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Effects of thermal ageing in water and ethanol environments on the compressive response of natural and agglomerated cork stoppers

Massimiliano Gerometta [a,b], Xavier Gabrion [b], Aurélie Lagorce [a], Aline Bonnotte [c], François Villette [b], Sébastien Thibaud [b], Thomas Karbowiak [a,*]

[a] Université Bourgogne Europe, Institut Agro, INRAE, UMR PAM, Dijon F-21000, France
[b] Université Marie et Louis Pasteur, SUPMICROTECH, CNRS, institut FEMTO-ST, Besançon F-25000, France
[c] Plateforme DImaCell, Université Bourgogne Europe, Institut Agro Dijon, INRAE, UMR Agroécologie, Dijon F-21000, France

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ABSTRACT

The ageing of cork stoppers is a critical issue for the oenology industry. This study employed a repeated loading method to characterise the evolution of the compressive behaviour of aged cork-based stoppers, addressing the lack of reliable mechanical indicators of ageing. First, natural and agglomerated cork stoppers, as well as polyurethane binder, were subjected to a 200-day ageing period at 50°C either in contact with water (liquid phase) or with ethanol (vapour or liquid phase). In addition to sorption, imbibition and swelling phenomena were observed. After the ageing period, the volume filled by water was estimated at 52% for natural, and of 75% for agglomerated cork. Higher values were estimated for ethanol, with 84% for the cork-based samples and 97% for the polyurethane binder. Second, after vacuum treatment to remove water and ethanol, the aged samples underwent 8 compression cycles at 43% Hencky strain. The tangent modulus was calculated to assess the instantaneous mechanical response, whereas the dissipated energy was calculated to characterise the evolution of the compressive behaviour over cycle repetitions. The results suggest that water and ethanol can interact with the components of a cork-based stopper and thus play a key role in altering their mechanical behaviour during ageing.

1. Introduction

Cork is a biological material obtained from the cork oak tree (*Quercus suber* L.) (Silva et al., 2005). The combination of properties such as low density (Pereira, 2007b), low permeability to liquids (Chanut et al., 2022), good chemical stability (Pereira, 2007c), thermal-acoustic insulation (Novais et al., 2021, Alves et al., 2024), a rather high barrier to gases (Crouvisier-Urion et al., 2018), and outstanding mechanical properties in compression (Lagorce-Tachon et al., 2015a), has led to the use of this material in many different applications. 200 thousand tons of cork are produced every year (APCOR, 2020). Cork is mainly used in the oenological sector, which account for 73.5% of global cork production. This corresponds to the manufacture of approximately 13 billion cork-based stoppers (natural and agglomerated) each year (APCOR, 2020, Amorim, 2024). In their use as wine stoppers, they are first compressed in the bottling machine (in the radial and tangential directions for natural cork) and then inserted into the glass bottleneck. For still wines, a 35% nominal strain is applied to the stopper by the bottling machine jaws (FFL, 2006), corresponding to a reduction in diameter from 24 ± 0.4 mm to 15.5 ± 0.5 mm. Then, it bounces-back to 18.5 ± 0.5 mm, which corresponds to the inner diameter of the bottleneck (FFL, 2006). This constant strain in the bottleneck (23% of nominal strain) is equivalent to a compression of 40% in volume. In the case of sparkling wine, the bottling machine compresses the stopper up to 50% nominal strain (diameter reduction from 31 ± 0.5 mm to 15.5 ± 0.5 mm) before it recovers to the inner diameter of the bottleneck at 17.5 ± 0.3 mm (43% of nominal strain). In this case, the volume reduction reaches 70% (AFNOR, 1995).

Wine is a water-ethanol solution obtained from the alcoholic fermentation of grape must, with an alcohol content of at least 8.5% v/v (OIV, 2024). It can be stored for a few months up to several years, depending on its chemical composition. However, phenolic compounds are particularly sensitive to oxidation. During storage, they continuously react with reactive oxygen species. In the presence of excessive oxygen, oxidation can lead to organoleptic changes in wine, thereby affecting its shelf life (Mercanti et al., 2024). Among the factors that govern wine

* Correspondence to: Université Bourgogne Europe, Institut Agro, INRAE, UMR PAM, 1 Esplanade Erasme, Dijon F-21000, France.
E-mail address: thomas.karbowiak@institut-agro.fr (T. Karbowiak).

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oxidation, environmental storage conditions play an important role. For instance, temperature impacts the rate of chemical reactions (Scrimgeour et al., 2015), and light exposure triggers the synthesis of reactive oxidative species (Echave et al., 2021). The closure is the most important factor in preserving wine from oxidation during storage in bottle, as it represents a barrier against oxygen ingress. The oxidation phenomenon during ageing can also be indirectly influenced by relative humidity. Indeed, it affects the mechanical (Lagorce-Tachon et al., 2015a; Lagorce-Tachon et al., 2016a) and barrier properties (Crouvisier-Urion et al., 2018) of cork-based stoppers.

Although visible modifications can be noticed on uncorked stoppers after several years of storage, to the best of our knowledge no specific studies on the effect of ageing on the structure and mechanical properties of cork-based stoppers is available in the literature. Research studies are mainly focused on the characterisation of its barrier properties. To better understand the relationship between the stopper and wine oxidation, different studies have been carried out on the barrier properties of the bottleneck-cork stopper system. Lagorce-Tachon et al. investigated the oxygen transfer through a corked bottleneck with natural stopper without surface treatment, using a manometric technique. They found that the diffusion coefficient of oxygen was 50 times higher compared to that obtained for the cork stopper alone (with interface glued) (Lagorce-Tachon et al., 2016b). In another work, Chanut et al. demonstrated that the surface coating of microagglomerated cork stopper significantly reduces oxygen transfer at the interface between the glass bottleneck and the stopper (Chanut et al., 2021). In a study conducted on aged bottles of white wine sealed with a natural cork stopper, Karbowiak et al. found that oxygen transfer at the glass-cork interface was 1000 times higher than through the cork stopper alone in oxidized wine, whereas it was only 10 times for non-oxidized wine (Karbowiak et al., 2019). These results further emphasize the critical role of the bottleneck-stopper interface during long-term ageing. In another ageing study, Chanut et al. also investigated the effect of different storage conditions on the oxygen barrier properties of a miniaturised bottleneck-stopper system (6 mm wafer, microagglomerated cork). They found that the presence of model wine and temperature had a significant effect on the oxygen transfer. At 20°C, no change in oxygen barrier properties was observed over a storage period of 24 months. At 35°C, a significant increase in oxygen transfer at the glass-cork interface was observed after 9 months of storage compared with samples stored at 20°C. At 50°C, this phenomenon occurred more rapidly, becoming evident after 3 months of storage. The partial melting of the surface treatment agent or the modification of the mechanical properties of the stopper were assumed to be responsible for changes in the oxygen barrier properties (Chanut et al., 2023).

Mechanical ageing of cork stoppers represents a critical issue in oenology and wine bottle storage, particularly because no reliable mechanical characterization currently reflects the ageing state of the material under various environmental conditions. In this context, this study aims to investigate the effects of ageing on the mechanical properties of cork-based stoppers after exposure to the main wine components, namely water and ethanol.

2. Materials and methods

2.1. Sample preparation

High-quality natural cork stoppers (24 mm diameter, 49 mm height) were supplied. Microagglomerated (*mi*) cork stoppers (31 mm diameter, 39 mm height, 20% w_{binder}/w_{cork} binder, particle size within 0.25–3 mm) and macroagglomerated (*MA*) cork stoppers (31 mm diameter, 39 mm height, 8% w_{binder}/w_{cork} binder, particle size within 3–7 mm) were also used in this study. A micro-milling machine (Kern micro GMBH, Germany) was used to manufacture $15 \times 15 \times 15$ mm^3 (from natural cork stoppers) and $11 \times 11 \times 11$ mm^3 (from agglomerated cork stoppers) cubes, depending on the initial height of the stopper. Polyurethane (PU) binder (toluene diisocyanate, TDI) was also analysed in this study. Samples dimensions were selected according to previous studies on mechanical properties of cork (Anjos et al., 2014; Lagorce-Tachon et al., 2015a). Cylindrical blocks of PU binder were left to polymerize at 25°C and 50% relative humidity (RH) for at least 3 days after ultrasonic treatment (30 min, 37 kHz) to eliminate air bubbles. Then, $10 \times 10 \times 10$ mm^3 cubes were cut manually. In this case, smaller samples were obtained in order to eliminate defects caused by the polymerisation process. All samples analysed in this study were sourced from Portugal.

2.2. Sorption kinetics of water and ethanol

After a two-week dynamic vacuum treatment applied to remove water (p ~1 mbar, 25°C), samples were aged at 50°C for 200 days in air-tight containers under different storage conditions: (i) completely immersed in deionized water, (ii) in contact with ethanol vapour, and (iii) completely immersed in ethanol (≥99.8%, CAS 64–17–5, Germany). The dimensions of samples were measured before the ageing test using a calliper. During the ageing period, cork samples were weighted at 25°C at $t = 0$ (before conditioning at 50°C) and every 11 days (using a Sartorius BP 211D balance; d = 0.01 mg). The six sides of the cubic sample immersed in water or ethanol were dried with paper towels to dry the surface before weighting. Each data point in the kinetics analysis is calculated as the mean value of at least five independent measurements for natural and agglomerated cork and at least three for PU binder sample. The kinetics are expressed as the uptake (C, $mol.g^{-1}$), of water or ethanol sorbed by the material as follows:

$$C = \frac{\left(\frac{m_t - m_{t_0}}{m_{t_0}}\right)}{M} \quad (1)$$

Considering the difference between the mass value at time t (m_t) and initial dry mass of the sample before ageing (m_{t_0}), normalised by m_{t_0}, and M the molar mass of water (18.02 g.mol^{-1}) or ethanol (46.07 g.mol^{-1}).

