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Selecting packaging material for dry food products by trade-off of sustainability and performance: a case study on cookies and milk powder

Maarten Baele[a,b], An Vermeulen[a,c], Dimitri Adons[d], Roos Peeters[d], Angelique Vandemoortele[b], Frank Devlieghere[a], Bruno De Meulenaer[b], Peter Ragaert[a,b,c*]

[a]Research Group Food Microbiology and Food Preservation (FMFP), Department of Food Technology, Safety and Health, Ghent University, Coupure Links 653, 9000 Ghent, Belgium (Partner of Food2Know)
[b]Research Group Food Chemistry and Human Nutrition (nutriFOODchem), Department of Food Technology, Safety and Health, Ghent University, Coupure Links 653, 9000 Ghent, Belgium (Partner of Food2Know)
[c]Pack4Food, Coupure Links 653, 9000 Ghent, Belgium (Partner of Food2Know)
[d]Hasselt University, IMO-IMOMEC, Packaging Technology Centre, Wetenschapspark 27, Diepenbeek, Belgium

Abstract (max 250 words):
Alternative packaging concepts for two dry, shelf-stable food products were evaluated. A trade-off between recyclability (monolayer materials) and performance (multilayered high-barrier materials) was made for the packaging materials. Caramellized cookies were packaged in flowpacks made of PP film (OTR 1307cc/m²/d, WVTR 5g/m²/d), acryl-coated PVdC/PP film (OTR 21.8cc/m²/d, WVTR 4.2g/m²/d) as a reference material and metallized PP (MPP) film (OTR 31.2cc/m²/d, WVTR 0.4g/m²/d) and stored at 22°C and 50% relative humidity. Texture was compromised after six months of storage for the former two materials, while the latter provided an extension of textural acceptability. Whole milk powder was packaged in unsealed PE bags as a reference, representing a typical paper bag with a PE liner that is stapled shut without a seal. Alternative packages were sealed PE bags (OTR 1464cc/m²/d, WVTR 3g/m²/d), PE/PA/EVOH/PA/PE (OTR 0.25cc/m²/d, WVTR 0.95g/m²/d) and PA/EVOH/PA/PE (OTR 1.24cc/m²/d, WVTR 8g/m²/d) multilayer bags, and PP/Al/PE (OTR 0.1cc/m²/d, WVTR 0.1g/m²/d) bags and stored at room temperature and relative humidity between 70 and 90%. Unsealed bags were found to be unacceptable for storage at high humidity, due to excessive caking, discolouration and mould growth. Sealed PE bags provided adequate protection against moisture, yet not against oxygen ingress, leading to oxidative off-odours. The barrier efficiency of PA/EVOH/PA/PE was compromised by the high humidity. Both PE/PA/EVOH/PA/PE and PP/Al/PE bags provided adequate protection for over a year.

Keywords: Packaging, oxygen transmission rates, water vapour transmission rates, cookies, milk powder

***Corresponding author.** E-mail: Peter.Ragaert@ugent.be

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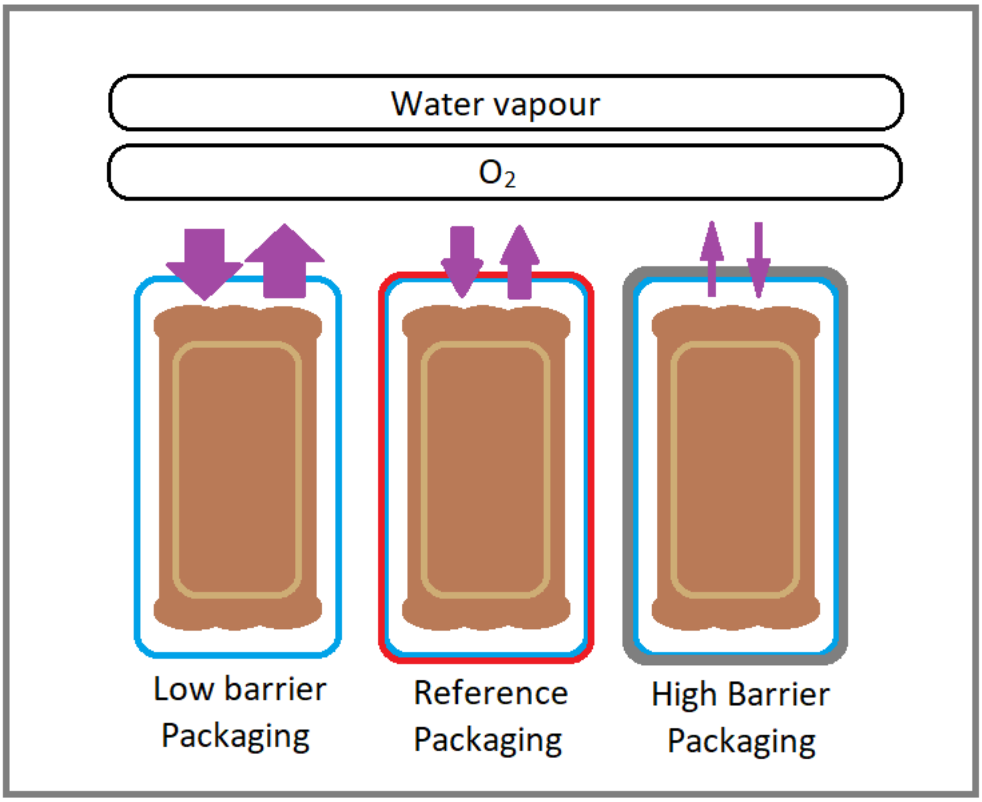
Balancing packaging sustainability and performance: a case study on dry food products

Maarten Baele[a,b], *An Vermeulen*[a,c], *Dimitri Adons*[d], *Roos Peeters*[d], *Frank Devlieghere*[a], *Bruno De Meulenaer*[b], *Peter Ragaert*[a,b,c*]

The effect of a typical reference and some alternative packaging materials on the shelf life of two shelf-stable products, cookies and milk powder, was evaluated. Cookies were packaged in PP film, acryl-coated PVdC/PP film and metallized PP film. Moisture content and texture evolution in the different materials were evaluated. Milk powder was packaged in unsealed PE bags, sealed PE bags, two multilayer bags and an aluminum laminate bag. Moisture content, lipid oxidation and colour were monitored.



Introduction

Dry food products are characterized by a low moisture content and low water activity and thus are not susceptible to spoilage through the growth of bacteria, yeasts and moulds. Their spoilage is caused by physical and chemical processes. Two such products, caramellized cookies and milk powder, were considered in this study. As these products often have a shelf life of multiple months up to over a year, it may often prove challenging for producers to guarantee a near-fresh experience for consumers throughout the whole shelf life. As the optimal storage conditions can not be guaranteed by the consumer, sufficient protection of the product through adequate packaging is required [1-5]. Most importantly, protection against oxygen and water vapour is needed.

Intense protection of these foods could rather easily be achieved by utilizing highly performant packaging materials with very low permeability to oxygen and water vapour, such as metal laminates [6, 7]. However, multi-layered materials are under a lot of pressure recently, especially since the European Commission has recently issued the decision that by 2030, all plastics placed on the European market should be either recyclable or reusable [8]. As such it is opportune to evaluate whether currently established packaging concepts may be optimized by, for example, switching to thinner or monolayered materials which are more easily recyclable and likely lower priced. However, maintenance of a proper shelf life should be paramount.

