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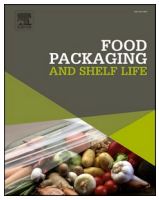

Moisture uptake during storage of coffee packed into compostable capsules decreases the quality of coffee brew

Marco Lopriore [a], Marilisa Alongi [a,*], Sonia Calligaris [a], Lara Manzocco [a], Giulia Ravaioli [b], Ada Nucci [b], Maria Cristina Nicoli [a]

[a] Department of Agricultural, Food, Environmental, and Animal Sciences, University of Udine, Via Sondrio 2/A, Udine 33100, Italy
[b] Lavazza Torino, S.p.A, Italy

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ABSTRACT

Compostable bioplastics for coffee capsule production should satisfy compostability requirements while providing a moisture barrier able to guarantee the espresso coffee quality. The present study aimed at exploring the time required for coffee packed in biobased PBS capsules and stored under different temperature and relative humidity to reach critical moisture levels triggering quality decay. Samples were stored in plastic boxes containing supersaturated solutions of $Mg(NO_3)_2$, $NaNO_2$ or NaCl guaranteeing 54, 65 or 75 % RH, placed at 20, 30 and 45 °C in thermostatic incubators. During storage, the coffee powder was analysed for moisture uptake and water activity, and the coffee brew was extracted to measure the pH, selected as the quality indicator. Over 18 months, moisture uptake rapidly increased, reaching critical levels within 3 weeks in the worst-case scenario (*i.e.*, 45 °C and 75 % RH). The evolution of pH presented an initial lag phase and a subsequent linear decay, which were respectively shorter (< 15 days) and faster (pH < 5.1 within 1 month) in the worst-case scenario. The findings highlight the role of T and RH in affecting coffee quality decay and emphasize the potential drawbacks of adopting biopolymer-based packaging. These outcomes could help food manufacturers in scouting new packaging materials for coffee capsule applications, evidencing the potential drawbacks of replacing conventional packaging materials with biobased ones. In this regard, it is recommended that a thorough cost-benefit analysis is carried out before transitioning from conventional to compostable packaging to ensure sustainability goals are effectively met while maintaining product quality.

1. Introduction

Coffee has become a global lifestyle product, with single-dose capsules significantly increasing its popularity due to the high-quality brews thereof extracted. This allows consumers to drink an espresso coffee with its typical sensory attributes (flavour, taste, foam) at home within seconds (Lopes et al., 2021).

Although directly linked to the characteristics and quality of the ground roasted coffee used, the sensory experience upon coffee brew consumption is also greatly affected by the changes occurring during the storage of the coffee capsules (Strocchi et al., 2022, Strocchi et al., 2023a, 2023b). The main changes are generally due to the development of oxidative reactions leading to the formation of hydroperoxides and off-flavours as well as acidity increase associated to organic acid hydrolysis (Goodman & Yeretzian, 2015; Strocchi et al., 2022; Strocchi et al., 2023a, 2023b). This phenomenon contributes to increase coffee acidity (Ginz et al., 2000; Santanatoglia et al., 2023) leading to an unpleasant flavor and aroma (Nicoli & Savonitti, 2005; Sivetz & Foote, 1963; Thomas et al., 2017) with a subsequent reduction of its acceptability (Manzocco & Nicoli, 2007). Besides the foam layer, body and uniformity are typically considered as indicators accounting for the quality of coffee brew (Mardjan & Hakim, 2019), acidity remains the most reliable sensory indicator accounting for coffee staling. In this regard, pH is the physical-chemical parameter which best correlates with perceived acidity (Ruthenberg & Chang, 2017; Santanatoglia et al., 2024).

Since roasted coffee is a dry product, oxygen and moisture are the major environmental factors affecting its stability during storage and hence its shelf life. Both factors can be taken under control by selecting proper packaging materials and technology. Traditional packaging materials such as polyolefins, polyvinyl chloride, ethylene vinyl alcohol, and composite polymer-aluminium foils continue to be the most

* Corresponding author.
E-mail address: marilisa.alongi@uniud.it (M. Alongi).

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effective solutions for meeting the requirements of both single and multi-dose ground coffee containers. Their primary advantage lies in the ability to combine various of the aforementioned materials, each with distinct barrier properties, to create multilayer laminate materials that provide an optimal high-barrier against oxygen and water vapor.

At the same time, additional interventions (*i.e.*, modified atmosphere, pressurization) are applied to maintain oxygen below the critical value triggering the development of oxidation. These packaging strategies have been used for decades to pack coffee allowing a very prolonged shelf life of around 18–24 months (Manzocco et al., 2019). However, the urgency of facing the issue of plastic pollution due to the non-biodegradability of conventional plastics, coupled with the inability to recycle packaging materials because of their multilayer structure (Marinello et al., 2021), led regulatory bodies to issue a directive (European Union, 2019) aimed at inverting this trend. These policies primarily target single-use plastics, and in the case of coffee, single-dose capsules. Consequently, policies promoting the transition to bioplastics, together with the growing market demand for more sustainable solutions, are significantly pushing the packaging industry to invest in bioplastics. However, transitioning to bioplastics is not yet an easy task. Not only these new packaging materials could pose unexpected drawbacks when exposed to real working conditions (*e.g.*, loss of mechanical strength and/or barrier properties during storage), but they could also require new dedicated handling procedures during processing and storage.