At $t = 200$ days, at the end of the ageing period, the mass and dimensions of samples were measured before and after applying a dynamic vacuum (p ~1 mbar, 25°C, 14 days) to remove water and ethanol, and before mechanical testing. The initial volume (before ageing, V_{t_0}) and the final volumes (after ageing, V_a, and after vacuum treatment, V_v) of the samples, were measured using a calliper.

The volume sorbed (V_s) of water or ethanol was first calculated as follows:

$$V_s = \frac{m_t - m_{t_0}}{\rho_{50°C\ W\ or\ E}} \quad (2)$$

With $\rho_{50°C\ W\ or\ E}$ the density of water (W) or ethanol (E) at 50°C. It is assumed that the density of water or ethanol sorbed in the cell wall is equal to that of the liquid in the lumen of cork cells.

Then, the filled volume (V_f) of water or ethanol in the sample was calculated as the ratio between the volume sorbed (V_s) to the volume of the sample measured at the end of the ageing test (V_a) prior to vacuum treatment:

$$V_f = \frac{V_s}{V_a} \times 100 \quad (3)$$

The phenomenon of imbibition of water and ethanol also induced swelling of the sample during ageing. To characterise this phenomenon, the relative volume variation (ΔV) was calculated as follows:

$$\Delta V = \left(\frac{V_t - V_{t_0}}{V_{t_0}}\right) \times 100 \quad (4)$$

With $V_t - V_{t_0}$ (mm^3) representing the difference between the final and initial volume of the sample, normalised by V_{t_0} (mm^3). V_t refers to two possible final states: either the volume after ageing (V_a) at 50°C for 200 days; or the volume after the vacuum treatment (V_v) applied

following the ageing process. The final volume considered is reported in each case.

The relative variation in mass of the sample (Δm) was calculated as follows:

$$\Delta m = \left(\frac{m_v - m_{t_0}}{m_{t_0}}\right) \times 100 \quad (5)$$

With $m_v - m_{t_0}$ (g) representing the difference between the final weight of the sample after vacuum treatment (m_v) and its initial dry mass before the ageing period (m_{t_0}), normalised by m_{t_0}.

2.3. Mechanical testing: repeated loading compression cycles

An MTS criterion 45 tensile machine, equipped with a 5 kN load cell, was used to perform uniaxial compression test on cork and binder samples, between two parallel steel platens at a crosshead displacement rate of 1 mm.min^{-1}. A 0.125 mm thick Polytetrafluoroethylene (PTFE) film was laid on the platens to reduce the friction coefficient with cork surface. Natural cork was compressed along the tangential direction. This was determined by observing the cell structure with a Keyence VHX−7000 digital microscope previous to mechanical testing. Mechanical tests were performed on at least five replicates of natural and agglomerated cork and at least three PU binder replicates for each storage condition.

For the analysis of the mechanical parameters required to characterise the material ageing, the following definitions of stress and strain were adopted. As the cross-sectional area variation cannot be measured during the test, the nominal stress, σ (MPa) is used and calculated according to:

$$\sigma = \frac{F}{S_0} \quad (6)$$

Where F is the load (N) measured by the tensile machine and S_0 the initial cross-sectional area of the sample (mm^2).

The Hencky strain ε (-) is given by Eq. 7:

$$\varepsilon = \ln\left(\frac{L}{L_0}\right) \quad (7)$$

L_0 is the initial height of the sample and $L = L_0 + \Delta L$, with $\Delta L < 0$ the displacement of the crosshead. A Hencky strain of 43% was applied to the samples, corresponding to the strain level of a cork stopper in the bottling machine according to the strain definition (FFL, 2006). The nominal stress and Hencky strain have been arbitrarily set as positive values.

First, the sample was compressed up to a set displacement and then returned to its initial position. Then, the same loading-unloading cycle was repeated eight times, referred to as repetitions *a-h*, as detailed in Fig. 1a. Eight cycle repetitions were selected as a compromise between scientific and technical considerations. From a scientific perspective, this number was considered sufficient to subject the material to stress and thereby better characterise its mechanical response over successive compressions, while avoiding the conditions of a mechanical fatigue test. From a technical perspective, the number of repetitions was also chosen with regard to the total duration of the mechanical test, ensuring a feasible experimental design across all ageing conditions investigated. Each repetition consisted of a loading (solid line) and an unloading (dashed line) curve (Fig. 1b). For each of the eight repetitions, four parameters were determined: (1) the tangent modulus (E_t) was calculated from the stress-strain unloading curve, following the same protocol as previously detailed in (Gerometta et al., 2023). It allows to determine the evolution of the material stiffness under repeated loading. (2) the dissipated energy (W), corresponding to the area under the loading-unloading curve was determined using the trapezoidal integration method; (3) the residual strain (ε_r) was calculated as the difference between the strain values corresponding to a stress of 0 MPa on the loading and the unloading curves; (4) the stress loss (σ_l) was determined as the difference between the maximum stress values of two successive repetitions for each cycle. An illustration of the parameters calculated for the b cycle repetition is presented in Fig. 1b.

2.4. Scanning electron microscopy

SEM images of aged natural and agglomerated cork samples, after repeated loading tests, were obtained using a field emission gun scanning electron microscope (FEG-SEM, TESCAN Clara) operated at an accelerating voltage of 0.5 kV. The observations were carried out under controlled temperature and pressure conditions at + 4°C and 500 Pa. Samples did not require metallization prior to SEM imaging. The SEM images were obtained using Gaseous detector Tescan.

2.5. Statistical analysis

A one-way analysis of variance (ANOVA) with Tukey's multiple comparison test (p value < 0.05) was used to compare each of the 4 parameters calculated from the repeated loading test performed in different storage conditions: tangent modulus, dissipated energy, stress loss and residual strain. The assumptions for applying of a one-way ANOVA test were first assessed, i.e. the normality of residuals, the homogeneity of variance of residuals, and the independence of measurements. In case where the ANOVA conditions were not satisfied, the non-parametric Kruskal-Wallis test was employed as an alternative statistical analysis.

3. Results and discussion

The transfer of matter within porous materials such as cork involves various physical mechanisms. To ensure a clear understanding of the phenomena discussed in this work, the terms *sorption*, *adsorption*, *absorption*, *imbibition*, and *swelling* are defined below according to their IUPAC definitions.

- *Sorption*: "The process by which a substance (sorbate) is sorbed (adsorbed or absorbed) on or in another substance (sorbent)" (IUPAC, 2025d).
- *Adsorption:* "An increase in the concentration of a dissolved substance at the interface of a condensed and a liquid phase due to the operation of surface forces. Adsorption can also occur at the interface of a condensed and a gaseous phase" (IUPAC, 2025b).
- *Absorption:* "The process of one material (absorbate) being retained by another (absorbent); this may be the physical solution of a gas, liquid, or solid in a liquid, attachment of molecules of a gas, vapour, liquid, or dissolved substance to a solid surface by physical forces, etc." (IUPAC, 2025a).
- *Imbibition:* "The uptake of a liquid by a gel or porous substance. It may or may not be accompanied by swelling" (IUPAC, 2025c).
- *Swelling:* "The increase in volume of a gel or solid associated with the uptake of a liquid or gas" (IUPAC, 2025e).

3.1. Sorption and imbibition phenomena of water in cork stoppers

The sorption kinetics of water (liquid phase) on cork and PU binder samples after an ageing period of 200 days at 50°C is shown in Fig. 2a (blue label). Natural cork sorbed 0.17 ± 0.03 mol.g^{-1} of water, but did not reach the equilibrium after 200 days. The microgglomerated (*mi*) cork samples sorbed 0.20 ± 0.02 mol.g^{-1} and reached the equilibrium already after 70 days. On the contrary, macroagglomerated (*MA*) samples did not reach the equilibrium after 200 days, sorbing 0.17 ± 0.01 mol.g^{-1} of water. A different behaviour was observed for PU binder, which sorbed a very low amount of water $4 \times 10^{-4} \pm 5 \times 10^{-4}$ mol.g^{-1} during ageing. In addition to the sorption kinetics analysis, the