Caramellized cookies are a common confectionary product to be served as a snack alongside coffee, and thus are often packaged as single servings. Two quality parameters are important for this type of product: aroma and texture [9]. First, the typical caramellized aroma should be preserved. Packaging materials with good gas barrier properties commonly imply good aroma barrier properties as well: most relevant aroma compounds are volatile organic substances typically with a higher molecular weight then oxygen and water vapour. Consequently they would permeate through the packaging material at a slower rate. Texture deterioration is due to uptake of moisture, which causes the starch to shift from a glassy to a rubbery state. To the consumer, this is translated as crisp and crumbly cookies turning soggy, tough, chewy and/or stale [10, 11].

The effect of storage conditions on texture of cookies is extensively studied in literature. However, the research is highly heterogenic, due to the immense amount of specific types of products to be considered. Some cookies are meant to bend and be soft, so moisture loss should be prevented to avoid hardening [10, 12]. Others are meant to be crispy and crunchy, so moisture ingress should be avoided [13-16]. Some products are sensitive to oxidation [1, 17-19]. Others are not in particular, as they may possess an intermediate water activity level at which oxidation rates are minimal [5, 19, 20]. This shows that packaging materials should provide a highly tailored protection.

As such, Romeo et al. [21] compared plastic trays open to ambient air, polyvinylchloride (PVC) film, aluminum foil and N_2-flushed trays in (polyamide/polyethylene) PA/PE film for storage of Italian almond pastries. The flushed overwrapped trays performed best, followed by aluminum foil packaging. Similarly, Piga et al. [12] compared PVC film and aluminum (Al) foil for soft italian almond cookies. Once more, PVC was outperformed by the aluminum foil in terms of preserving the cookies' texture (in this case, through prevention of moisture loss). Romani et al. [5] compared metallized polypropylene (MPP)/paper films, metallized polylactic acid (M-PLA)/paper and an oxo-degradable MPP/paper with a pro-oxidant additive for biscuits. Despite the PLA-based material being more permeable, the authors found no significant differences in quality parameters dependent on moisture and oxygen ingress between the different packaging types during an accelerated storage test. It should be mentioned though that oxodegradable films has become very controversial due to the formation of microplastics during degradation [8]. Nagi et al. [22] showed that both high density polyethylene (HDPE) and aluminum laminate were appropriate for storage of cereal bran cookies.

Milk powder, commonly produced by spray-drying of whole milk, is a free-flowing powder consisting of milk proteins and milk fat globules embedded in an amorphous lactose matrix [23-25]. Three phenomena dictate the loss of milk powder quality during its storage [24-26].

The most crucial one is the crystallisation of the otherwise amorphous or glassy lactose. Crystallisation only occurs once the glass transition temperature of lactose is exceeded. This temperature depends, amongst other factors, upon the moisture content: an increase lowers the glass temperature [26-28]. Thus, if powder is kept at a constant temperature, initially below the glass transition temperature, crystallisation may occur due to moisture sorption. As amorphous lactose is very hygroscopic, sorption of moisture will occur very rapidly provided the availability. Crystallisation of lactose greatly alters the functionality of the powder, leading to decreased flowability, decreased solubility and caking. A second phenomenon which can occur is discolouration due to nonenzymatic browning [25]. This defect is due to the formation of brown pigments as a result of the Maillard reaction, in this case the result of a condensation of lysine and lactose [24]. The consequence is twofold: sensory rejection increases due to visual browning, and the nutritional value of the powder decreases as lysine is an essential amino acid and thus a relevant nutrient in dairy products [3]. The third relevant phenomenon is lipid oxidation. This is the reaction of mostly unsaturated lipids with oxygen. Advanced lipid oxidation leads to decreased nutritional value, as vitamin A and essential fatty acids are degraded. In addition, rancidity develops due to the generation of off-odours [29-33].

Rehman et al. [4] found similar performance for kraft paper bags and LDPE/PP bags for skim milk powder storage. Lim et al. [34] found paper/PE packaging material to be inferior to Al-PE laminate and paper/PA/PE during storage at 40°C, but not at 20°C. Camargo Novaes et al. [35] compared metallized polyethylene terephthalate (M-PET)/PE and PP/PE bags, and composite and metal cans for the storage of whole milk powders at elevated temperatures and high humidity. The water vapour barrier of PP/PE proved insufficient, leading to caking of the powder. An et al. [36] determined water vapour and oxygen barrier requirements, based on the onset of lactose crystallization, for single-serving milk powder for infants to achieve a shelf life over six months. Requirements towards oxygen transmission rates (OTR) and water vapour transmission rates (WVTR) were very strict due to high surface area/product ratio. As such, metal or composite cans or aluminum-laminated flexible films were proposed.

The aim of the current study was to evaluate a range of well-defined alternative packaging materials spanning a range of OTR and WVTR values as compared to a reference material. This is done for caramellized cookies and whole milk powder stored in controlled temperature and humidity conditions. Complex multilayered packaging materials have the benefit of providing superior water vapour and gas barrier properties. For some products, the use of these packaging materials may provide an extended shelf life as compared to using less complex, low-barrier packaging concepts. Less complex materials, and in particular monomaterial packages, trade off barrier properties for improved recyclability.

For cookies packaged per unit in flowpack wrappers, PP film and metallized PP film (further referred to as MPP film) were compared to an acryl-coated PP/PVdC film (further referred to as reference film), specifically focusing on texture and moisture content. For whole milk powder, an unsealed PE bag (representing a paper bag with plastic liner that is glued or stapled shut) was compared to sealed PE bags (representing sealed common plastic liners), two multilayer bags (PE/PA/EVOH/PA/PE and PA/EVOH/PA/PE) and a PP/Al/PE bag. In this case, moisture content, colour, caking and lipid oxidation were the considered parameters. The set-up, product types and packaging types of this test were selected in close collaboration with packaging and food producers as part of a broader research project aiming to optimize packaging and storage concepts for different food products.

Materials & methods

Food products and packaging

Caramellized cookies contained 4.9% protein, 19% fat and 72.6% carbohydrate, of which 38.1% sugars (data provided by the producer). The cookies were packaged individually in flowpack wrappers on an industrial form-fill-seal line by the producer. Packaging was performed in ambient air, no gas flushing of the packages was performed. Three different films were used: the first was a PP film with an acryl/PVdC coating, which is a very common material for packaging of cookies and will henceforth be called the 'reference film' [5, 37]. The other two were a standard PP film (having lower water vapour barrier properties than the reference), and metallized PP (MPP) (having higher water vapour barrier properties, but lower oxygen barrier properties than the reference). Water vapour transmission rate (WVTR) of the materials were gathered from the material's technical sheets. For the O_2 transmission rate (OTR) of the films, the technical sheets did not provide consistent measurement conditions. Thus, the OTR was experimentally determined according to ASTM standard F1927 using a Mocon Ox-Tran 2/21 (Mocon, Minneapolis, USA). 99.9% pure O_2 was used as a test gas. Measurements were performed at 23°C, at 0% relative humidity at the inside of the test material and 50% at the outside of the test material. These conditions were chosen to reflect a real storage situation. The transmission properties of the materials are provided in Table 1.

