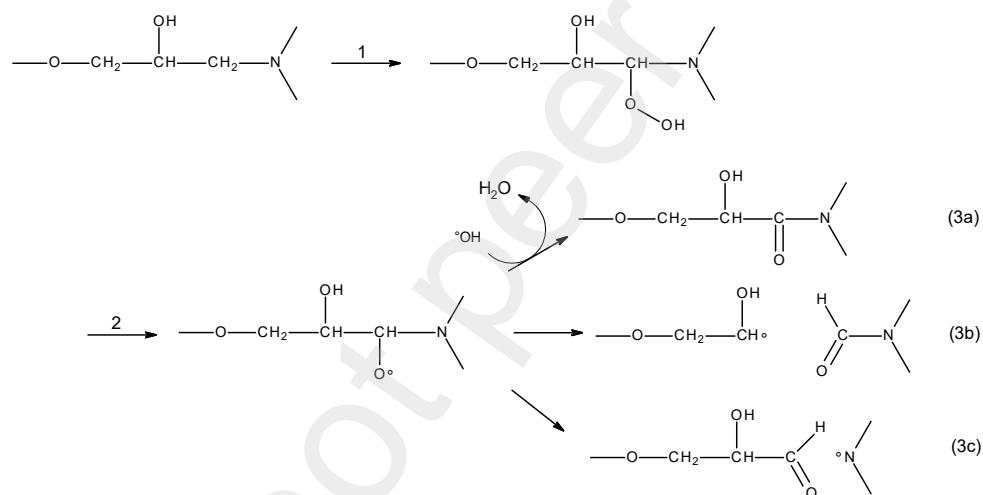
The possible influence of plasticizer loss seems easier to discuss at 100°C. According to Figure 6b, plasticizer is lost after 200 h of ageing for a 1 mm thick plate. In the same time, Figure 3 and 4 show that that barrier properties are barely increased in the early ageing time corresponding to plasticizer loss, and continue to degrade significantly more at longer time, where oxidation starts to become significant. In other words, oxidation seems the most plausible explanation to the loss of barrier properties.

Let us now turn to oxidation, which is expected to be the only possible cause of failure at 100°C. Oxidation is in essence a heterogeneous phenomenon described by the reaction diffusion coupling of oxygen. Bulky samples are oxidized in surface, whereas deeper layers are less degraded. The thickness of oxidized layer is given by:

$$TOL^2 = \frac{D_{O_2} \cdot [O_2]}{r_{OX}} \quad (6)$$

Where TOL is the thickness of oxidized layer, D_{O_2} the oxygen diffusivity, $[O_2]$ the equilibrium oxygen concentration (i.e., at the surface of a thick sample) and r_{OX} the oxidation rate. The sum of activation energy of oxygen diffusivity and solubility is lower than the value for oxidation rate so that TOL increases when lowering temperature [28]. At 200°C, the thickness of oxidized layer is about 150 μm (see Supplementary information -2). It can hence be considered that samples under investigation (presented in Figure 4, 5, 11, 12) are almost homogeneously degraded.

In such samples, the assumption can be made that end of life (in terms of mechanical properties or permeability properties) is associated to a « critical » chemical state [29] which can be interpreted from the oxidation mechanism (Scheme 1): the hydroxypropyl ether groups responsible of sub-glassy mobility is progressively destroyed. Its disappearance provokes the depletion of the β relaxation amplitude (and thus an increase in elastic modulus) together with the loss of mobility and thus of plastic deformation.



Scheme 1. Simplified oxidation mechanism of epoxies.

Let us now turn on the consequences of ageing in terms of barrier properties. At first, it can be recalled that some previous papers showed that permeability was decreased after oxidation [14], which is, in appearance, in contradiction with our data, but was observed in the case of other polymer systems than epoxies. It is also well established that TETA group favors chain scission [30] creating empty space where oxygen can more easily diffuse. At 80°C or 100°C, the permeability of epoxy coated concrete is drastically increased. It calls for the following comments:

① It remains speculative to directly correlate permeability changes with amide concentration in the epoxy. It seems actually that the degradation of the permeation properties is faster for the concrete + epoxy than for the epoxy alone. According to Eq. 1, an increase of epoxy permeability by a factor 2 induces an increase of epoxy concrete by a factor 2. However, when looking at permeability values after 500 h, one sees that epoxy permeability is multiplied by almost 3 meanwhile permeability of concrete + epoxy is multiplied by a 1000 factor, i.e., the permeability of epoxy coated concrete is very close of the value expected for concrete alone.