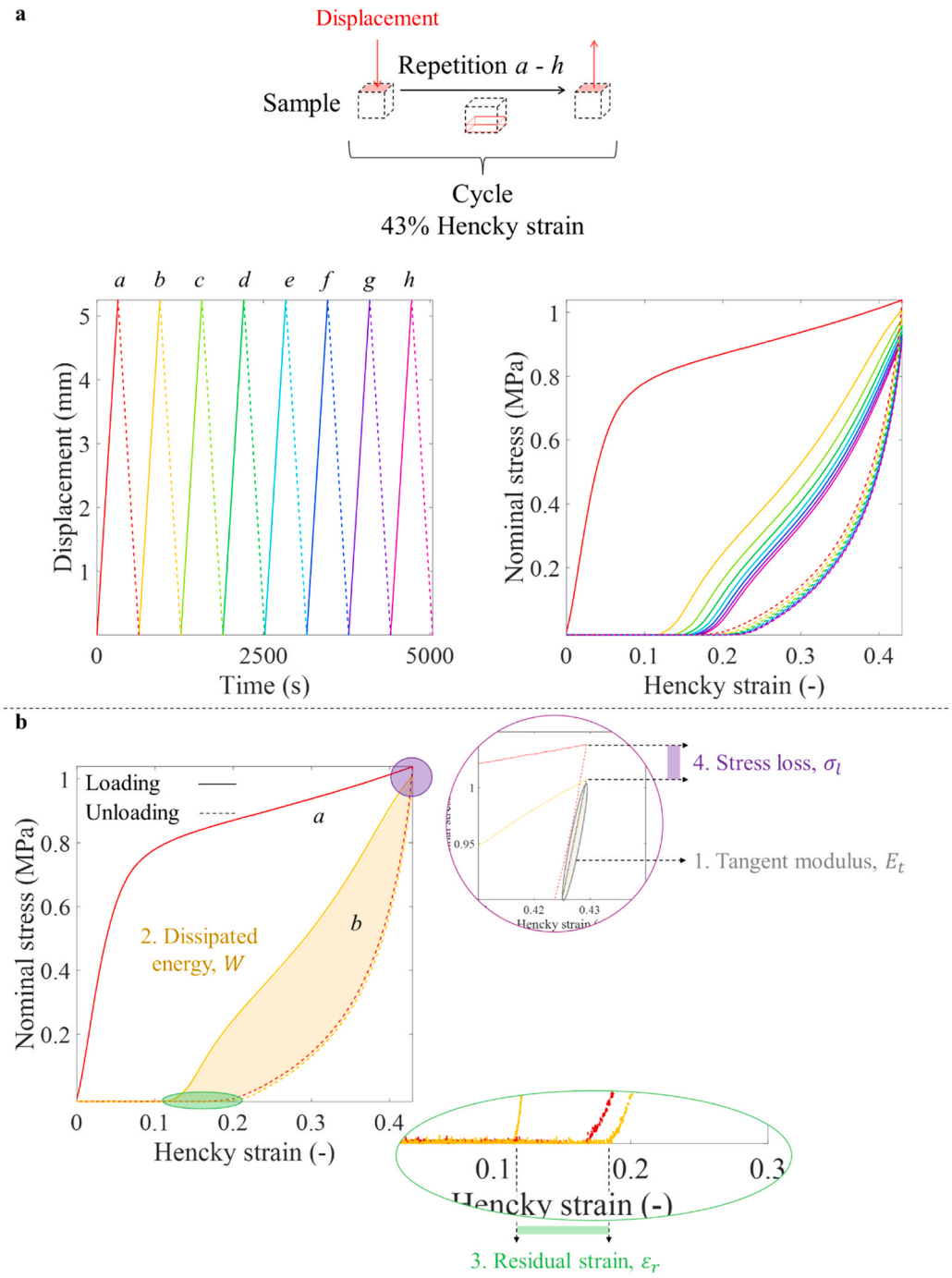

Fig. 1. (a) Schematic diagram of the repeated loading test performed at 25°C: the displacement values as a function of time for the eight cycle repetitions applied to the sample are displayed on the graph (left). The corresponding characteristic stress-strain curve obtained from these eight cycle repetitions is also shown (right). (b) Parameters determined for each cycle repetition: (1) tangent modulus (E_t), (2) dissipated energy (W), (3) residual strain (ε_r), (4) stress loss (σ_l).

filled volume (V_f) after the ageing period was calculated and is presented in Fig. 2b. After 200 days at 50°C, water occupied 52.6 ± 7.7% of the final volume of natural cork samples. For agglomerated cork, the filled volume after the ageing period was higher than for natural cork, reaching 75.6 ± 5.6% and 68.6 ± 2.4% for *mi* and *MA* samples, respectively (Fig. 2b, blue label). In the case of PU binder, sorbed water occupied a negligible volume (0.8 ± 1%). This result is in line with the kinetics observed for samples immersed in water.

In a previous thermodynamic study on the sorption of water vapour by cork, Lequin et al. observed that the amount of water sorbed by cork (phellem + lenticels) near saturation was 6 mmol.g^{-1} at 25°C. In the same study, the water sorption by lenticels (8 mmol.g^{-1}) was higher than that measured for cork, indicating that interaction with water is stronger for lenticular cells than cork (phellem). However, they stated that the influence of the presence of lenticels on the sorption properties of high-quality cork was negligible, due to the low lenticel content (Lequin et al., 2010). In another study, Lagorce-Tachon et al. calculated for the best quality (class 0) natural cork stoppers, a macroporosity value of 5.9% v/v, using neutron tomography. They also highlighted that lenticels in a cork stopper are not interconnected (Lagorce-Tachon et al., 2015b). This suggests that the phenomenon of water sorption through lenticels or lenticels filling with liquid water cannot account for such a large amount of water sorbed by cork-based stopper after being aged at 50°C completely immersed in water. Therefore, a phenomenon of

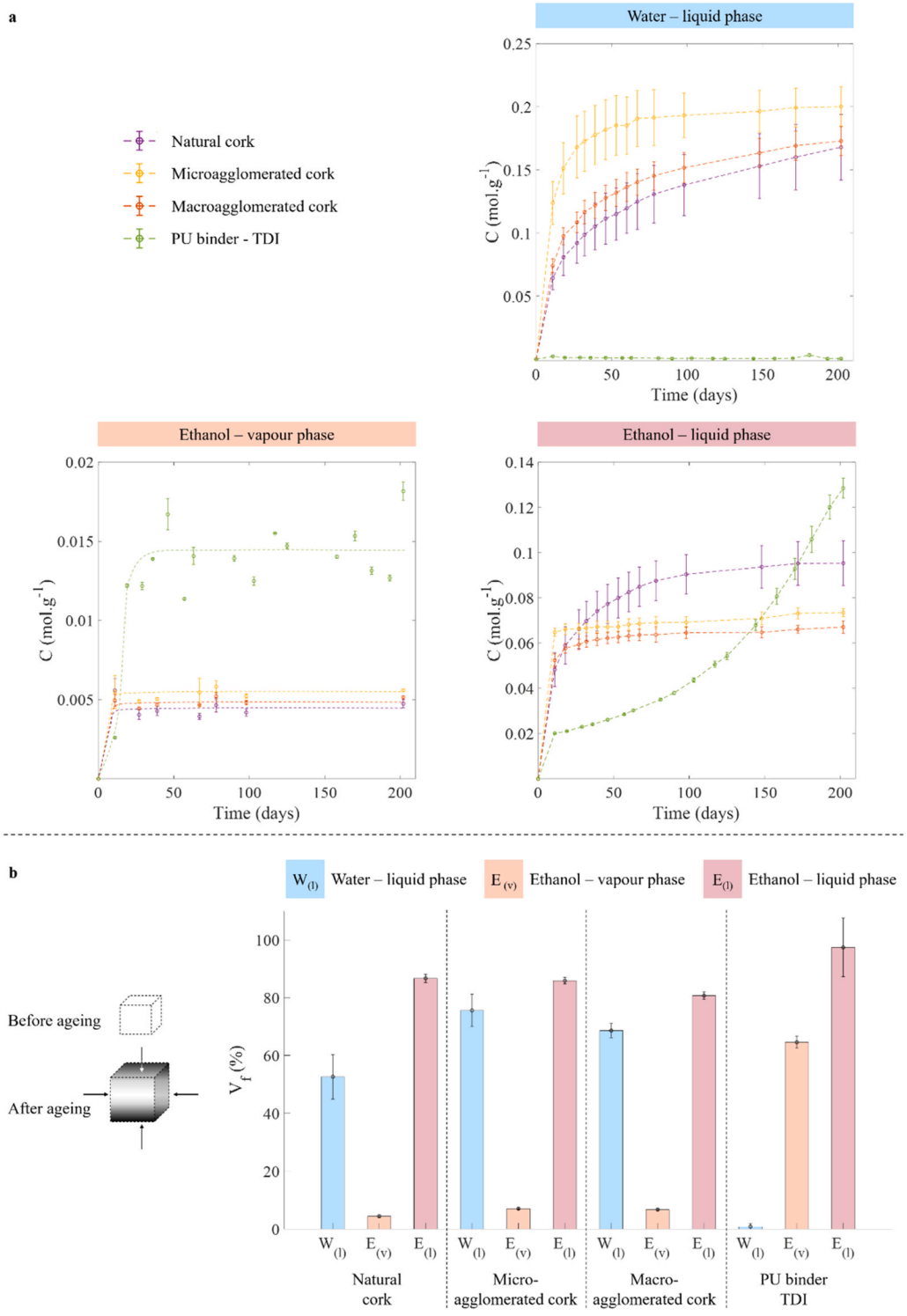

Fig. 2. (a) Kinetics of sorption and imbibition (C) of water in liquid phase, ethanol in vapour phase and ethanol in liquid phase for different samples: natural cork (n = 6), microagglomerated cork (n = 5), macroagglomerated cork (n = 5), and PU binder (n = 4 for contact with water in liquid phase; n = 3 for contact with ethanol in vapour or liquid phase) during a 200-day ageing test at 50°C (dashed line is a guide to the eyes). (b) Filled volume (V_f) of water or ethanol in the samples calculated prior to vacuum treatment.

diffusion through the cell wall of phellem and the imbibition of the cell lumen occurred. Although the studies of Castilho Pereira Santos Gomes et al. (1993) and of Abenojar et al. (2014) have reported that cork is a hydrophobic material, Chanut et al. (2022) demonstrated that cork exhibits an intermediate behaviour, and its hydrophobic or hydrophilic character depends on the scale probed. At the macroscopic scale, the honeycomb structure and the roughness of the cell walls give cork a hydrophobic character with a water contact angle close to 90°. However, two-photon microscopic observations showed that, when a water drop is deposited on the cork surface, it completely fills the first layer of open cells of the cork surface (50 μm) (Chanut et al., 2022).