Milk powder was delivered in 25kg paper bags. Based on the specification sheet, the powder contained 2.67% moisture, 26.4% fat, 24.6% protein and 39.9% lactose. After delivery, the milk powder was weighed in 1 kg portions in paper bags lacking any water vapour or gas barrier. These were used to contain the portions and to prevent dusting of the powder during further handling. The portions, as contained in the paper bags, were stored in three types of plastic bags (as shown in Table 2) and sealed using a Multivac C300 vacuum packaging machine (Multivac, Mechelen, Belgium). Before sealing, the machine's chamber was subjected to a vacuum step at

5 mbar, flushed with a modified atmosphere packaging (MAP) gas mixture (30% CO_2, 70% N_2) until a pressure of 350 mbar, after which the bags were sealed and the vacuum was compensated in the chamber. The gas mixture was created using a Witt MG18-3MSO gas mixer (Gasetechnik, Germany). CO_2 was included in the MAP gas mixture as suggested by the milk powder supplier, who empirically found improvements in keeping quality of the milk powder (lipid oxidation) due to CO_2 inclusion. As a reference, PE bags that were kept unsealed were used to represent a package lacking any barrier against oxygen and water vapour (Table 2), such as the paper bags in which the powder was supplied [4]. The WVTR of the materials were determined according to ASTM standard F1249 using a Mocon Perma-tran 700 (Mocon, Minneapolis, USA). Measurements were performed at 38°C, at 0% relative humidity at the inside of the test material and 90% at the outside of the test material. The OTR of the materials was determined as described above. As a final fifth alternative, PP/Al/PE bags with superior oxygen and water vapour barrier properties (data collected from the supplier's technical data sheets) were used.

Storage and sampling

The cookies were stored in a dry climate chamber at 22°C for the first two months of storage. For the remainder of the test, the cookies were moved to tightly sealed cabinets containing jars with an aqeous saturated NaBr (Sigma-Aldrich, Overijse, Belgium) solution, allowing for a controlled relative humidity (RH) equilibrium set at 50% [38]. Measurements showed that the actual RH fluctuated between 40 and 60%. The cabinets were kept in 22°C incubators (KB8400, Termaks, Bergen, Norway). These conditions were chosen to simulate a typical storage period in a European retail environment.

The milk powder bags were stored in a tightly sealed container, located within a climate room. The amount of sample bags had to be limited due to size restraints of this container. The temperature of this room was set at 30°C for the first two months of storage, then at 22°C for the remainder of the test. The elevated temperature was included to simulate a period of temperature abuse during storage or transport [4]. Below a perforated grid supporting the bags, the bottom of the cabinet was filled with an aqueous saturated KNO_3 (VWR international, Leuven, Belgium) solution, allowing a relative humidity equilibrium within the cabinet in the order of 90% RH [38]. Measurements revealed that the relative humidity started at approximately 70% and only slowly rose to 90% during the test. These conditions, including temperature abuse and high humidity, were chosen to simulate overseas container transport.

Temperature and relative humidity within the storage cabinets were monitored using a Testo 623 temperature-humidity logger (Testo, Ternat, Belgium).

Once per month over the span of one year, samples were removed from storage for analysis. For the cookies, multiplicates were used and one analysis was performed per sample, for multiple samples. For the milk powder, one bag was opened per analysis day per treatment (packaging type). On these samples, analyses were performed at least in triplicate. In this case, the amount of samples was smaller due to space restrictions of the climate cabinet and the large size of the individual bags. It should be mentioned that this results in reduced robustness of the statistical analysis of these results.

Analyses

Fatty acid composition

Lipids were extracted from the cookies using the Bligh and Dyer method, in which chloroform was substituted by dichloromethane [39]. Fat from the milk powder was extracted using the IDF method 265 [40]. Fatty acid composition was determined using AOCS method Ce 1b-89 [41] using capilary gaschromatography as described by Mestdagh et al. [42]. The fatty acid composition of the cookies is shown in Table 3. The fatty acid composition of the milk powder is shown in Table 4.

Moisture content, water activity and moisture sorption

Before analysis of the cookie samples, the cookies were ground into powder using a pestle and mortar. Moisture content was determined by mixing approximately 5g of sample with sand in a metal cup. The sand had been dried at 105°C for 24h in advance and cooled to room temperature in a dessicator prior to use. The mixture of sand and sample was dried for 2h at 105°C, cooled down in a dessicator and weighed. The sample was then dried for another 30 minutes, cooled and reweighed. This drying and weighing was repeated until the weight stabilised [43]. The cookies were ground into powder before this analysis.

Water activity at 25°C was determined using an Aqualab Vapor Sorption analyzer (Decagon Devices Inc., Meter Group Europe, München, Germany).

The same apparatus was used to determine the adsorption-type vapour sorption isotherms using the dynamic dewpoint isotherm (DDI) method. The adsorption was started at the experimentally determined initial a_w and moisture content values. The sorption data were analysed using the VSA downloader software (Decagon Devices Inc., Meter Group Europe, München, Germany).

Texture measurements

Cookies were subjected to a three-point bend test using an Instron 5942 Single Column system (Instron Benelux, Boechout, Belgium) [5, 14, 15, 21]. Using a 500N load cell, a plastic blade (CNS Farnell, UK) was lowered onto the sample at a constant rate of 1mm/s. The cookie was supported on the two opposite ends at exactly 5 cm apart. Care was taken so that the probe was lowered onto the middle of the cookie. The measurement initiated as soon as the measured force reached 0.1N. The required force (N) to maintain the probe at a constant speed was returned as a function of the displacement (mm). The test ended as soon as the force decreased to 5% of the maximum force measured during the test. The data was gathered in the Instron Bluehill 3 software. ‘Hardness’ was defined as the value of the peak force (N) applied during the test [5, 44]. This peak force was registered right before the cookie breaks. ‘Fracturability’ was defined as the inverse of the displacement of the probe (or deformation of the cookie) right before the cookie breaks, when peak force is registered. An arbitrary threshold was set at 0.6 mm deformation, as none of the fresh cookies extended past this point before breaking during the initial measurements. The product of hardness and fracturability can be defined as the 'rigidity' (stress/strain or peak force in N/displacement at peak force in mm) [45]. The 'end of test' extension was used as an extra measure for the brittleness of the cookies: for a brittle cookie, the test will end very quickly after the peak force is registered, as both halves of the now broken cookie will fall off the support and no longer exert a pressure on the probe. When the cookie has become less brittle, it keeps exerting force on the probe as it bends, and thus the apparatus will keep registering force at higher deformation. As such, extreme values found in these texture measurements cannot be regarded as statistical outliers, but are rather real cases of failure.

Headspace oxygen concentration

Oxygen concentrations within the milk powder bags were monitored non-destructively with the aid of OxyDot sensors on the inside of the bags, read out optically using the Oxysense 210T system (Oxysense Inc., Dallas, US) [46]. These measurements were not performed for the opaque PP/Al/PE bags, as transparency of the bags was a requirement to allow the sensors to be read out.

Hexanal

Hexanal, a reaction product from the oxidation of linoleic acid, was monitored as a marker for the extent of lipid oxidation in milk powder [47]. Lipid oxidation was also identified by the supplier of the milk powder as a highly common index of failure. Hexanal concentration was determined using headspace solid-phase microextraction (HS-SPME) coupled with a gas chromatograph with mass spectrometer (GC-MS).