As a response to these concerns and uncertainties, some coffee companies are exploring ways to balance product protection and sustainability by replacing petroleum-derived capsules with compostable biobased alternatives, while concomitantly studying their potentialities. Some examples of bioplastics are polybutylene succinate (PBS), polylactic acid (PLA), and polybutylene adipate terephthalate (PBAT) (European Bioplastics, 2022). Among these, PBS is gaining popularity in the food industry due to its processing flexibility, making it easy to manufacture using standard plastic processing methods like extrusion, injection molding, and blow molding. PBS application is particularly convenient due to its good mechanical properties (*i.e.*, tensile strength and flexibility), high melting point and thermal stability, which make it well-suited for coffee brewing. Moreover, its ability to blend with other biopolymers or traditional plastics is of significant importance, enabling the development of customized materials and biocompatible blends tailored for specific applications (Aliotta et al., 2022). However, the only current application of PBS in the food sector concerns the production of active packaging containers to extend the shelf-life of fresh products (*e.g.*, red grapes and fresh pasta) (Hernández-García et al., 2023; Hu et al., 2023). Besides guaranteeing satisfactory processability and mechanical properties, bioplastics such as PBS also provide a barrier against oxygen that, in some cases, is even higher than that provided by conventional petroleum-based polymers (Wu et al., 2021). The permeability of PBS to water vapor is crucial to guarantee the overall efficiency and success of the composting process, which requires proper moisture levels to facilitate the breakdown of the organic waste and the packaging material itself (Folino et al., 2020). Nevertheless, the permeability of PBS to water vapour may present a significant drawback, since the moisture entering the capsule might be absorbed by coffee, leading to the increase of a_w above the critical monolayer value and the depression of T_g below room temperature. The resulting coffee plasticization may cause the acceleration of the alterative events leading to pH decrease (Manzocco & Nicoli, 2007; Anese et al., 2005).

Some works in literature already highlighted the potential drawbacks of biopolymer-based packaging intended for packing dry foods (Lee & Robertson, 2021; Macedo et al., 2012). In particular, Strocchi et al., (2023a, 2023b) observed significant moisture increase and pH decrease during 90-day storage under stress conditions (*i.e.*, 45 °C and 65 % RH) of coffee packed in compostable capsules made of a non-specified biopolymer.

Nevertheless, to the best of our knowledge, no investigation has been carried out to study the time required by coffee packed in biobased capsules and stored under different temperature and RH conditions to reach the critical moisture triggering plasticisation and pH decrease.

In light of these considerations, this study aims to address the following questions: (i) "how long does it take for coffee packed in biobased PBS capsules to reach critical moisture levels during shipping and storage?"; (ii) "what is the rate and extent of quality decay in the coffee brew associated with moisture uptake?". Therefore, the effect of moisture uptake during storage of ground roasted coffee packed in biobased capsules made of PBS on the quality of the espresso coffee brew was investigated. To this purpose, the modified state diagram of ground roasted coffee was firstly determined to have insights on the glass transition temperature and sorption isotherm of coffee as a function of water activity. Then, the roasted and ground coffee was packed in capsules, which were stored at different temperature (20, 30, 45 °C) and RH (54, 65 and 75 %) to simulate different environmental conditions possibly experienced by capsules during storage. The changes in moisture and water activity of roasted coffee during storage were then investigated as well as the pH changes of the coffee brew obtained from coffee capsules having different storage time under the considered environmental conditions.

2. Materials and methods

2.1. Chemicals

Lithium chloride (LiCl, purity ≥ 99 %), magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\ H_2O$, purity ≥ 99 %), sodium chloride (NaCl, purity ≥ 99 %), and potassium chloride (KCl, purity ≥ 99 %) were purchased from Merck KGaA (Darmstadt, Germany). Potassium acetate ($C_2H_3O_2K$, purity = 98 %), magnesium chloride hexahydrate ($MgCl_2 \cdot 6\ H_2O$, purity ≥ 97 %), potassium carbonate (K_2CO_3, purity ≥ 99 %), and sodium nitrite ($NaNO_2$, purity ≥ 97 %) were purchased from Avantor (Radnor, USA). Potassium sulphate (K_2SO_4, purity ≥ 99 %) was purchased from Carlo Erba (Rodano, Italy). Water was purified with a Milli-Q system (Millipore, Bedford, MA, USA).

2.2. Coffee capsule storage

Freshly produced coffee capsules from the same batch were provided by Lavazza Torino S.p.A. Capsules were made of polybutylene succinate (PBS).