In the case of PU binder, only a very small amount of sorbed water

was measured over the ageing period (Fig. 2b, blue label). Similar results were obtained by Le Gac et al., who studied the sea water sorption of methylene diphenyl diisocyanate (MDI), another type of PU, during ageing at temperatures between 25 and 120°C for 18 months. They found that the maximum water uptake was 1×10^{-3} mol.g^{-1} (1.8% w/w), regardless of the storage temperature (Le Gac et al., 2013). Comparable values were also reported by Huacuja-Sánchez et al. for MDI aged for 15 days by immersion in water at 25, 40 and 60°C, with water uptake ranging between 1.38×10^{-3} mol.g^{-1} and 1.48×10^{-3} mol.g^{-1} (2.48–2.67% w/w) (Huacuja-Sánchez et al., 2016). The results are comparable to those obtained in the present study, even though the ageing durations and temperature conditions vary between studies.

As already discussed for natural cork, the porosity of agglomerated corks plays a marginal role in water imbibition. For *MA* cork stoppers, Crouvisier-Urion obtained an intergranular porosity value of 3.7% v/v. The same author also assessed the "open" (accessible) porosity by helium pycnometry, finding a much lower value of 1.8 ± 1.2% v/v (Crouvisier-Urion, 2019). For *mi* cork stoppers, this value was lower and close to zero. Furthermore, given the low affinity of PU for water, as evidenced by the kinetics (Fig. 2a), it can be assumed that water sorption and imbibition mainly occurred through the cork particles that are not fully coated by the PU binder. Crouvisier-Urion reported local inhomogeneities of the PU binder around the cork particles of a *MA* cork stopper, observed in 2D tomography section (Crouvisier-Urion, 2019). In this study, a slightly higher filled volume for *mi* cork, which contains 20% w/w of PU binder, was noted than that of *MA* cork, containing 8% w/w of adhesive (Fig. 2b). This led to the hypothesis that, regardless of the percentage of PU binder in cork-based stoppers, water sorption and imbibition phenomena occurs through the cork material. In particular, the smaller the particle size ([0.25–3] mm < [3–7] mm < bulk), the easier the water sorption and imbibition into the material ($V_{f\,(\text{water, }mi)} > V_{f\,(\text{water, }MA)} > V_{f\,(\text{water, natural})}$), with the cell wall acting as the primary limiting factor in imbibition process.

3.2. Sorption and imbibition phenomena of ethanol in cork stoppers

After 200 days in contact with ethanol (vapour phase) at 50°C, natural, *mi* and *MA* cork samples exhibited similar kinetics (Fig. 2a, orange label), with sorbed amount of $5 \times 10^{-3} \pm 2 \times 10^{-4}$ mol.g^{-1}, $6 \times 10^{-3} \pm 9 \times 10^{-5}$ mol.g^{-1} and $5 \times 10^{-3} \pm 0.7 \times 10^{-4}$ mol.g^{-1}, respectively. The equilibrium was achieved after only 25 days. Interestingly, PU binder sorbed an amount of ethanol ~4 times higher, reaching a constant value of $0.02 \pm 6 \times 10^{-4}$ mol.g^{-1}. Although comparable ethanol uptake was calculated for cork-based samples, the filled volume (V_f) for natural cork (4.5 ± 0.4%) was lower compared to *mi* (7.0 ± 0.3%) and *MA* cork (6.7 ± 0.4%). In the case of the PU binder, it reached 64.6 ± 2.1%. This suggests that PU binder can favour a faster ethanol sorption on the *mi* and *MA* cork compared to natural cork (Fig. 2b, orange label).

The kinetics were even more pronounced when samples were placed in contact with ethanol in liquid phase (Fig. 2a, red label). Natural cork sorbed on average 0.10 ± 0.01 mol.g^{-1} after 150 days. *mi* and *MA* agglomerated cork exhibited similar kinetics, sorbing $0.07 \pm 2 \times 10^{-3}$ mol.g^{-1} and $0.07 \pm 3 \times 10^{-3}$ mol.g^{-1} in 18 days. It is interesting to note that, for PU binder, the amount of ethanol sorbed increased markedly to $0.13 \pm 4 \times 10^{-3}$ mol.g^{-1} without ever reaching equilibrium after 200 days. These results obtained for ethanol storage in liquid phase confirm that, in addition to sorption, a phenomenon of imbibition occurred during ageing. Indeed, the filled volume by ethanol after 200 days was of 86.7 ± 1.4% for natural cork. The presence of lignin in the cell wall may have favoured the diffusion through the cell wall and the imbibition in the cell lumen compared to water. Indeed, lignin is a hydrophobic molecule composed of phenylpropane units, originated from three aromatic alcohol precursors (*p*-coumaryl, coniferyl and sinapyl alchols) (Laurichesse and Avérous, 2014). Consequently, it has high affinity in organic solvents such as ethanol, which is even used in the lignin extraction process (El Hage et al., 2009, Bui et al., 2015).

To analyse agglomerated cork, two factors need to be considered: the particle size and the presence and content of the PU binder. Despite the difference in particle size, they exhibited similar ethanol uptake (Fig. 2b, red bar), resulting in a filled volume of 85.9 ± 1.1% for *mi* cork and 80.7 ± 1.3% for *MA* cork. Interestingly, the results suggest that the faster ethanol sorption and imbibition could be favoured by the presence of PU binder compared to water. Indeed, for PU binder samples ethanol filled the entire volume of the sample reaching 97.4 ± 10.1%, whereas a negligible filled volume was calculated when in contact with water in liquid phase (Fig. 2b). The different contents of PU binder used in the production of *mi* (20% w/w) and *MA* (8% w/w) cork stoppers, do not appear to play a decisive role in the ethanol imbibition phenomenon. This can be explained by considering the binder content in terms of volume, where the difference between *mi* and *MA* samples is much smaller, at approximately 5% v/v and 1% v/v, respectively.

3.3. Swelling of the material upon exposure to water and ethanol

The phenomena of sorption and imbibition of water and ethanol also induced swelling of cork and binder samples during ageing, as shown in Fig. 3.

The first graph in Fig. 3a shows the variation in volume of the samples after contact with water, or ethanol at 50°C for 200 days (ΔV_a). The water and ethanol uptake caused the sample to swell, resulting in an increase in volume after the ageing period. After complete immersion in water, natural cork samples exhibited a very low swelling (2.8 ± 2.8%), whereas it was clearly observed in *mi* and *MA* cork samples with a swelling of 23 ± 10% and 22 ± 1.6%, respectively. For agglomerated cork samples, PU binder did not played an important role in the water sorption and imbibition phenomena, as shown in Fig. 2a. This was probably due to the grinding process of cork particles, which increased the specific surface available for water sorption and imbibition, thus favouring the swelling phenomenon. In another study, Lequin et al. observed that the adsorbed amount of water on cork powder, obtained by grinding a cork stopper, was higher than that on cork plates, whatever the relative pressure (Lequin et al., 2010).

During ageing in contact with ethanol vapour (Fig. 3a, orange bar), a volume increase of 2.2 ± 1.6%, 14.7 ± 2.5% and 28.2 ± 4.1% was noted for natural, *mi* and *MA* samples, respectively. Lequin et al. demonstrated that the sorption mechanism of ethanol on natural cork was characterized by an hysteresis phenomenon between sorption and desorption. This hysteresis was attributed to the swelling of the material (Lequin et al., 2013). From the present results, it is worthy to note that *mi* and *MA* cork underwent greater swelling than natural cork, suggesting that the adhesive probably plays an important role in this phenomenon. Indeed, PU binder samples, exhibited a strong affinity for ethanol, leading to a storage volume increase of 87.2 ± 12.6% when exposed to ethanol vapour. When cork-based samples were completely immersed in ethanol, similar trends were observed (Fig. 3a, red bar). Only a slight swelling was noticeable for natural cork (1.2 ± 1%), while *mi* and *MA* cork increased in volume by 29.3 ± 1.3% and 30.7 ± 2.1%, respectively. Particularly, for PU binder, a tremendous swelling of approximately 800% was observed during ageing. An example of PU binder swelled after contact with ethanol (vapour and liquid phase) is illustrated in figure 13 (Appendix M). It is also important to note that, agglomerated cork stoppers have different adhesive content, equal to 20% w/w for *mi* and 8% w/w for *MA*. However, the comparable swelling values for this samples suggest that the percentage of adhesive did not affected this phenomenon, as previously discussed in Section 3.2.