Phosphate buffer was prepared by dissolving 8.95g/L disodium hydrogen phosphate dodecahydrate (Chem-lab Analytical, Zedelgem, Belgium) and 3.04g/L potassium dihydrogen phosphate (Chem-lab Analytical, Zedelgem, Belgium) in water and adjusting to pH 2 with orthophosphoric acid (Fischer Scientific, Merelbeke, Belgium). Antioxidant solution consisted of 0.25g butylated hydroxyanisole (Sigma-Aldrich, Overijse, Belgium) in 0.5ml HPLC grade methanol (Fischer Scientific, Merelbeke, Belgium). Internal standard solution consisted of 25mg/ml hexanal-d12 (CDN Isotopes, Quebec, Canada) in HPLC grade methanol further diluted to 37.5µg/ml in water. A calibration standard solution was prepared from a 0.815mg/ml solution of hexanal (Sigma-Aldrich, Overijse, Belgium) in HPLC grade methanol, further diluted to 0.815µg/ml in water.

Samples were prepared by adding 1g of milk powder to a 20 ml glass headspace vial, also containing 4ml of phosphate buffer, 5µl of antioxidant solution and 15µl of internal standard solution. External calibration curves were created by standard addition, through adding 0-75-150-300-450-600µl of this standard solution to headspace vials containing 1g of milk powder (that had been stored in vacuum prior to use, to avoid excessive oxidation of these samples), 5µl of antioxidant solution, 15µl of internal standard solution and 4ml of buffer solution. The vials were sealed with PTFE/silicone caps (Agilent Technologies, Palo Alto, CA).

The HS-SPME process was performed automatically by a CTC-CombiPAL autosampler (Agilent Technologies, Palo Alto, CA). The samples were pre-incubated at 75°C for 5 minutes, whilst being agitated at 500 rpm. Extraction was done for 10 minutes with a DVB/CAR/PDMS gray fiber (Supelco, Bellefonte PA, US). The fiber was desorbed for 2 minutes at 250°C in the inlet. For chromatographic analysis, an Agilent 7890A GC with a 5975C mass spectrometer (Agilent Technologies, Palo Alto, CA) and equipped with an Agilent J&W DB-624 60m, 0.25mm, 1.40µm capillary column was used. Helium was used as carrier gas at a constant flow rate of 1.3ml/min. The oven temperature was programmed as follows: initial temperature 50°C, hold time 5 min; ramp up to 140°C at 4.5°C/min. The mass spectrometer detector (MSD) conditions were the following: transfer line to MSD, 280 °C; ionization energy, 70 eV;

operating in selective ion mode (SIM). The selected ions monitored were m/z 44, m/z 46, m/z 56 and m/z 64, quantifiers were m/z 56 for hexanal and m/z 64 for hexanal-d_{12}.

Oxidation was not evaluated for the cookies. The extent of lipid oxidation in a food product is based on many factors such as fatty acid composition, the level and kind of pro- and antioxidants, presence of free fatty acids. Based on internal experience, the producer specified that oxidation is not a specific point of failure for their cookies, while texture was the key concern. Sakač et al. [16] stored cookies in 40µm PP film and only detected significant oxidation after 14 months of storage. Romani et al. [5] found little difference in hexanal formation when comparing cookies stored in packaging materials with OTR ranging from 1.6 to 15 cc/m²/d.

Colour

Colour evolution of the milk powder was monitored using a Konica Minolta CM2500-D (Konica Minolta Sensing Europe, Bremen, Germany) handheld colour analyser set at D65 illuminant and 10° standard observer. Measurements were performed on a sample of powder that had been placed in transparent bags, in a layer of at least 2cm thick. The results were rendered as tristimulus colour parameters in the CIELAB colour space, and resulted from averaging 10 measurements per sample. The cookies' colour was not analyzed instrumentally in this test.

Statistics

Data were analysed using R Statistics 3.5 [48]. Significance of the main effects 'packaging type', and 'time of storage' and the interaction effect were evaluated using analysis of variance (ANOVA) on univariate general linear models. The appropriateness of these models was checked using a histogram of the residuals. A main effect was interpreted as a global difference over all levels of the other factor. An interaction effect was interpreted as an evolving effect of packaging type over time. Levene's test was used to check homogeneity of variances. Estimated marginal means were used to compare pairs of levels of one factor for all levels of the other two factors. Comparisons were based on Fischer's least significant difference test (LSD).

Results

Cookies

Moisture content and water activity

The cookies' moisture sorption isotherm is shown in Figure 1. The isotherm showed a type III shape, as classified by Brunauer et al. [49]. While type II isotherms are also reported for biscuits and cookies, this is a common finding for sugary confectionery products [13, 50-53]. As discussed by Lewicki et al. [54], these curves possess inflection points that indicate crucial moisture levels. Exceeding these levels imparts critical physical changes to the product. These were automatically calculated by the data gathering software, showing two inflection points in the curve: one at a_w 0.45 and 3.5% moisture content, and one at a_w 0.80 and 16% moisture content. The latter seems rather irrelevant, as the cookies would be far from acceptable from a consumer's point of view at this level of moisture content. Thus, a water activity of 0.45 and moisture content of 3.5% was regarded as a preliminary index of failure for the cookies. As an extra control, a GAB model was fitted to the curve [53-55]. A good overall fit was achieved and an inflection point at 4.5% moisture and a_w 0.50. This would indicate that for the cookies, a critical range exists between 3.5 and 4.5g moisture per 100g dry matter, or between a water activity of 0.45-0.50. The lower value of this range will be used as an indicative critical point.

Figure: FIGURE_1

Figure 1: Moisture sorption isotherm of crumbled cookies. The dotted lines indicate the curve's two inflection points.

The initial moisture content of the cookies was between 1.3% and 1.9%, corresponding to a water activity of 0.14±0.03. As there was little difference in WVTR between the PP film and the reference film, moisture content of the cookies packaged in these two films progressed similarly. Cookies packaged in PP film surpassed a moisture content of 3.5% after 3 months, cookies packaged in the reference film after 4 months (Figure 2). Analysis of variance showed no significant difference in change over time when comparing only these two packaging types (p=0.069). Cookies packaged in the MPP film had an overall lower moisture content and reached 3.5% moisture after about 8 months of storage.

Figure: FIGURE_2

Figure 2: Moisture content (dry matter base) of cookies packaged in (left) PP film, (middle) reference film and (right) MPP film as a function of storage time. The dotted line indicates a critical moisture content, determined from the moisture sorption isotherm.

Figure: FIGURE_3

Figure 3: Water activity of cookies packaged in (left) PP film, (middle) reference film and (right) MPP film as a function of storage time. The dotted line indicates a critical water activity, determined from the moisture sorption isotherm.