Each capsule contained 7 g of ground-roasted coffee blend (*i.e.*, *Coffea arabica* and *Robusta*) packed under nitrogen with an oxygen residue below 1 %. Coffee capsules were stored in 9 different environmental conditions by combining 3 different temperatures (*i.e.*, 20, 30, and 45 °C) and 3 different environmental relative humidities (54, 65 and 75 % RH). The RH values were guaranteed, during the whole storage interval, by placing at the bottom of hermetically closed plastic boxes a thin layer of supersaturated solutions of $Mg(NO_3)_2$, $NaNO_2$ or NaCl for the 54 %, 65 % or 75 % RH, respectively. Coffee capsules were placed on a suspended perforated tray in the boxes, to prevent any direct contact with the supersaturated solution.

To ensure that coffee samples were maintained at the selected temperatures (*i.e.*, 20, 30, and 45 °C) during storage, the plastic boxes were stored in dark conditions in three thermostatic incubators (Pol-Eko, Wodzislaw Slaski, Poland) set at 20, 30, or 45 °C (±1 °C). Specifically, three boxes, each containing samples equilibrated at the three different RH, were allocated in each incubator. At different storage times, coffee capsules were collected and used to determine the water activity (a_w) and the moisture content (M) of coffee powder and to measure the pH of the extracted coffee brew. The sampling frequency, reported in Table S1, was defined on a case-by-case basis, depending on the results obtained.

2.3. Water activity of coffee powder

At each storage time, coffee powder was removed from the capsule and the a_w was measured using a dewpoint measuring instrument (AQUALAB 4TE, Astori Tecnica s.r.l., Poncarale, Italy). The results are reported as the average of 3 measurements obtained on the powder from 3 different coffee capsules, and the percentage of the coefficient of variation was less than 7 %.

2.4. Moisture of coffee powder

Moisture was determined by gravimetric method according to (AOAC, 2005). In particular, 1 g of coffee powder removed from the coffee capsule was dried at 75 °C and 1.32 kPa for 12 hours using a vacuum oven (Vuotomatic 50, Bicasa, Milan, Italy). After the drying period, the sample was cooled and weighed. Moisture was calculated as the percentage ratio between the water content in the initial sample, obtained as the difference between sample weight before and after drying (g), and the initial weight of the sample (g). The results are reported as the average of 3 measurements obtained on the powder from 3 different coffee capsules, and the percentage of the coefficient of variation was less than 9 %.

2.5. pH of coffee brew

Coffee brewing was performed by solid/liquid extraction, using a domestic espresso machine (Lavazza Jolie, Lavazza S.p.A., Torino, Italy). A volume of 30 mL deionized water was used for coffee brewing, in agreement with the producer's indication. The temperature of water during brewing was about 92 °C, according to machine specifications. After extraction, the coffee brew was rapidly cooled down to 20 °C by means of a blast chiller (Air-O-Chill, Electrolux Professional, Pordenone, Italy). The pH of the brew was measured with a pH-meter (HI5221, HANNA Instruments, Padova, Italy). The results are reported as the average of 3 measurements obtained on the brew extracted from 3 coffee capsules, and the percentage of the coefficient of variation was less than 5 %.

2.6. Moisture adsorption isotherm of coffee powder

Coffee powder was collected from freshly prepared coffee capsules and aliquots of 1 g were put in Petri dishes placed on a suspended perforated tray in desiccators hermetically closed and containing supersaturated solutions of inorganic salts providing a RH ranging from 11 up to 97 %. The salts, with relevant RH in brackets, were used as follows: LiCl (11 %), $C_2H_3O_2K$ (23 %), $MgCl_2$ (32 %), K_2CO_3 (43 %), $Mg(NO_3)_2$ (54 %), $NaNO_2$ (65 %), NaCl (75 %), KCl (85 %), and K_2SO_4 (97 %). Samples were stored at 20 °C until the equilibrium with RH was reached. To this aim, samples' weights was monitored during storage and samples were considered at equilibrium when their weight did not change by more than 2 mg/g_{dw} between two consecutive measures (Jowitt & Wagstaffe, 1989). Calorimetric analyses were conducted by means of a differential scanning calorimeter (DSC3+, Mettler Toledo, STAR^e System, Greifensee, Switzerland). After the equilibrium was reached, the final value of moisture (M, g_{H2O}/g_{dw}) of each sample was calculated by means of Eq. 1:

$$M = \frac{(w_f - w_i)}{w_i} \quad (1)$$

where w_i and w_f are the initial and final weight of coffee samples respectively. The calculated value of M was, hence, averaged and plotted with the corresponding a_w to build the sorption isotherm. Sorption data were modelled by using the Guggenheim-Anderson-De Boer (GAB) equation (Eq. 2), which has previously been used to describe the isothermal sorption behaviour of coffee (Anese et al., 2006; Iaccheri et al., 2019):

$$M = \frac{m_0 \cdot b \cdot C \cdot a_w}{(1 - b \cdot a_w) \cdot (1 - b \cdot a_w + C \cdot b \cdot a_w)} \quad (2)$$

where m_0 represents the moisture content at monolayer level (g_{H2O}/g_{dw}), and b e C are fitting parameters.