Let us assume that a common amide concentration value describes an end of life criteria: for instance, 0.25 mol l^{-1} corresponds to a severely degraded epoxy at 80°C (with permeability multiplied by a decade) and even more degrade at 100°C (where barrier properties of epoxy are almost completely vanished). The extrapolation of time to reach this concentration to lower temperature remains challenging, having in mind that the use of Arrhenius law for lifetime value is discussable (Figure 12b).

CONCLUSIONS

This paper deals with the multiscale study of the complex ageing mode of epoxy coatings with a focus on the reasons responsible for the loss of barrier properties. For that purpose, epoxy concrete coatings were aged together with some thin plates.

It was mainly shown that physical ageing by structural relaxation, and/or loss of plasticizer had a very limited effect on mechanical and barrier properties. On the contrary, oxidation (even if slow) can provoke the embrittlement of coatings.

It remains now to investigate the effect of coupled ageing, in particular where structural relaxation occurs on oxidized samples. The existence of chain scission may alter the macromolecular mobility, the rate of relaxation and the nature of the equilibrium state, i.e. finally the effect of ageing on mechanical and permeation properties. Reversely, the effect of structural relaxation and/or plasticizer loss on the oxidation rate is worth to be investigated. At last, in order to get closer of real conditions, the effect of humid ageing on barrier and mechanical properties should also be investigated.

ACKNOWLEDGEMENT

The Agence Nationale de la Recherche is gratefully acknowledged for funding the project ANR DUREVE (ANR 18-CE06-0028 - 2019-2022), and this work.

REFERENCES

- ¹ A. Saccani, V. Magnaghi. Durability of epoxy resin-based materials for the repair of damaged cementitious composites. *Cement and Concrete Research* 29(1), 1999, 95-98.
- ² M. M. El-Hawary, A. Abdul-Jaleel. Durability assessment of epoxy modified concrete. *Construction and Building Materials* Volume 24(8), 2010, 1523-1528.
- ³ A.A. Almusallam , F.M. Khan, S.U. Dulaijan, O.S.B. Al-Amoudi. Effectiveness of surface coatings in improving concrete durability, *Cement and Concrete Composites* 25(4-5), 2003, 473-481.
- ⁴ M.C. Celina. Review of polymer oxidation and its relationship with materials performance and lifetime prediction. *Polymer Degradation and Stability* 98(12), 2013, 2419-2429.
- ⁵ E. Ernault, E. Richaud, B. Fayolle. Origin of epoxies embrittlement during oxidative ageing. *Polymer Testing* 63, 2017, 448-454.
- ⁶ D. Hou, Q. Yang, P. Wang, Z. Jin, M. Wang, Y. Zhang, X. Wang. Unraveling disadhesion mechanism of epoxy/CSH interface under aggressive conditions. *Cement and Concrete Research* Volume 146, 2021, 106489
- ⁷ L. Dobircan, N. Delpouve, R. Herbinet, S. Domenek, L. Le Pluart, L. Delbreilh, V. Ducruet, E. Dargent. Molecular mobility and physical ageing of plasticized poly(lactide). *Polymer Engineering and Science* 55(4), 2015, 858-865.
- ⁸ Kits d'étanchéité de toitures par application liquide ETAG 005. Révision mars 2004 <https://www.eota.eu/etags-archive>
- ⁹ M. Savvilitidou, A.P. Vassilopoulos, M. Frigione, T. Keller. Effects of aging in dry environment on physical and mechanical properties of a cold-curing structural epoxy adhesive for bridge construction. *Construction and Building Materials* 140, 2017, 552-561.
- ¹⁰ S. Shaikh, M. Yaqoob, P. Aggarwal. An overview of biodegradable packaging in food industry. *Current Research in Food Science* 4, 2021, 503-520.
- ¹¹ D.W. van Krevelen, K. te Nijenhuis. *Properties of Polymers - Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions*. 4th Edition - February 9, 2009
- ¹² M.C. Celina, A. Quintana. Oxygen diffusivity and permeation through polymers at elevated temperature *Polymer* 150, 2018, 326-342.
- ¹³ X. Colin, F. Essatbi, J. Delozanne, G. Moreau. Towards a general kinetic model for the thermal oxidation of epoxy-diamine networks. Effect of the molecular mobility around the glass transition temperature. *Polymer Degradation and Stability* 181, 2020, 109314.
- ¹⁴ J.-L. Gardette, A. Colin, S. Trivis, S. German, S. Therias. Impact of photooxidative degradation on the oxygen permeability of poly(ethyleneterephthalate). *Polymer Degradation and Stability* 103, 2014, 35-41.
- ¹⁵ E. Ernault, E. Richaud, B. Fayolle. Thermal-oxidation of epoxy/amine followed by glass transition temperature changes. *Polymer Degradation and Stability* 138, 2017, 82-90.
- ¹⁶ S. Kunze, R. Groll, B. Besser, J. Thoming. Molecular diameters of rarefied gases. *Scientific Reports* 12, 2022, 2057.
- ¹⁷ S. Le Cruz, R.A. Pethrick. Solvent Effects on Cure 1-Benzyl Alcohol on Epoxy Cure. *International Journal of Polymeric Materials and Polymeric Biomaterials*. 60, 2011, 441-455.