Considering water activity (Figure 3), analysis of variance showed no significant difference in change over time between the PP film and reference film (p=0.111). The a_w 0.45 threshold was passed between 7-9 months of storage. Cookies packaged in the MPP film did not exceed an a_w of 0.45 within the duration of the test. The results for water activity showed discrepancies from the expectations based on the moisture adsorption isotherm and the moisture content during storage (Figure 4). This indicates that in reality, the cookies' water activity after certain storage periods corresponded with somewhat higher moisture contents than found in the moisture sorption isotherm. This is illustrated in Figure 4. It should be noted however that in order to determine the sorption characteristics of the biscuit, the sample was ground in a mortar into a powder, thus increasing considerably the specific surface of the matrix and also removing possible 'capillary' effects within the cookie. It is therefore expected that the number of sorption places increased in parallel and thus that at a particular moisture content, a lower water activity is observed for the powdered cookie on which the sorption isotherm was determined compared to the stored biscuit. The opposite was observed however, especially at water contents lower than 6 % (on db). This deviation can be explained based on the recent report of Karrila and Karrila (2020) [56]. In their study using the same instrument and DDI method to determine the sorption isotherm it was observed the sorption characteristics of a powdered starch based snack was dependent upon the particle size. At the same moisture content powders with a particle size was < 180 µm had a lower water activity compared to powder of the same snack of which the particle size was 3000 µm. These authors explained this phenomenon by the absence of rate effects in the absorption process of water to its binding places if the particle size of the powder is small enough, while these are relevant if the particle size of the powder is too big. Most likely the powder size of the ground biscuits was too high to neutralise such rate effects in our conditions.

Figure: FIGURE_4

Figure 4: Moisture sorption isotherm (line) of crumbled cookies and measured a_w - moisture content (dry basis) couples of intact cookies stored in PP film (●), reference film (○) and MPP film (▼) during the storage test. The lines indicate the critical a_w and moisture content as derived from the isotherm.

Texture measurements

Textural attributes of bakery products are highly product-specific and often hard to interpret and relate to consumer experience [15, 45, 57, 58]. Fresh caramellized cookies are characterised by a 'snap' when force is applied by the consumer's teeth. In texture measurements, this was reflected by three characteristics: 1) a high peak force, 2) a low deformation at peak force and 3) a sharp and immediate drop in force after the cookie breaks (Figure 5). A loss of 'snap' was expected after absorption of a certain amount of moisture. This was reflected by a lower peak force, higher deformation (due to the cookie bending rather than breaking) and a tail on the texture curve, due to the force required to further bend the cookie as illustrated in Figure 5. This figure shows results for a cookie that was kept without packaging material at room temperature for 2 weeks.

Figure: FIGURE_5

Figure 5: Comparison of typical texture profiles of fresh or 'breaking' (-●-) and failed or 'bending' (-×-) cookies. The 'failed' were kept without packaging at room temperature for two weeks before analysis.

Despite obvious sensory changes on the texture of the cookies throughout storage, little conclusion could be made from the evolution of the cookies' hardness (Figure 6). Due to the high variability of the data, detecting statistically significant trends was hindered. Analysis of variance showed no overall effect of packaging type on hardness ($p=0.257$), but it did affect the changes throughout time ($p=0.016$) (see Supplemental Table 1). When the hardness was divided by the deformation at peak force, negative trends appeared for all packaging types (Figure 7). The decrease in rigidity was exhibited a less pronounced trend for the MPP film, which may be linked to its better moisture barrier. Between 7 and 8 months a pronounced drop in the rigidity was observed, most notably for the cookies packaged in PP film. From a sensory point of view, loss of rigidity would mean that the cookies became tougher and less crispy. This corresponds better with the observed water activity evolution (Figure 3) than with the moisture content (Figure 2). Most notably for PP films, water activity levels consistently exceed a_w 0.45 after 8 months of storage, corresponding to the rigidty drop mentioned above. For the PP film and reference films, the moisture level had indeed exceeded 3.5% (Figure 2), but this had happened some months before, indicating that critical moisture could be at a higher level than initially proposed. The deformation at peak force (Figure 8) for the PP film and reference film packaged cookies consistently surpassed the arbitrary threshold mentioned earlier, indicating that from this point the cookies were no longer as crispy as if fresh. Apart from some outliers, cookies packaged in the high-moisture barrier MPP film did not exceed this threshold as consistently. The 'end of test' extension (Figure 9) followed a course highly similar to the extension at peak force. After 5 months in the case of the reference packaging and 6 months in the case of PP film packaging, no measurements were below the 0.6mm threshold and multiple high deformation values (over 1mm and up to 15mm) were measured. It is remarkable that this occurred earlier for the reference film, since this film has better moisture barrier than the PP film (Table 1). This observation may be influenced by the sampling times being 1 month apart from each other and test variability. More frequent analysis may have provided smoother curves showing clearer results. The values for cookies packaged in MPP film started showing outliers and increased towards the end of the storage period, but not as consistent and pronounced as for the other two packaging types. It is likely that some outliers were due to microleaks, allowing more water vapour to enter the packages. As the metallization imparted some more rigidity to the films, it is possible that seals were not as complete as they were on the PP and reference films, as they were all packaged on the same packaging lines regardless of the material used.

Figure: FIGURE_6

Figure 6: Hardness of cookies stored in PP film (left), reference film (middle) and MPP film (right) as a function of storage time.

Figure: FIGURE_7

Figure 7: Rigidity of the cookies stored in PP film (left), reference film (middle) and MPP film (right) as a function of storage time.

Figure: FIGURE_8

Figure 8: Deformation at peak force of cookies stored in PP film (left), reference film (middle) and MPP film (right) as a function of storage time. The dotted line represents an arbitrary threshold based on measurements on the fresh cookies.

Figure: FIGURE_9

Figure 9: Deformation at end of test for cookies stored in PP film (top left), reference film (top middle) and MPP film (top right) as a function of storage time, and detail of the same plots at low extension (bottom row). The dotted line represents an arbitrary threshold based on measurements on the fresh cookies.

For the sake of completeness, it is important to notice that from a sensory point of view, the cookies did not simply progress towards lower hardness and higher deformation at peak force. For example, the cookies packaged in PP film evolved from hard and crispy to soft and bendable (mosts clearly illustrated in Figure 8 by the dip in rigidity for PP film packaged cookies during months 6-8) further towards tough and chewy, illustrated by the return to higher rigidity during months 9-12. Most likely, this is due to redistribution of moisture and subsequent recrystallisation of sugar [12].

Milk powder

Oxygen concentration

Oxygen concentrations measured in three of the used bags are shown in Figure 10. For the unsealed bags, no concentrations were monitored as these bags were constantly subjected to atmospheric oxygen due to the lack of a seal. The PP/Al/PE bags were not monitored as the bags needed to be transparent to be able to read out the oxygen sensors. Despite the PE, PE/PA/EVOH/PA/PE and PA/EVOH/PA/PE bags having the same thickness, differences in measured oxygen concentration were massive. Due to the very high oxygen permeability (Table 2), milk powder packaged in PE bags was exposed to near-atmospheric oxygen concentrations. However, towards the end of the test the concentrations in some of the bags dropped. The cause of this is unclear, as oxygen consumed by the powder would be expected to be repleted through permeation through the PE bag. Concentrations in the PE/PA/EVOH/PA/PE multilayer bags remained below 1% for the majority of the test period, with a minor downward trend. The other type of multilayer bags was highly similar in composition, only missing a PE layer on the outside of the material. As PA and EVOH are polar polymers, and a high humidity was maintained throughout the test, moisture affected the EVOH and PA barrier layers, where it increased its permeability to oxygen, as seen in Figure 10 [59].