2.7. Time needed to reach monolayer

To estimate the time (t) needed for coffee to reach the monolayer ($a_{w,m}$), the hydration number (h) (Oswin, 1946) was calculated for all the a_w values considered in the study according to Equation 3.

$$h = \frac{a_w}{1 - a_w} \quad (3)$$

Following, h was plotted against time and a linear regression was applied to calculate the slope (k, day^{-1}) by fixing the intercept to h_0, which is the hydration number of the fresh coffee powder. The time needed to reach the monolayer ($t_{a_{w,m}}$) was then calculated by Equation 4:

$$t_{a_{w,m}} = \frac{h_m - h_0}{k} \quad (4)$$

where h_m is the hydration number at the monolayer.

2.8. Calorimetric analysis

Amounts of 20 mg of sample were weighed in 100 μL aluminium pans. Aluminium pans were hermetically closed with aluminium lids and an empty aluminium closed pan was used as a reference. Samples were heated from – 80–160 °C at 10 °C/min. Thermograms were analysed for the onset temperatures of glass transition (T_g) using STAR^e software. The results are reported as the average of at least 2 replicates, and the percentage of the coefficient of variation was less than 5 %. The T_g curve was fitted by the Gordon and Taylor (1952), according to Eq. 5:

$$T_g = \frac{CT_{gc} + \varepsilon W T_{gw}}{C + \varepsilon W} \quad (5)$$

where T_{gc} and T_{gw} are the glass transition temperatures of anhydrous coffee and water, respectively, C and W are the mass fraction of coffee solids (g_{solids}/g_{tot}) and water (g_{H2O}/g_{tot}), and ε is the Gordon-Taylor parameter. The model parameters T_{gs} and k were estimated while considering that the T_{gw} is −135 °C.

2.9. Statistical analysis

Data were subjected to one-way repeated measures analysis of variance (ANOVA) and Turkey's Honest Significant Differences test ($p < 0.05$). Correlation was measured by the Pearson coefficient. All the statistical computations were conducted using R version 4.3.2 for Windows (The R foundation for statistical computing, Vienna, Austria) through RStudio environment (version 2023.09.1 – 494). Graphs were produced by using the *ggplot2* library (version 2.26.27) (Wickham, 2016).

3. Result and discussion

3.1. Modified state diagram of coffee powder

The storage of coffee at various RH might alter its water content, affecting its physical state and making it prone to the development of alterative reactions. In particular, upon water absorption and transition from glass to rubber, the molecular mobility of coffee is expected to increase, triggering the development of chemical reactions and thus accelerating alterative events (Dawidowicz & Typek, 2017; Goodman & Yeretzian, 2015; Jaiswal et al., 2012; Strocchi et al., 2023a). Therefore, in the initial part of the study, the modified state diagram of ground

coffee, concomitantly showing the onset glass transition temperature (T_g) as a function of a_w and its sorption isotherm, was determined (Fig. 1).

As expected, at low a_w, the slope of the isotherm curve was low and increased rapidly when a_w overcame a value of about 0.60. The GAB constants C and b were 2.11 and 0.95, respectively, and the GAB monolayer value, m_0, was found to be 0.033 g_{H2O}/g_{dw}, which corresponded to a water activity at monolayer level, a_{w0}, equal to 0.43. This result is in agreement with literature evidences, reporting m_0 of ground roasted coffee to range from 0.023 to 0.038 g_{H2O}/g_{dw} (Anese et al., 2006; Hayakawa et al., 1978; Mutlu et al., 2020), depending on biological (*e.g.*, cultivar) and technological (*e.g.*, roasting conditions, particle size) factors.

Since a_w is a ratio between pressures, it is known that the isotherm does not change drastically due to temperature increase (Labuza et al., 1985). However, to verify the constancy of the isotherm within the temperature range applied for sample preservation in this study (*i.e.*, 20–45 °C), additional tests were conducted by assessing the isotherm at 45 °C. As expected, no significant differences among the isotherms were observed with the temperature range here tested (data not shown). Thus, the sorption isotherm shown in Fig. 1, although referring to data acquired at 20 °C, was actually applicable in the entire range of temperature considered for coffee storage in the present work.