The second graph in Fig. 3b shows the variation in volume after vacuum treatment (ΔV_v, pressure p ~1 mbar, 25°C, 14 days) performed on aged samples. When stored in contact with water (liquid phase), a slight reduction in volume was observed compared to the volume measured before the ageing test: 8.7 ± 3.8% for natural cork, 17.0 ± 3% for *mi* cork, and 12.7 ± 2.8% for *MA* cork. In contrast, the variation for

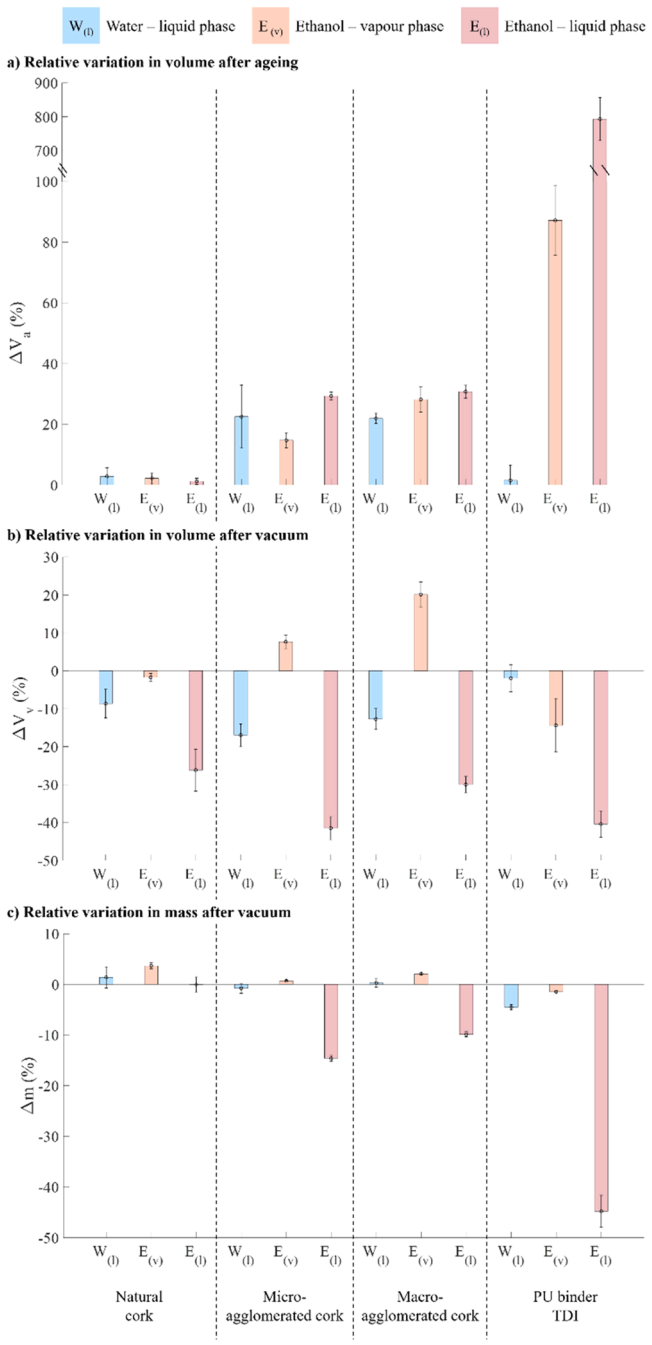

Fig. 3. (a) Relative variation in volume after 200 days-ageing period at 50°C (ΔV_a), and (b) relative variation in volume after vacuum treatment (ΔV_v, p ~1 mbar, 25°C, 14 days) as a function of storage conditions. (c) Relative variation in mass (Δm), calculated as the difference between the final weight of the sample after vacuum treatment and its initial weight before the ageing period as a function of storage conditions. Natural cork (n = 6), microagglomerated cork (n = 5), macroagglomerated cork (n = 5) for all storage conditions. PU binder (n = 4 for contact with water in liquid phase; n = 3 for contact with ethanol in vapour or liquid phase).

PU binder samples was negligible (|ΔV| of 1.9 ± 3.5%). This phenomenon was more pronounced for samples completely immersed in ethanol. The volume of natural cork decreased moderately by 26.1 ± 5.5%, while stronger reductions were observed for *mi* cork (41.5 ± 3.0%), *MA* cork (30.0 ± 2.1%), and PU binder (40.4 ± 3.5%). In the latter case, both ethanol exposure and vacuum treatment caused damage to the PU polymer structure, leading to collapse. X-ray tomography was used for volume measurement as reported in figure 13d (appendix M). Interestingly, for samples exposed to ethanol vapour, two different phenomena were observed. Natural cork and PU binder exhibited a reduction in volume of 1.7 ± 1.0% and 14.4 ± 7.0%, respectively. In contrast, an increase in volume was noted for *mi* cork (7.7 ± 1.8%) and for *MA* cork (20.1 ± 3.3%).

To further discuss the results presented in Fig. 3b, it is important to compare with Fig. 3c, which shows the variation in mass calculated as the difference between the final weight of the sample after vacuum treatment and its initial weight before the ageing period. Mass reduction was very low for natural and agglomerated cork samples after complete immersion in water, whereas PU binder exhibited a mass loss of 4.5 ± 0.6%. This could be attributed to hydrolysis reaction occurring during the ageing period. Le Gac et al. reported that PU immersed in seawater at temperatures between 25 and 120°C for 18 months underwent hydrolysis. This process led to chain scission in the polymer (urethane linkage), which caused a significant modification of the tensile behaviour (stress at break decreased, elongation at break increased followed by a drastic drop). Hydrolysis of PU can be described using the Arrhenius law, with a first order reaction rate k of 2.8×10^{-12} s^{-1} at 70°C (Le Gac et al., 2013). The reaction also occurs at lower temperatures, albeit at much slower rates: at 50°C, which corresponds to the ageing temperature used in the present study, the reaction rate is about 14 times lower ($k = 2.3 \times 10^{-13}$ s^{-1}) than at 70°C, while at 25°C it is approximately 400 times lower ($k = 6.3 \times 10^{-15}$ s^{-1}).

Interestingly, in Fig. 3c, even after vacuum treatment, cork-based samples in contact with ethanol vapour exhibited the opposite phenomenon to that observed after complete immersion in water. Natural, *mi* and *MA* cork samples showed a slight increase in mass of 3.7 ± 0.6%, 0.7 ± 0.1%, and 2.0 ± 0.2%, respectively. This is due to the ethanol vapour sorption on cork. Indeed, cork has been demonstrated to have strong affinity with ethanol in the vapour phase. At 25°C and for a relative ethanol pressure of 0.7, the sorbed amount of ethanol is ~1 $mmol.g^{-1}$ (Lequin et al., 2013). Furthermore, Lequin et al. found that a chemisorption mechanism occurs in addition to physisorption, meaning that the sorption-desorption phenomenon is not reversible. The amount of ethanol that remained chemically bonded to the cork surface was about ~0.25 $mmol.g^{-1}$ (25% of the total sorbed quantity) (Lequin et al., 2013). In contrast, for PU binder stored in ethanol vapour, a mass loss of 1.5 ± 0.2% was noted. This could be attribute to a degradation phenomenon.

A negligible reduction in mass (0.03 ± 1.5%) was observed for natural cork samples completely immersed in ethanol. However, an extraction phenomenon of cork compounds may have occurred as a brown colour of the liquid was observed at the end of the ageing period. For PU binder, a mass loss of 44.8 ± 3.2% was observed, suggesting partial solubilization or degradation of the adhesive. For *mi* and *MA* cork, a reduction in mass of 14.6 ± 0.6% and 9.9 ± 0.5% was observed, respectively. Even for cork-based samples a brown colour was observed, suggesting an extraction phenomenon on cork compounds and/or potential degradation of PU binder (Fig. 3c). This result correlates with the corresponding volume reduction shown in Fig. 3b.

Six et al. has reported a possible migrants from synthetic products (adhesives, surface treatment and lubricants) used for cork stopper, simulating long-term storage condition in 12% ethanol for 10 days at 40°C (Six and Feigenbaum, 2003). More recently, Corrias et al. performed a release test on a one-piece agglomerated cork stopper immersed in white wine (10.5% v/v) and ethanol (96%) for 48 h at room temperature. They found that ethanol had a higher extraction capacity on PU isocyanates compounds (2,4 TDI and 2,6 TDI) than white wine (Corrias et al., 2021). In another study, Non-Intentionally Added Substances (NIAS), formed by the reaction between ethanol and diisocyanates, were detected in champagne bottle (20 cL) following a 10 days storage period at 60°C in horizontal position (Canellas et al., 2021). However, it should be emphasized that, in the context of the present work, no direct analysis of the liquid phase was performed, and

therefore no definitive conclusions can be drawn regarding the degradation or migration of PU components under the tested conditions.

3.4. Mechanical response of the different type of aged cork stoppers

The mechanical response to repeated loading cycles of natural and agglomerated cork as well as PU binder was studied after ageing (200 days at 50°C). Prior to the mechanical analysis, samples were vacuum treated (p ~1 mbar, 25°C, 14 days) in order to remove water or ethanol, and to focus on the mechanical behaviour of the sole material. The mechanical ageing of the cork stopper was discussed based on two parameters: the tangent modulus, which characterises the material's stiffness and the dissipated energy, which reflects the evolution of its compressive behaviour over the cycle repetitions. Data on residual strain and stress loss are provided in the appendices for the interested reader (A-H). Fig. 4 shows the tangent modulus values obtained for the first cycle repetition (*a*) at 43% Hencky strain. The data relative to the successive cycle repetitions (*b* to *h*) are presented in appendices (A-H). The samples from the different ageing storage conditions were compared with non-aged samples stored at 25°C and 50% RH.