Figure: FIGURE_10

Figure 10: Oxygen content measured within the headspace of (left) PE bags, (middle) PE/PA/EVOH/PA/PE bags, (right) PA/EVOH/PA/PE bags during storage of milk powders.

Moisture content and water activity

The milk powder manifested a combined type I – type II moisture sorption isotherm behaviour (Figure 11) [49, 60]. Literature often finds type II isotherms for whole milk powder, and critical points are found at a water content approaching 8% and a water activity of 0.50 [3, 25, 26, 61]. At this point amorphous lactose, which is crucial for physical properties such as flowability, will start to crystallise.

Figure: FIGURE_11

Figure 11: Moisture sorption isotherm of milk powder.

Both moisture content and water activity were clearly affected by packaging type (p=0.000 in both cases, see Supplementary Table 2). Initial moisture content was 2.7%. As expected, moisture was absorbed rapidly by the powder in the unsealed bags during the first 4 months of storage (Figure 12). A maximum in moisture content between 8 and 9% was reached after the fourth month of storage. During the following two months, a decrease in measured moisture content was observed. This was due to the crystallisation of lactose in the powder, after a critical amount of moisture had been reached. This corresponded with critical moisture contents found in literature [25, 61] and with the observed isotherm (Figure 11). After this drop, the moisture content increased again slowly during the remainder of the test. The observed evolution of the moisture content in the unsealed bags showed that a sealed packaging system providing a moisture barrier is really required for keeping milk powder in the high relative humidity conditions used in this test. None of the powder samples stored in sealed plastic bags showed a similarly pronounced phenomenon during the test. It took less than two months for a difference to appear between the powder stored in PE bags as compared to the PE/PA/EVOH/PA/PE multilayer bags. At the end of the storage test the difference in moisture content was not greater than 1%. After 12 months of storage, the PE/PA/EVOH/PA/PE bags reached approximately 4% of moisture. For the PA/EVOH/PA/PE bags, this level was already surpassed after 2 months of storage. Just over 6% of moisture was measured in the powder stored in the PA/EVOH/PA/PE bags at the end of the test. For the aluminum laminate bags, the initial moisture content of the milk powder was well retained (Figure 12).

Figure: FIGURE_12

Figure 12: Moisture content of milk powder stored in (top left) unsealed PE bags, (top middle) PE/PA/EVOH/PA/PE multilayer bags, (top right) PA/EVOH/PA/PE multilayer bags, (bottom left) PE bags, (bottom right) aluminum laminate bags.

Initial water activity (Figure 13) of the milk powder was just below 0.3. Powder stored in the unsealed bags showed a sharp rise in a_w after the first month of storage. Coincident with the drop in moisture content, the water activity of these powders dropped and rose back to the former level after 7 months of storage. The high relative humidity of the storage atmosphere and high water activity of the powder in these bags allowed moulds to start growing on the surface of the powder, visually noticeable from the 10th month of storage. For the powder in PA/EVOH/PA/PE bags, a notable increase in a_w was observed towards the end of the test. For the powder in aluminum laminate bags, the a_w changed very little. Despite the 3-fold difference in water vapour barrier of the PE/PA/EVOH/PA/PE multilayer bags and the PE bags (Table 2), the a_w evolution was highly similar between these two packaging types. Only at month 4 and month 11 significant differences were found. Yet, no moisture-related cases of failure occurred for these packaging types, implying that transmission rates of 0.95 and 3 g/m²/d are acceptable transmission rates for milk powder stored in these conditions. Between the PE bags and the PA/EVOH/PA/PE bags (WVTR 3 and 8 g/m²/d, respectively) there is also an almost 3-fold difference in transmission rate, while in this case the water activity results do follow a different trend. The absolute difference in WVTR between these two packaging types seems more crucial, implying that the minimal WVTR for this case is somewhere between 8 and 3 g/m²/d.

Figure: FIGURE_13

Figure 13: Water activity of milk powder stored in (top left) unsealed PE bags, (top middle) PE/PA/EVOH/PA/PE multilayer bags, (top right) PA/EVOH/PA/PE multilayer bags, (bottom left) PE bags, (bottom right) aluminum laminate bags.

The importance of moisture and crystallisation of lactose was reflected in the fact that powder stored in unsealed PE exhibited strong caking. Apart from being an obvious visual index of failure, this caking also greatly imparted the solubility of the powder. This was observed after 6 months of storage. The sorption isotherm shown in Figure 11 indicates an inflection point at an a_w value of 0.40. Treatments showing caking indeed had water activities exceeding a_w 0.4, indicating a critical a_w value existing around that point.

Lipid oxidation

Hexanal was monitored as a marker for secondary lipid oxidation. It is only one of many different compounds formed during lipid oxidation, but it is one of the most predominant compared to other secondary oxidation products and imparts a distinct grassy or hay-like smell [29-33]. The significant increase over time measured in the sealed PE bags stands out (Figure 14). Oxidation was likely significant for this packaging concept due to the high amount of oxygen available within these bags (Figure 10), and these values correspond with findings from Lloyd et al. for ambient-packaged whole milk powder in 5kg portions stored for one year in bags with OTR 1.5cc/m²/d [32]. The unsealed bags were also exposed to high oxygen levels, but no corresponding high hexanal measurements were observed. A possible explanation for this is that hexanal was formed but already decomposed further [32]. Another possibility is that the formed hexanal was lost to the atmosphere, due to the volatility of this compound and the lack of a seal that could restrain the hexanal within the packaging system. There was little difference between the hexanal concentrations measured for the other packaging concepts. Lloyd et al. also found that when a modified atmosphere with lowered oxygen content (<4%) is preserved, formation of hexanal is mitigated [32]. 50ng/g was found to be a sensory threshold for hexanal in milk [31, 62]. Seen as the powder is meant to be reconstituted as one part powder for 9 parts water, 500ng/g was used as threshold for the powder. This was only exceeded in the case of the powder packaged in sealed PE bags, after 6 months of storage. Despite other bags having oxygen concentrations exceeding 5% over the course of the storage period (Figure 10), no effect on hexanal formation could be observed, which was rather unexpected.

Figure: FIGURE_14

Figure 14: Hexanal content of milk powders stored in unsealed bags (○), PE bags (●), PE/PA/EVOH/PA/PE multilayer bags (▼), PA/EVOH/PA/PE multilayer bags (△) and Aluminum laminate bags (×).

Colour

As seen in Figure 15, milk powder stored in unsealed bags exhibited a clear decrease in L* value (lightness) and increase in a* (redness) and b* value (yellowness), already during the first few months of storage. Visually, this was clearly noticeable as the powder takes a more yellow-brown hue. These findings correspond to findings by Celestino [63]. Moisture is important for the colour of milk powder: the rate of Maillard reaction, responsible for browning, increases with water activity [25, 64]. This is due to increased mobility of reagents due to increased water availability. No visually noticeable colour defects were observed in other packaging concepts, which was confirmed by the limited difference in tristimulus colour parameters.

Figure: FIGURE_15

Figure 15: Colour evolution of milk powder packaged in unsealed bags (○), PE bags (●), PE/PA/EVOH/PA/PE multilayer bags (▼), PA/EVOH/PA/PE multilayer bags (△) and Aluminum laminate bags (×).