The modified state diagram (Fig. 1) also shows T_g of coffee samples having increasing a_w. As expected, the glass transition temperature of ground roasted coffee decreased with increasing a_w (and M), indicating coffee plasticization upon moisture uptake. Experimental T_g values of ground coffee having different a_w were fitted according to the Gordon-Taylor model (Eq. 5). The relevant parameters T_{gc} and ε were 61.2 and 4.2, respectively, in line with literature data (Iaccheri et al., 2019). The T_g at the monolayer was 34 °C. Considering the RH values of the present study, and thus theoretical equilibrium a_w values of 0.54, 0.65 and 0.75, the corresponding T_g values were 23.1, 10.5, and 5.4 °C, respectively. These results indicate that when coffee reaches the equilibrium with environmental RH, in the temperature range considered in this study most samples are in a rubber state, with the only exception of the sample stored at 20 °C and 54 % RH which is ~3 °C below T_g. This means that, with this only exception, should coffee monolayer be exceeded, the physical state of the system would not prevent the development of alterative events. In other words, when coffee moisture exceeded the monolayer one and was stored at temperature above T_g, the mobility of the reactants was not kinetically hindered. This would result in the formation of caffeic acid upon chlorogenic acid hydrolysis, resulting in a lower pH of coffee brew, which is known to compromise the overall quality of the beverage. These changes, coupled with a high moisture content, may also trigger oxidative reactions causing the formation of primary and secondary oxidation products (Cincotta et al., 2020; Ginz et al., 2000; Strocchi et al., 2023a, 2023b; Yeager et al., 2023).

3.2. Water activity of coffee packed in compostable capsules

The increasing trend of replacing conventional packaging materials with compostable ones, especially PBS, has recently expanded to the coffee capsules market. However, PBS susceptibility to moisture, which is needed to guarantee the composting process, can also induce moisture uptake by coffee during storage, triggering the subsequent pH decrease and thus coffee quality. This study, for the first time to the best of our knowledge, addressed the impact of using PBS to produce coffee capsules on moisture uptake during storage. To this purpose, a wide range of RH and storage temperatures was investigated, simulating conditions relevant to both distribution and domestic use, considering a realistic long-term storage. Results reported in Fig. 2a and Figure S1 show, respectively, the increase of a_w and M of ground coffee packed in PBS capsules during storage.

The initial a_w of coffee powder was 0.090 ± 0.004, which, according to the coffee isotherm (Fig. 1) corresponded to a M of 0.0027 ± 0.0002 g_{H2O}/g_{dw} and a T_g of 52 °C. These values are in line with those previously reported by other authors for freshly produced ground roasted coffee (Anese et al., 2006; Iaccheri et al., 2019) and account for a high stability of the product. However, the a_w (and M, Figure S1) of ground roasted coffee packed in PBS dramatically increased under all storage conditions, confirming that this packaging solution was not able to prevent moisture uptake. Strocchi et al. (2023a) reported analogous findings, showing that moisture uptake in coffee packed in compostable capsules was higher than in coffee packed in conventional multilayer single-dose capsules. Figure S1 also showed that, in all cases, a_w progressively increased approaching RH. It must be underlined that the a_w could not reach the exact equilibrium with the environment due to food matrix and packaging effects (Sun & Woods, 1993). Nevertheless, the time required to approach equilibrium considerably varied depending on both storage temperature and RH.

Under the same storage temperature, it can be noticed that the higher was the RH, the faster increased a_w, due to the stronger driving force, *i.e.*, the gap between initial coffee a_w and environmental RH. For instance, when coffee capsules were stored at 20 °C and 54 % RH, the maximum a_w value (*i.e.*, 0.52) was reached after over 16 months. When the RH increased to 65 and 75 %, the same a_w value of 0.52 was reached within just 8 and 5 months, respectively. Not only RH, but also temperature affected the rate of moisture uptake by coffee, with a faster

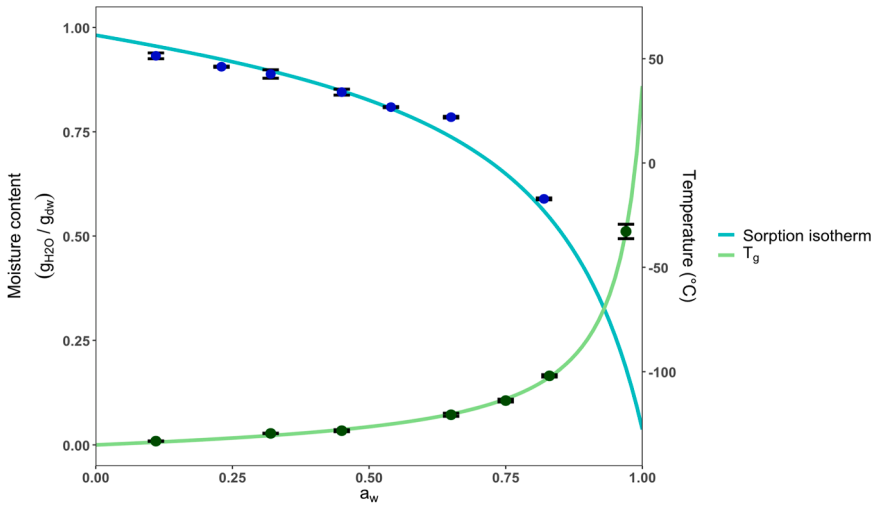

Fig. 1. Modified state diagram showing the sorption isotherm and the glass transition temperature (T_g) as a function of water activity (a_w) of ground roasted coffee.