At the macroscopic scale, when natural cork was aged in contact with water (liquid phase), a significant increase in stiffness was observed from mechanical testing. The tangent modulus reached 29.1 ± 4.0 MPa. This is approximately 1.7 times higher than that of the reference sample (16.9 ± 4.6 MPa), indicating an increased rigidity of the material. To the best of our knowledge, very little is known about the ageing of cork in contact with liquid water, and no specific study has been reported in the literature. Although no direct comparison can be made, previous

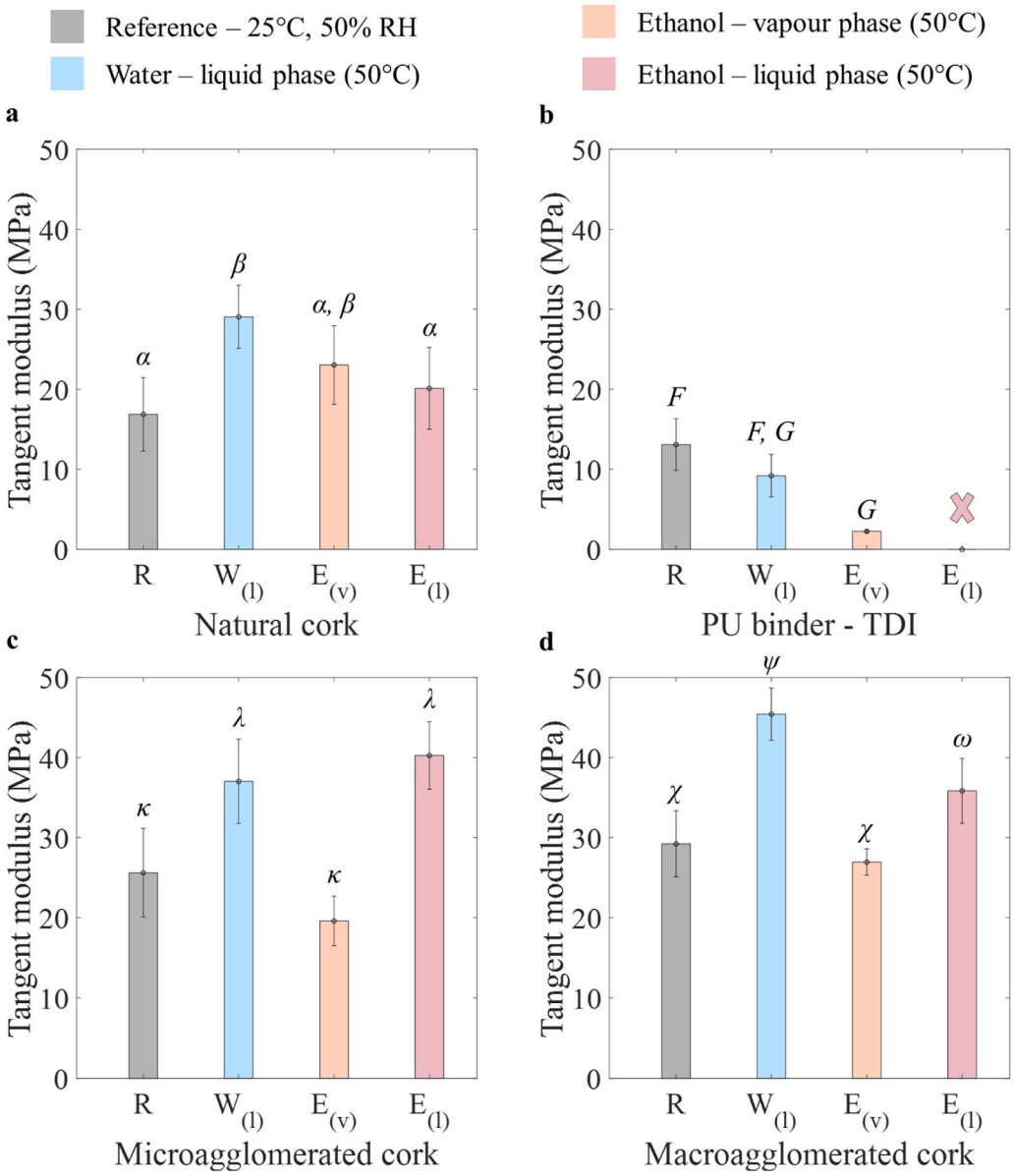

Fig. 4. Tangent modulus values calculated from the 1st cycle of a repeated loading test at 43% Hencky strain performed at 25°C on (a) natural cork (n = 6), (b) PU binder (reference: n = 6; water – liquid phase: n = 4; ethanol – vapour phase: n = 3) and (c, d) agglomerated cork (n = 5) samples aged in contact with water (liquid phase) or ethanol (vapour or liquid phase) for 200 days at 50°C. No repeated loading test was conducted on PU binder samples aged in contact with ethanol (liquid phase) due to collapse of the structure following the vacuum treatment. The Mechanical analysis of the aged samples was carried out after removing the water or ethanol by vacuum treatment. Statistics: one-way ANOVA comparing storage conditions for the first cycle repetition. Significant differences (p value < 0.05) are indicated by different letters for natural cork (α, β), for microagglomerated cork (κ, λ), and for macroagglomerated cork (χ,ψ,ω). Kruskal-Wallis test was used for PU binder samples (F, G).

studies on natural cork (Lagorce-Tachon et al., 2015a) and cork-based stoppers (Lagorce-Tachon et al., 2016a) can be used as a basis for discussion. In these two studies, samples were stored at 25°C for at least three months under controlled relative humidity conditions (0% - 100% RH). Quasi-static compression test was then performed at a crosshead displacement rate of 60 mm·min^{-1} (sixty times higher than that used in the present work). These works highlighted the plasticizing effect of water on the compressive mechanical response of cork. For natural cork in the tangential direction, the elastic modulus decreased significantly—by approximately a factor of three—in the 50–100% RH range, from 22 MPa to 6.6 MPa. In contrast, within the 0–50% RH range, no plasticizing effect of water was observed, as the elastic modulus remained approximately 22 MPa (Lagorce-Tachon et al., 2015a).

In the present work, when considering hydration states comparable to those investigated by Lagorce-Tachon et al.—namely ~0% RH for aged, dehydrated cork and ~50% RH for the non-aged reference—a significant increase in stiffness by a factor of 1.7 was observed for aged samples after mechanical testing, suggesting a possible ageing effect in natural cork. At the microscopic scale, SEM observations of samples aged by complete immersion in liquid water and subsequently dehydrated revealed delamination between cell walls (0.2–0.6 μm) after mechanical testing (Fig. 5b), compared to the reference (50% RH) (Fig. 5a). This phenomenon can be attributed to the combined effect of mechanical compression and the low hydration state of the material. Similar features have been observed after compression testing of non-aged, dehydrated natural cork at 25°C (Lagorce-Tachon et al., 2015a).

Therefore, the ageing effect should be investigated at the molecular scale. The prolonged exposure of natural cork to liquid water for 200 days at 50°C may have induced modifications in certain cell wall components. Lagorce-Tachon et al. reported a glass transition temperature (Tg) in cork of approximately −9.5 ± 1.5°C, close to saturation at 97% RH (Lagorce-Tachon et al., 2015a). Under the conditions of the ageing test, the corresponding amorphous polymer fraction of cork was therefore well above its glass transition and existed in a rubbery state. In this state, the polymer chains exhibit high mobility, enabling molecular rearrangements within the cell wall network. However, the vacuum treatment applied to remove water prior to mechanical testing led to an increase in Tg (with a reported value of 26.5 ± 1.3°C at around 0% RH (Lagorce-Tachon et al., 2015a), shifting from rubbery to glassy state at the temperature of measurement.

The increased stiffness can also result from the hydrolysis of cork components (suberin, lignin, polysaccharides) that may occurred during ageing. Simoes et al. studied the effect of the hydrothermal treatment on the structural components of cork, applying different temperatures (from 120°C to 180°C) and time conditions (60, 120, 180 and 240 min) (Simões et al., 2024). Hemicelluloses were completely hydrolysed under the most severe conditions. Suberin, in contrast, exhibited high chemical resistance, remaining stable up to 160°C, with depolymerisation occurring only under more extreme conditions. Lignin, however, remained stable regardless of the treatment applied (Simões et al., 2024). Although the experimental temperature in the present study was lower than that of Simões et al., the much longer exposure time may have contributed to this phenomenon. Indeed, the ageing test was conducted over a period approximately 1200 times longer than the treatments reported by Simões et al.

When aged in contact with ethanol, the tangent modulus values measured following vapour phase exposure (23.0 ± 4.9 MPa) and complete immersion (20.1 ± 5.1 MPa) did not differ significantly from the reference (16.9 ± 4.6 MPa). The effects of ethanol exposure may have been partially masked by the high variability observed in the cork's compression behaviour. Indeed, regardless of storage conditions, it should be noted that it exhibited a rather high variability, which is typical of biological materials (Fig. 4a). Calculated coefficients of variation were of 27% for the reference (25°C and 50% RH), and of about 23% for aged samples in contact with ethanol (vapour and liquid phase). These values are consistent with those reported in the literature for the compressive behaviour of natural cork, ranging from 16% to 38% (Gibson et al., 1981, Pereira et al., 1992, Anjos et al., 2014, Oliveira et al., 2014). At the microscopic scale, ethanol vapour storage did not affect the cork cell walls of dried natural cork sample, as shown in the SEM images in Fig. 5c. In contrast, for natural cork completely immersed in ethanol, delamination between cell walls of dried natural cork was noted (Fig. 5d), as previously reported for samples aged in water (liquid phase). Interestingly, when cork was in contact with ethanol in the liquid phase, the cell wall underwent degradation, as evidenced by straight lines marks (length: 0.9–3.7 μm, thickness: ~0.1 μm; Fig. 5e, f, g). This effect was not observed for samples aged in water (Fig. 5b), suggesting that cork react differently with ethanol and water.