Discussion

The initial comparison of fresh and failed cookies texture measurements as shown in Figure 5 seemed clear, but during the the actual storage test results were harder to interpret, mostly due to the intrinsic variability associated to these measurements [5]. Despite this, it was rather clear that cookies packaged in PP film and reference film started showing consistent textural failure after six months. Rigidity, deformation at peak force and deformation at end of test seemed useful measurements to determine this. Hardness or peak force was not as useful, as this did not change as much or as clearly as anticipated. The fact that the producer’s logo was baked into the cookies, providing an irregular elevation, provided extra variability. Further studies should consider extensive preliminary testing to get to know the variability and textural changes to be expected for a certain kind of product.

Some caution had to be taken with the proposed moisture content threshold at 3.5% and water activity threshold of 0.45. The latter was not achieved for the MPP film packaged cookies, while texture failures did appear for these samples. Figure 4 suggests that during the actual storage test, the moisture content of 3.5% corresponded with a water activity of just below 0.300, so this may well be a more realistic threshold. Ideally, sorption isotherms should be determined on the product as it is: crumbling the cookie for the determination of the isotherm may have influenced the isotherm in the current study.

Romeo et al. [21] found that PA/PE film and aluminum foil was to be preferred over PVC film to prevent texture change during storage of soft almond cookies. Nitrogen flushing of packages provided additional benefits. Likewise, Piga et al. [12] found that storage in PVC film brought about rapid texture deterioration in cookies and preferred aluminum foil. Mandala et al. [15] experienced problems when attempting to relate moisture content to textural properties. Small changes in moisture did not translate to significant changes in texture properties, due to high intrinsic variability. Careful, product-specific interpretation of the data was needed. Romani et al. [5] found that a metallized PLA/paper laminate may be suitable as a replacement for metallized PP/paper laminate with comparable barrier properties for storage of biscuits. In the current study, the MPP film provided some shelf life extension based on moisture-related spoilage phenomena. However, due to the processing properties of this film, further optimization of the packaging infrastructure was needed for this film to avoid microleakage.

It should be remarked however that consumer appreciation and shelf life of cookies is however more complex than texture alone: despite lipid oxidation not being a primary concern of the cookie producer, a certain degree of gas barrier may be beneficial to maintaining the cookie’s lipid quality and overall aroma. Therefore it would be interesting to include evaluation of aroma evolution in future testing. This would require the use of a trained sensory panel.

Another remark is that these single-cookie packages are usually wrapped in a bundle film. This imparts an extra hurdle for transmission of vapour and gases. The internal atmosphere in the bundle film will be different from the ambient air, thus a different gradient will be present, slowing down transmission. However, it is entirely possible that a consumer may open and discard the bundle film shortly after purchase, so as a measure of precaution the shelf life should be determined for the single-packaged rather than the bundle-packaged cookies. With this in mind, the use of PP film would trade in only a fraction of the shelf life for an improved recyclability of the packaging material.

It is clear that unsealed bags were not appropriate for storage of milk powder in conditions of relative humidity above 70%. Moisture content increased rapidly, and crystallisation of lactose occurred after 4 months of storage. By then, browning had already set in as well. Due to severe caking further in storage, moisture could no longer easily redistribute within the powder and accumulated on the surface allowing the growth of moulds.

Though observations were few in number, milk powder in PA/EVOH/PA/PE failed due to discolouration, caking and loss of solubility at the end of the shelf life. This points towards insufficient protection for storage in conditions of high humidity. Meanwhile, milk powder in PE bags (WVTR 3g $H_2O/m^2/d$) did not show any moisture-related signs of failure. However, off-odours were formed due to lipid oxidation in this type of bag. Thus, OTR should certainly be lower than 1464cc $O_2/m^2/d$. The packaging types with drastically lower OTR (0.1 - 1.2cc $O_2/m^2/d$) showed no signs of failure only due to lipid oxidation. Thus, an adequate packaging material should provide an OTR lower than 1464cc $O_2/m^2/d$, but on the basis of these experiments the highest acceptable OTR could not be determined.

Conclusions

Investigations on cookies were focused on water vapour permeability of the packaging materials. Texture measurements proved a valuable tool in determining shelf life of cookies, despite large variations in the measurements. Texture was not significantly improved by the improved moisture barrier that the reference film (4.2g $H_2O/m^2/d$) provided over the PP film (5g $H_2O/m^2/d$). Thus, recyclability of this packaging system may be improved by choosing the PP film, which is a monomaterial, for a trade-off of a fraction of the shelf life. The tenfold superior moisture barrier of the MPP film (0.4g H_2O/m²/d) did provide an extension of the shelf life based on texture, but isolated failures were still present.

Two shortcomings of the current test set-up on milk powders should be pointed out: the limited amount of replications per treatment, and incomplete follow-up of in-package oxygen levels. Missing data on in-package oxygen levels in the current study was due to opaque packages and insufficient package headspace, which interfered with our measurement methods. Anyhow, some important observations can still be made from the current study. If high humidity is to be expected during the storage of milk powder, for example due to export to tropical regions, a tightly sealed bag providing moisture and oxygen barrier is insurmountable. If a stapled or glued bag is used, moisture can easily enter the bag leading to crystallisation of lactose, caking, discolouration and promotion of oxidation, severely limiting the shelf life. Shelf life of milk powder stored in PE bags was cut short only due to formation of off-odours as a result of lipid oxidation. This shows that the water barrier was adequate, but a higher gas barrier was required. PA/EVOH/PA/PE bags also did not provide adequate protection, as the barrier properties of the polar layers were compromised due to high humidity conditions during storage. PE/PA/EVOH/PA/PE bags and aluminum laminate bags both provided superior protection. With material reduction (which can be linked to sustainability and cost-efficiency) in mind, the PE/PA/EVOH/PA/PE film is definitely to be preferred for long-term storage of milk powder in humid environments as it is more material-efficient (56µm less thick) and does not include the aluminum component.

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Tables

Table 1: Specifications of the cookie packaging films

Material	Thickness (µm)	OTR[a] (cc/m^2/d)	WVTR[b] (g/m^2/d)
PP *(Jindal Films, Virton, Belgium)*	25	1307.1 ± 28.0	5.0
Acrylic – PVdC coated PP *(Jindal Films, Virton, Belgium)*	26	21.8 ± 0.3	4.2
Metallized PP *(Taghleef GmbH, Holzhausen an der Heide, Germany)*	30	31.2 ± 1.8	0.4

[a]Measured at 23°C, 50%RH at the outside of the material, 0%RH at the inside. Measured with 99.9% O_2 gas flow
[b]Measured at 38°C and 90%RH. Data gathered from the material's technical sheet

Table 2: Specifications of the milk powder packaging bags

	Thickness (µm)	OTR (cc/m^2/d)	WVTR (g/m^2/d)
Unsealed PE *(Mondi, Poperinge, Belgium)*	80	∞	∞
PE *(Mondi, Poperinge, Belgium)*	80	1464 ± 43[a]	3.00 ± 0.03[c]
PE/PA/EVOH/PA/PE *(Mondi, Poperinge, Belgium)*	80	0.25 ± 0.02[a]	0.95 ± 0.01[c]
PA/EVOH/PA/PE *(Obermühle GmbH, Pößneck, Germany)*	80	1.24 ± 0.06[a]	8.00 ± 0.23[c]
BOPP/Al/LDPE *(Goglio S.p.A., Milan, Italy)*	136	0.1[b]	0.1[d]