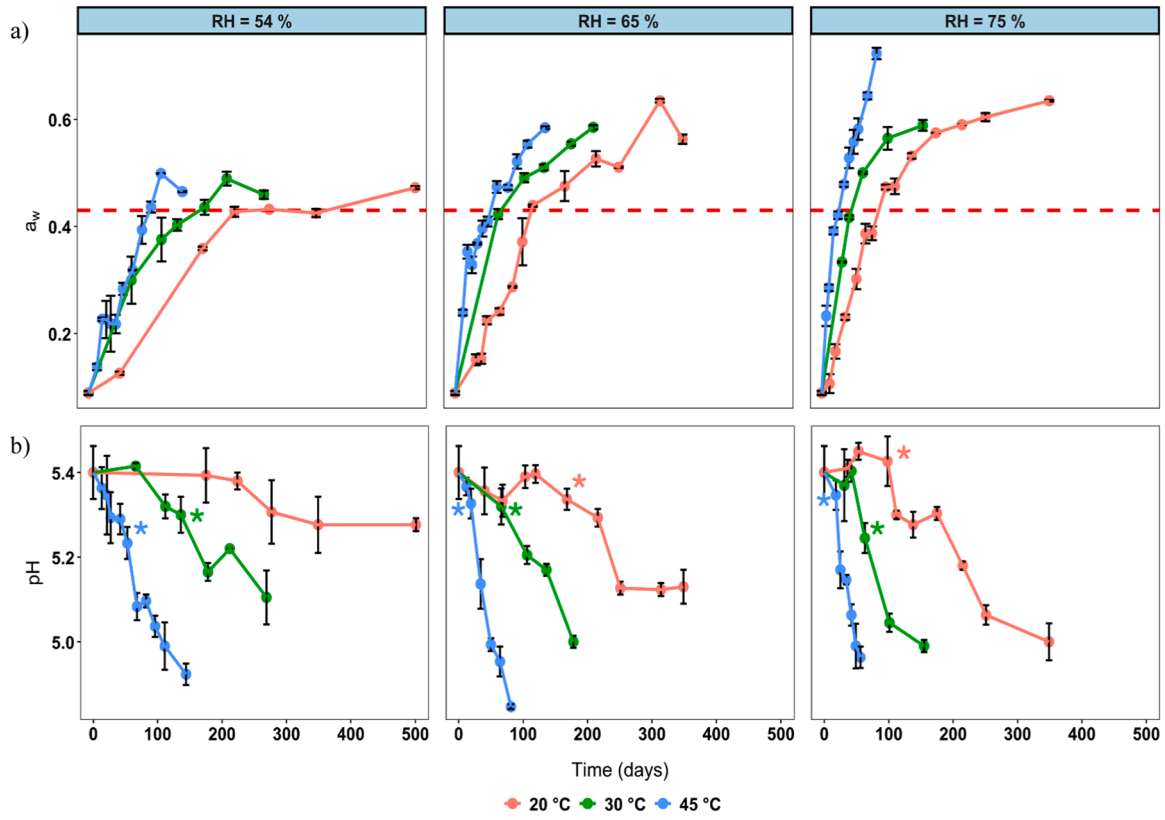

Fig. 2. (a) Water activity (a_w) and (b) pH of the brew of ground coffee packed in PBS capsules during storage at different RH values (54, 65, 75 %) and temperatures (20, 30 and 45 °C). In (a), the dashed red line represents a_w at the ground coffee monolayer ($a_{w0} = 0.43$); in (b), * indicates the first significant difference ($p < 0.05$) observed between two consecutive pH values within each sample.

increase in a_w at higher storage temperature. Since coffee capsules are typically attributed a shelf life even exceeding 18 months (Cincotta et al., 2020), acquired results point out that the increase in a_w suffered by ground roasted coffee packed in PBS capsules (Fig. 2a) was far from being negligible during the theoretical lifetime of the product.

In agreement with the increasing a_w trend observed in Fig. 2a, it must also be mentioned that if stored at RH above 75 %, mold growth could occur, bringing about also hygiene implications (Labuza & Dugan, 1971).

The m_0 and a_{w0} of ground roasted coffee were matched with the results showing the evolution of coffee a_w during storage (Fig. 2a) according to Equation 4, to estimate the time required for roasted coffee packed in PBS capsules to reach the monolayer values under varying environmental conditions. Table 1 reports the time required for ground roasted coffee to reach the monolayer values under different storage conditions.

It can be noted that coffee reached the monolayer largely before the expected shelf life of the product (*i.e.*, 540 days) under all the considered environmental conditions, with just 3 weeks being necessary to reach the monolayer in the worst-case scenario (*i.e.*, 45 °C and 75 % RH). Strocchi et al. (2023a) reported similar findings for coffee packed in an eco-friendly material and stored at 45 °C and 65 % RH. Despite the different coffee blend and packaging material of the capsules, also in this case the equilibrium was achieved within few weeks. These results confirm that bioplastics cannot protect ground coffee from moisture uptake during storage. In this regard, it must be pointed out that although coffee capsules are not expected to be stored at 45 °C and 75 % RH during their entire life, they could experience these extreme conditions for times long enough to trigger quality decay (Fig. 2a and S1), such as during the shipping process, which is performed under uncontrolled environmental conditions and typically lasts around 3-weeks.