Ethanol is one of the solvents employed to extract lignin from plant biomass (Bui et al., 2015, Tong et al., 2024). In this experiment, although this reaction is limited at 50°C, weak extraction may occur over 200 days. The lignin extraction caused by the reaction with ethanol could favoured a weakening of cell walls. Thus, during the repeated loading test, an enhanced contact between cell walls could explain the increase in cork rigidity. This hypothesis is supported by the results obtained by Pereira, who reported that, without lignin, cork cells collapse (Pereira, 2007a). Looking at the elastic modulus calculated in the elastic zone of the stress-strain curve for the first loading cycle (figure 14, appendix N), it can be observed that natural cork aged in ethanol (liquid phase) exhibits a lower value (5.6 ± 1.5 MPa) compared to the reference (9.9 ± 4.5 MPa). This reduction in elastic modulus suggests that ethanol may have damaged the cork cells walls. Consequently, under repeated loading, earlier buckling of the cork structure could promote greater contact between the cell walls, leading to earlier densification of the material. This densification may account for the higher tangent modulus observed after the first unloading cycle and, consequently, the increased stiffness of the material.

For the PU binder, a significant reduction of the tangent modulus by a factor 5.7 was calculated for aged samples exposed to ethanol vapour (2.3 ± 0.2 MPa) compared to non-aged samples (13.1 ± 3.2 MPa) (Fig. 4b). This indicates a strong interaction and/or reactivity between polyurethane binder with ethanol, as previously shown in Fig. 2a. This phenomenon was even more pronounced when the binder was completely immersed in ethanol. In this case, the sample reached a critical stage, causing the structure to collapse after vacuum treatment (figure 13, appendix M). Consequently, mechanical testing could not be performed on the affected samples. On the contrary, when stored in contact with water (liquid phase) no statistically significant difference was observed between the reference (13.1 ± 3.2 MPa) and aged samples (9.2 ± 2.7 MPa). However, it is noteworthy that a slight decrease in tangent modulus was observed for aged samples. This suggests that hydrolysis of urethane linkage could occur as previously described in Section 3.3.

The tangent modulus values calculated for *mi* cork aged samples completely immersed in water (37.0 ± 5.3 MPa) or ethanol (40.3 ± 4.2 MPa), were significantly higher than that of the reference (25.6 ± 5.5 MPa). In contrast, no significant difference was observed between samples exposed to ethanol vapour (19.6 ± 3.1 MPa) and the reference (Fig. 4c). *MA* cork exhibited the similar behaviour of *mi* cork after ageing. Significantly higher tangent moduli were obtained for samples after complete immersion in water (45.4 ± 3.3 MPa) or ethanol (35.8 ± 4.1 MPa) compard to the reference (29.2 ± 4.1 MPa). Samples exposed to ethanol vapour (27.0 ± 1.7 MPa) did not differ significantly from the reference (Fig. 4d).

These findings suggest that, according to the storage condition, various phenomena may occur during ageing, potentially affecting both the cork and the polyurethane (PU) binder. Considering cork, the grinding process may partially damage the cork particles, increasing their surface area in contact with water or ethanol. This may favoured hydrolysis and extraction phenomena by ethanol, as previously hypothesized. Considering the PU binder, structural modifications likely occurred during ageing in contact with ethanol (liquid phase), leading to

the collapse of the structure after vacuum treatment, as shown in figure 13 (appendix M). Therefore, in *mi* and *MA* samples, this could lead to increased friction between the cork particles, which contributed to the higher stiffness. In contrast to the results observed in liquid simulant, no significant difference was found between the reference and the aged samples stored with ethanol vapour. In this case the amount of ethanol sorbed does not seem to be sufficient to exert a significant influence on the mechanical behaviour of *mi* and *MA* corks stoppers.

From repeated loading test, the dissipated energy (*W*) parameter was also analysed. It highlights the evolution of the compressive behaviour over the cycle repetitions (*a-h*). Fig. 6a, b reports the dissipated energy values from the 8 repetitions obtained for natural cork and PU binder

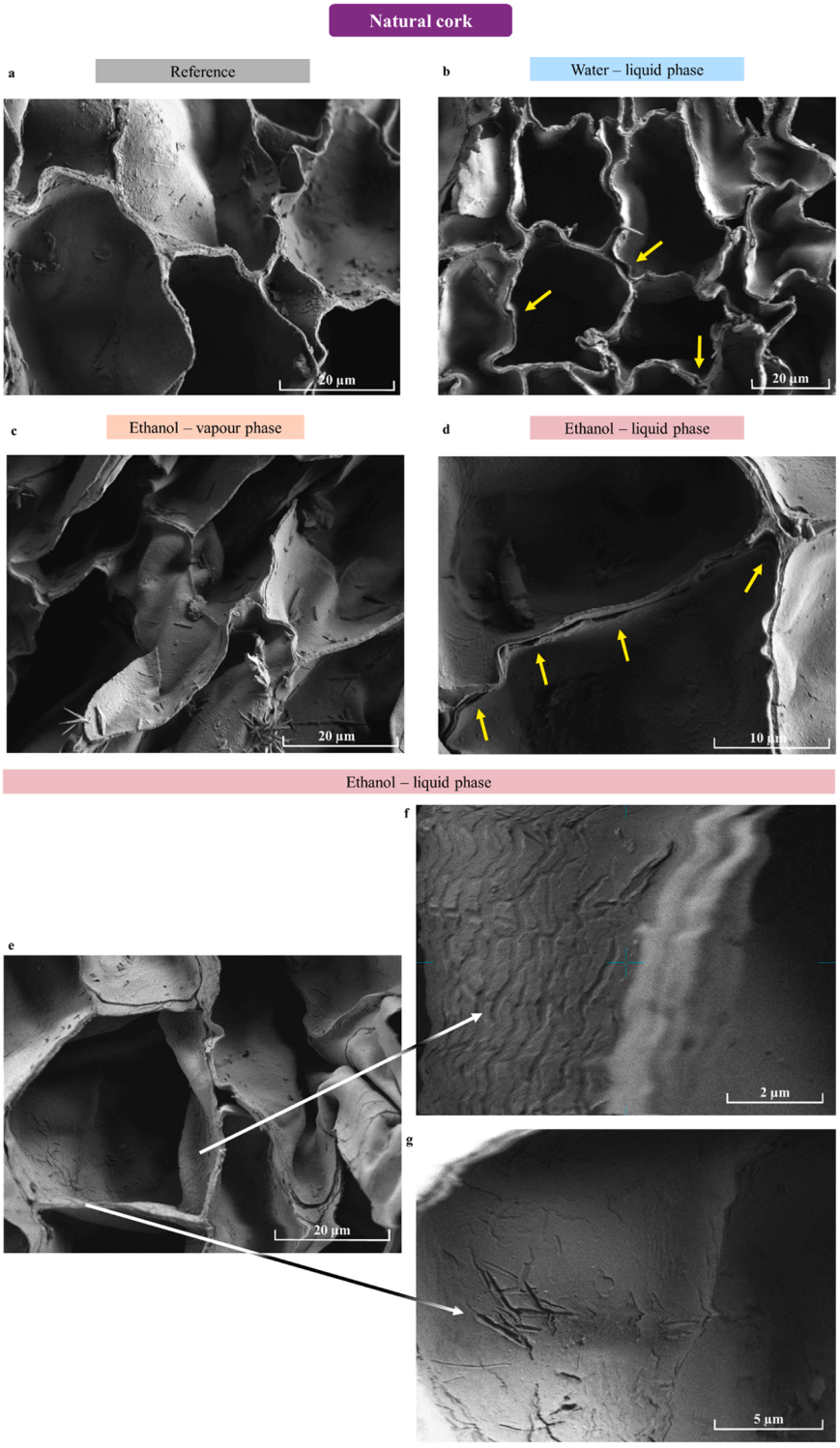

Fig. 5. Scanning electron microscopy images observed at T = 4°C, and p = 500 Pa of natural cork samples after repeated loading test performed at 25°C (eight cycle repetitions at 43% Hencky strain): (a) Reference material (stored at 25°C, 50% RH); and a aged, vacuum-treated samples during 200 days at 50°C in contact with (b) water (liquid phase), (c) ethanol (vapour phase), (d, e) ethanol (liquid phase). (f, g) Enlarged views on the cell wall after ageing in complete immersion in ethanol. Yellow arrows clearly show the occurrence of delamination phenomena between cell walls.