-
- ¹⁸ N. Gay, T. Lamouchi, F. Agostini, C. Davy, F. Skoczylas. Hydrogen diffusion through polymer membranes. *MATBUD'2020*, Oct 2020, Cracow, Poland. pp.01044, [10.1051/mateconf/202032201044](https://doi.org/10.1051/mateconf/202032201044). ([hal-03182683](https://hal.archives-ouvertes.fr/hal-03182683))
- ¹⁹ H.S. Wong R.W. Zimmerman, N. Buenfeld. Estimating the permeability of cement pastes and mortars using image analysis and effective medium theory. *Cement and Concrete Research* 42(2), 2012, 476–483.
- ²⁰ Y. Pei, F. Agostini, F. Skoczylas. Rehydration on heat-treated cementitious materials up to 700 °C-coupled transport properties characterization. *Construction and Building Materials* 144, 2017, 650-662.
- ²¹ E. Fonseca, V. Demétrio da Silva, J.S. Klitzke, H.S. Schrekker, S.C. Amico. Imidazolium ionic liquids as fracture toughening agents in DGEBA-TETA epoxy resin. *Polymer Testing* 87, 2020, 106556.
- ²² R. Delannoy, V. Tognetti, E. Richaud. Structure–Properties Relationships Involved in the Embrittlement of Epoxies. *Polymers* 14, 2022, 4685.
- ²³ X. Monnier, N. Delpouve, A. Saiter-Fourcin. Distinct dynamics of structural relaxation in the amorphous phase of poly(l-lactic acid) revealed by quiescent crystallization. *Soft Matter* 16(13),2020, 3224–3233.
- ²⁴ M.C. Celina, E. Linde, E. Martinez. Carbonyl Identification and Quantification Uncertainties for Oxidative Polymer Degradation. *Polymer Degradation and Stability* 188, 2021, 109550.
- ²⁵ M.C. Celina, E. Linde, E. Martinez. Carbonyl Identification and Quantification Uncertainties for Oxidative Polymer Degradation. *Polymer Degradation and Stability* 188, 2021, 109550.
- ²⁶ K. Frank, C. Childers, D. Dutta, D. Gidley, M. Jackson, S. Ward, R. Maskell, J. Wiggins. Fluid uptake behavior of multifunctional epoxy blends. *Polymer* 54(1), 2013, 403-410.
- ²⁷ C. Damian, E. Espuche, M. Escoubes. Influence of three ageing types (thermal oxidation, radiochemical and hydrolytic ageing) on the structure and gas transport properties of epoxy–amine networks. *Polymer Degradation and Stability* 72(3), 2001, 447-458.
- ²⁸ M.C. Celina, A. Quintana. Oxygen diffusivity and permeation through polymers at elevated temperature. *Polymer* 150, 2018, 326-342.
- ²⁹ C. Rouillon, P.-O. Bussiere, E. Desnoux, S. Collin, C. Vial, S. Therias, J.-L. Gardette. Is carbonyl index a quantitative probe to monitor polypropylene photodegradation? *Polymer Degradation and Stability* 128, 2016, 200-208.
- ³⁰ F. Benard, I. Campistrone, A. Laguerre, G. Vigier, F. Laval. Influence of silica fillers during the electron irradiation of DGEBA/TETA epoxy resins, part II: Study of the thermomechanical properties. *Polymer Degradation and Stability* 91(9), 2006, 2119-2125.