Considering the best case (*i.e.*, 20 °C and 54 % RH) the time required to reach the monolayer was still below the 18-month shelf life. Therefore, long before reaching its shelf life, the product would be characterized by physical and chemical properties not able to limit the alterative events.

These results are concerning since these environmental conditions could be easily suffered by the product, especially during shipping and storage, given that for shelf stable dry food, such as ground roasted coffee, RH and T control are generally not required.

Table 1
Time required by ground coffee packed in PBS capsules and stored at different temperature (20, 30, or 45 °C) and RH (54, 65, or 75 %) to reach the monolayer (*i.e.*, $a_{w0} = 0.43$ and $m_0 = 0.033$ g_{H2O}/g_{dw}).

Temperature (°C)	Time (days)		
	RH = 54 %	RH = 65 %	RH = 75 %
20	327	142	89
30	120	76	56
45	103	59	26

3.3. pH of the brew obtained from coffee packed in compostable capsules

It can be hypothesized that once the monolayer is exceeded the interaction between the reactants is favored, triggering the hydrolysis of the ester bond of the chlorogenic acids and forming caffeic and quinic acid (Dawidowicz & Typek, 2017). This phenomenon is known to be associated with a decrease of the pH of the brew extracted thereof (Clarke & Macrae, 1985). Thus, brew pH is recognized as a feasible indicator of coffee quality and consumer sensory acceptability (Manzocco & Nicoli, 2007; Manzocco & Lagazio, 2009, Santanatoglia et al., 2024; Strocchi et al., 2023a). Based on this consideration, PBS coffee capsules stored for increasing time under different environmental conditions

were used to extract the brew and measure its pH (Fig. 2b).

The brew obtained from freshly produced coffee capsules presented a pH of 5.40 ± 0.06, in agreement with the literature (Manzocco & Nicoli, 2007). During storage, the pH of coffee brew decreased with a rate and extent that varied depending on the storage conditions suffered by the capsules. The trend was similar to that observed for a_w and M increase (Fig. 2a and S1), with a clear dependence on both RH and T. Overall, the higher was the RH, the faster was the pH drop at the same T. Similarly, the higher was T at the same RH, the more quickly the pH dropped. In the worst-case scenario (*i.e.*, 45 °C and 75 % RH) the pH dropped below 5.1, a value accounting for unacceptable quality, within 1 month, that is far below the 18-month shelf life conventionally attributed to coffee capsules (Cincotta et al., 2020). This value is in agreement with the one observed by Strocchi et al. (2023a) for coffee stored at 45 °C and 65 % RH in eco-friendly capsules. It can also be noticed that the pH decay was not linear but presented a lag phase, whose length differed among samples. The duration of the lag phase was quantified as the time required to observe a significant ($p < 0.05$) decrease in the pH of the brew (Fig. 2b) and results are reported in Table 2.

The time required before any significant change in the pH of coffee brew was observed spanned from less than 15 days to over 16 months.

Interestingly, the time required to reach the monolayer values (Table 1) and the time necessary for the onset of pH decrease (Table 2), were in the same order of magnitude and the correlation between these timespans was very strong ($r = 0.98$).

In addition, the time necessary for the onset of changes in pH appeared to depended on temperature, according to a relation resembling the William-Landel-Ferry one (Williams et al., 1955). To this regard, Fig. 3 shows the time required to observe a significant ($p < 0.05$) decrease in the pH of the brew as a function of the distance of storage temperature (T) from the glass transition temperature of coffee (T_g) stored at different RH.

As evidenced in Fig. 3, samples in a rubbery state ($T - T_g > 0$) required from few days to about 170 days of storage before showing significant changes in pH. However, when the T_g was overcome, as it happened for coffee stored at 20 °C and 54 % RH ($T_g = 23.1$ °C), an abrupt increase in the time needed for alteration (> 500 days) was detected, suggesting that alterative events were kinetically hindered in the coffee powder that remained glassy during storage. Interestingly, differences in pH lag phase were also observed within rubber samples. In particular, the higher was the difference between storage temperature and coffee T_g (*i.e.*, increase in $T - T_g$), the shorter was the time necessary to onset pH decay, further confirming the crucial role of molecular mobility on the development of alterative events.

Overall, acquired results indicate that storage in packaging materials not adequately preventing moisture uptake, especially if associated with high storage temperature, might dramatically change the molecular mobility of reactants in ground coffee, becoming a major driver in determining the development of alterative events and finally impairing the quality of the brew.

4. Conclusions

The results presented in this work evidenced the detrimental effect

Table 2
Time (days) required to observe a significant ($p < 0.05$) decrease in the pH of the brew obtained from ground roasted coffee packed in PBS capsules and stored at different temperature (T; 20, 30, or 45 °C) and relative humidity (RH; 54, 65, or 75 %).