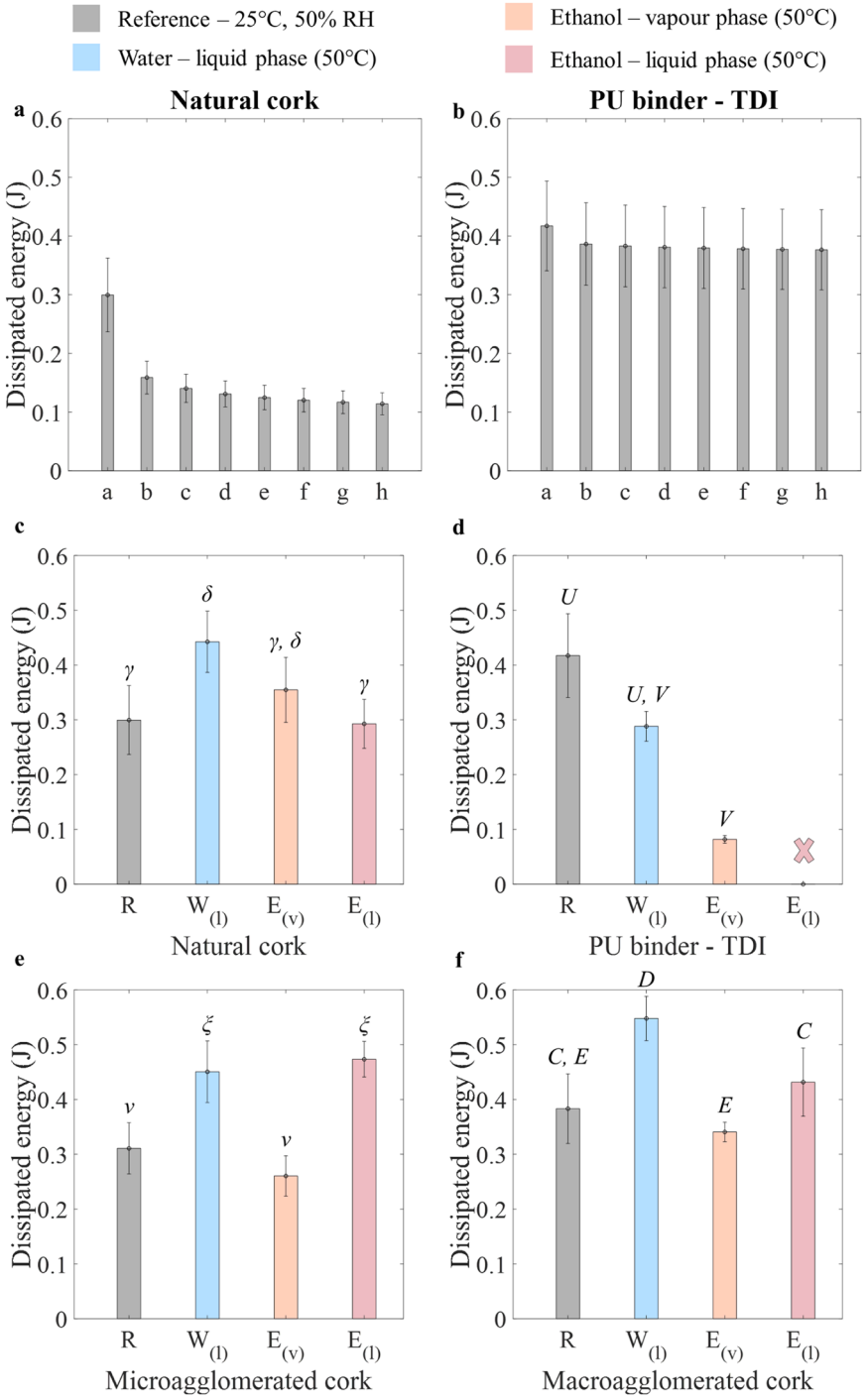

Fig. 6. Dissipated energy calculated for the eight cycle repetitions from a repeated loading test performed at 25°C on (a) natural cork (n = 6), (b) PU binder stored at 25°C, 50% RH (reference: n = 6; water – liquid phase: n = 4; ethanol – vapour phase: n = 3). (c, d, e, f) Dissipated energy values calculated from the 1st repetition of a repeated loading test performed on natural cork, PU binder, microagglomerated (n = 5) and macroagglomerated cork (n = 5) samples aged in contact with water (liquid phase) or ethanol (vapour or liquid phase) for 200 days at 50°C. No repeated loading test was conducted on PU binder samples aged in contact with ethanol (liquid phase) due to collapse of the structure following the vacuum treatment. The Mechanical analysis of the aged samples was carried out after removing the water or ethanol by vacuum treatment. Statistics: one-way ANOVA comparing storage conditions for the first cycle repetition. Significant differences (p value < 0.05) are indicated by different letters for natural cork (γ, δ), for microagglomerated cork (ν, ξ), and for macroagglomerated cork samples (C, D, E). Kruskal-Wallis test was used for PU binder (U, V).

stored at 25°C and 50% RH (references). The greatest reduction in dissipated energy for natural cork occurred between the first (*a*) and second (*b*) repetition: 46% for the reference (non-aged), 47% for ethanol (liquid phase), 56% for ethanol (vapour phase), and 57% for water (liquid phase). A smaller decrease of about 15% was observed between third (*c*) and eighth (*h*) repetitions. This pronounced initial reduction suggests that accommodation mechanisms occurred in the material from the first cycle repetition onwards (*b*). For example, such changes may reflect plastic deformation, in which part of the strain becomes permanent; damage on the material structure; and viscous effects, which are time-dependent and release energy more slowly. Each of these mechanisms contributes to the material's reduced ability to recover elastic

energy during cyclic loading. Similar behaviour was observed for agglomerated cork (figure 12, appendix L).

However, it is also important to note that even after eight compression repetitions, the cork material maintained approximately 30% of its initial energy storage capacity for all storage conditions. On the contrary, PU binder shown a relatively stable ability to store energy over the eight cycle repetitions. Only a slight reduction of approximately 10% was observed compared to natural cork (Fig. 6b). For *mi* and *MA* samples, composed of cork and PU binder, the trend observed over the cycle repetitions was similar to that observed for natural cork, suggesting that their compressive behaviour is mainly driven by the cork component (figure 12, appendix L).

The dissipated energy values for the first (*a*) repetition for natural cork, PU binder, *mi* cork and *MA* cork samples are shown in Fig. 6c, d, e, f, respectively (data related to repetitions *b-h* are presented in figure 11 and figure 12 in appendices I and L). Considering the ageing conditions, a significant difference in dissipated energy during the first loading cycle values was observed for water-aged natural cork samples, showing a higher dissipated energy capacity than the reference. This is consistent with the results obtained for the tangent modulus. No significant difference was observed for ethanol-aged samples compared to the reference (Fig. 6c). Conversely, when exposed to ethanol, the compressive behaviour of PU binder was strongly affected, resulting in a fivefold reduction of dissipated energy capacity compared to unaged sample (Fig. 6d). For *mi* cork, samples aged in contact with water or ethanol (liquid phase) showed significant differences compared to the reference, whereas those exposed to ethanol vapour exhibited no noticeable variation (Fig. 6e). For *MA* cork, only water-aged samples differed significantly from the reference, whereas no significant differences were observed between the reference and ethanol-aged samples (Fig. 6f). In agglomerated cork stoppers, the cork particles exhibit all three possible orientations (tangential, radial, and axial) that can confer more isotropy to the material at macroscale (Chanut et al., 2021). The effect of storage conditions on the dissipated energy capacity of *MA* cork stoppers may therefore be masked.

4. Conclusions

First, water and ethanol sorption kinetics in both vapour and liquid phase were investigated for natural and agglomerated cork stoppers, as well as on the polyurethane (PU) binder under accelerated ageing conditions (200 days at 50°C). Sorption occurred in all materials upon exposure to water or ethanol associated with swelling, especially for samples stored in liquid phase. During ageing in contact with ethanol (vapour phase), the PU binder sorbed approximately four times more ethanol than natural and agglomerated cork stoppers. In liquid water, the volume occupied ranged from 45% to 81%, coupled with swelling of 12–17% for cork-based stoppers, whereas the PU binder showed negligible water uptake and swelling. When in contact with ethanol (liquid phase) the volume filled reached 79–88%, coupled with stronger swelling up to ~30%. In contrast, for the PU binder it achieved ~97%, couple with remarkable swelling of approximately 800%.

Second, a repeated loading test was performed to better understanding changes occurring in the compressive behaviour of aged samples. The instantaneous mechanical response was characterised by the tangent modulus. A stiffening of the aged cork-based stoppers was observed after complete immersion in water and ethanol. The PU binder was strongly affected by exposure to ethanol vapour, with a decrease in tangent modulus by a factor of 5.7. The evolution of the mechanical response overs the cycle repetitions (*a-h*) was characterised by the dissipated energy. Approximately half of reduction occurred between *a* and *b* cycle repetitions. This suggests that accommodation mechanisms occurred in the material (e.g. plasticity, viscous or damage effects). In contrast, the PU binder ability to store energy remained relatively stable over the eight repetitions.

To go further, structural investigations of cork-based stoppers could be conducted using image analysis techniques at the microscopic scale to directly observe the buckling phenomenon. Such observations would also provide deeper insight into the sorption and imbibition processes occurring within the cork structure after contact with water or ethanol. In addition, chemical characterisation of the extracted components could help elucidate the impact of ageing on the compressive behaviour of cork-based stoppers.

CRediT authorship contribution statement

Sébastien Thibaud: Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Karbowiak Thomas:** Writing – review & editing, Validation, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Aline Bonnotte:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis. **François Villette:** Writing – review & editing, Validation, Software, Methodology, Formal analysis, Conceptualization. **Xavier Gabrion:** Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Aurélie Lagorce:** Writing – review & editing, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Massimiliano Gerometta:** Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2026.101813.

Data availability

Data will be made available on request.

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