RH (%) T (°C)	54	65	75
20	> 500	168	98
30	136	66	63
45	42	19	18

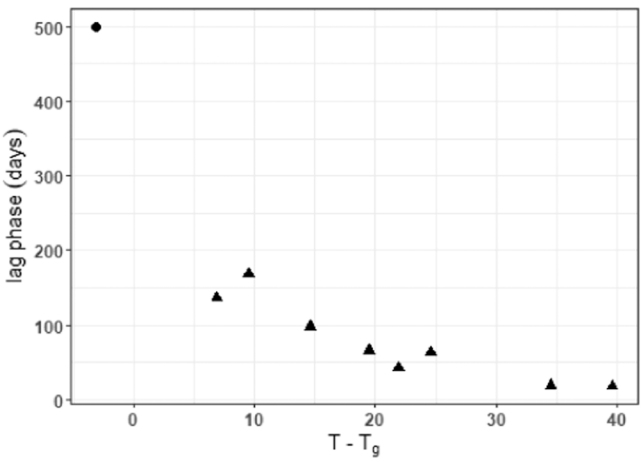

Fig. 3. Time required to observe a significant ($p < 0.05$) decrease in the pH of the brew obtained from ground roasted coffee packed in PBS capsules (lag pH) as a function of the difference between storage temperature and the glass transition temperature ($T - T_g$). ●: coffee sample in glassy state (20 °C and 54 % RH) ▲: coffee samples in rubber state.

that the use of bio-based packaging materials may have on the quality of coffee brew extracted from coffee exposed to different relative environmental humidity and temperature, mimicking those experienced during shipping and storage. Due to its intrinsic (compostable) nature, the bio-based material used to produce the capsules considered in the present study allowed moisture uptake by the packed coffee.

When coffee powder stored in PBS capsules absorbed enough water to overcome the monolayer and the glass transition temperature, hydrolytic reactions were triggered, ultimately resulting in a decrease of coffee brew pH. The rate and extent of these changes was deeply affected by the storage conditions, producing a significant pH drop within a time that in most cases was far below the shelf life typically attributed to coffee packed into capsules made of non-renewable oil-based materials.

In addition, if the food reaches the equilibrium with an environmental humidity above 75 %, a shift from a quality issue, typical of shelf stable dry food, to hygienic concerns may even arise.

The outcomes of the present study point out that the ongoing efforts aimed at improving the sustainability of packaging cannot lose track of its primary role that is protecting food from the external environment.

Although our findings could be in principle extended to numerous dry foods, where the quality decay might heavily depend on moisture uptake, a major limitation lies in the fact that additional research is needed to quantify the extent of moisture uptake and its impact on the shelf life of other dry foods. Moreover, depending on the food matrix under investigation, other real-world scenarios (*e.g.*, tropical and cold countries environmental conditions) may need to be taken into account.

Another limitation regards the specificity of the study, since the criticalities relevant to PBS capsules cannot be inferred to other biobased materials that in turn require dedicated studies. The latter should also take into account possible changes of mechanical behaviour under different storage conditions, which were not here addressed.

These limitations also point out that when biobased packaging materials are brought into play, the interactions among packaging, environment, and food cannot be neglected and the boundaries of the "shelf stable" concept need to be reframed. Fostering the replacement of conventional plastics with biobased materials for food packaging, brings thus about the need for a new approach to shelf-life estimation. This must take into account the dynamic changes occurring in food and the possibility that the alterative event may also suffer a shift. The shortcomings of the present study could be overtaken by further studies may be then required considering other factors that could affect coffee quality, such as light exposure and oxygen.

These outcomes could help food manufacturers in increasing their

awareness about the potential drawbacks of replacing conventional packaging materials with biobased ones, eventually including shelf life reduction and/or need for a secondary packaging (*e.g.*, pouches) able to avoid/delay moisture uptake. In addition, acquired findings underline the importance of raising consumer awareness of the trade-offs associated with purchasing dry foods in eco-friendly packaging. Indeed, only when properly protected, dry foods maintain their quality during storage, thereby reducing the likelihood of being wasted at domestic level, which would make contradict the sustainability push.

To avoid making vain the efforts of increasing food packaging sustainability, it is necessary to carefully evaluate not only the direct impact of packaging on the environment but also the increase of food wasting risk due to the reduction in both quality and safety of food stored in biobased packaging materials.

CRediT authorship contribution statement

Ada Nucci: Writing – review & editing, Resources. **Maria Cristina Nicoli:** Writing – review & editing, Project administration, Methodology, Funding acquisition, Conceptualization. **Marilisa Alongi:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis. **Sonia Calligaris:** Writing – review & editing, Supervision, Methodology. **Lara Manzocco:** Writing – review & editing, Supervision, Methodology. **Giulia Ravaioli:** Writing – review & editing, Resources. **Marco Lopriore:** Writing – review & editing, Writing – original draft, Visualization, Investigation, Formal analysis, Data curation.

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.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2024.101403.

Data availability

The data that has been used is confidential.

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