[a]Measured at 23°C, 50%RH at the outside of the material, 0%RH at the inside. Measured with 99.9% O_2 gas flow
[b]From technical sheet. Measured according to ASTM D3985-95 at 23°C and 0%RH
[c]Measured at 38°C, 90%RH at the outside of the material, 0%RH at the inside.
[d]From technical sheet. Measured according to ASTM F1249-90 at 38°C and 90%RH

Table 3: Fatty acid composition of the cookies, average of 6 measurements

Fatty acid	Percentage		
C14:0	1.0	±	0.1 %
C16:0	39.4	±	0.7 %
C18:0	6.5	±	1.1 %
C18:1	40.5	±	1.0 %
C18:2	12.1	±	0.2 %

Table 4: Fatty acid composition of the milk powder, average over 5 measurements

Fatty acid	Percentage
C4:0	3.8 ± 0.2 %
C6:0	3.3 ± 0.2 %
C8:0	1.0 ± 0.2 %
C10:0	3.4 ± 0.1 %
C12:0	4.1 ± 0.1 %
C14:0	12.5 ± 0.1 %
C14:1	1.1 ± 0.1 %
C16:0	33.6 ± 0.3 %
C16:1	1.6 ± 0.1 %
C18:0	11.1 ± 0.2 %
C18:1	22.4 ± 0.4 %
C18:2	1.8 ± 0.1 %
C18:3	0.6 ± 0.1 %

Supplementary materials

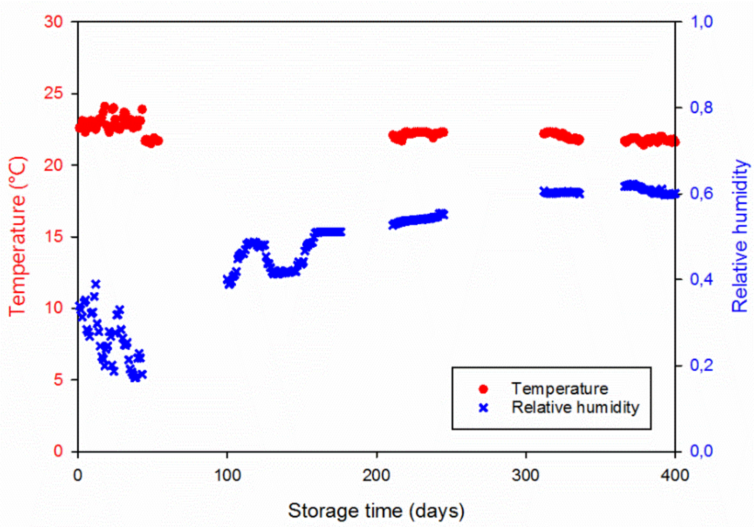

Figure 16: Temperature (●) and humidity (×) conditions during the cookie storage test

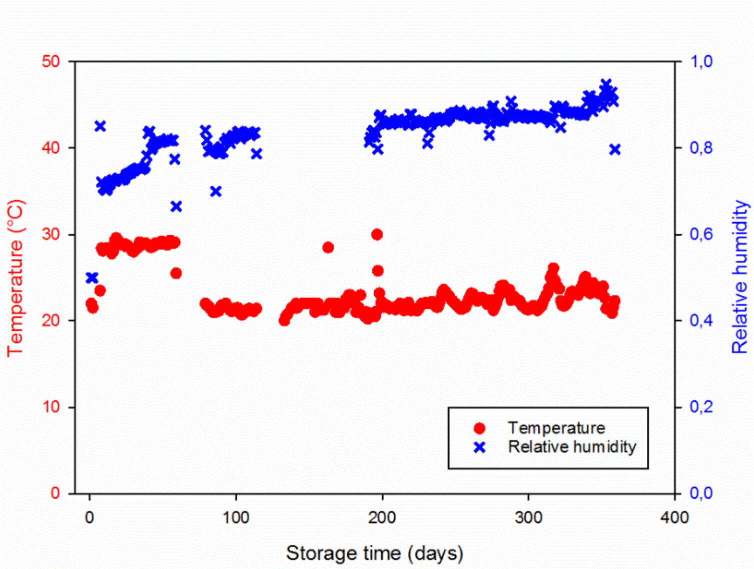

Figure 17: Temperature and humidity conditions during the milk powder storage test

References

1. Lu, L.-X. and F. Xu, *Effects of initial oxygen concentration and oxygen-barrier property of film on fat oxidation rate of packed cookies.* European Food Research and Technology, 2010. **231**(2): p. 347-351.
2. Kilcast, D. and P. Subramaniam, *The Stability and Shelf Life of Food*. Woodhead's food science, technology and nutrition. 2000, Boca Raton - Cambridge England: CRC Press, Woodhead Publishing Limited. 344.
3. Robertson, G.L., *Food Packaging and Shelf Life: A Practical Guide*. 2009: CRC Press. 408.
4. Rehman, S.-U., N.Y. Farkye, and A.A. Schaffner, *The effect of multiwall Kraft paper or plastic bags on physico-chemical changes in milk powder during storage at high temperature and humidity.* International Journal of Dairy Technology, 2003. **56**(1): p. 12-16.
5. Romani, S., et al., *Effect of different new packaging materials on biscuit quality during accelerated storage.* Journal of the Science of Food and Agriculture, 2015. **95**(8): p. 1736-1746.
6. Massey, L.K., *Permeability properties of plastics and elastomers: a guide to packaging and barrier materials. Second edition*. 2003, Norwich, NY: Plastics Design Library/William Andrew Publishing.
7. Robertson, G.L., *Food Packaging - Principles and Practice*. 3 ed, ed. G.L. Robertson. 2013: CRC Press.
8. European Commission, *A European Strategy for Plastics in a Circular Economy: Communication from the commission to the European Parliament, the Council, the European Economic and Social Committee and the Comittee of the Regions*, E. Commission, Editor. 2018: Brussels.
9. Smith, J.P., et al., *Shelf Life and Safety Concerns of Bakery Products—A Review.* Critical Reviews in Food Science and Nutrition, 2004. **44**(1): p. 19-55.
10. Roman, L., et al., *Nutritional and physical characterization of sugar-snap cookies: effect of banana starch in native and molten states.* Food & Function, 2019. **10**(2): p. 616-624.
11. Slade, L., et al., *The glassy state phenomenon in applications for the food industry: Application of the food polymer science approach to structure–function relationships of sucrose in cookie and cracker systems.* Journal of the Science of Food and Agriculture, 1993. **63**(2): p. 133-176.
12. Piga, A., et al., *Texture evolution of "Amaretti" cookies during storage.* European Food Research and Technology, 2005. **221**(3): p. 387-391.
13. Martínez-Navarrete, N., et al., *Water sorption and the plasticization effect in wafers.* International Journal of Food Science & Technology, 2004. **39**(5): p. 555-562.
14. San José, F., M. Collado-Fernández, and R. López, *Texturometric determination of digestive biscuits.* Journal of Food Measurement and Characterization, 2018. **12**(1): p. 412-425.
15. Mandala, I.G., C.A. Ioannou, and A.E. Kostaropoulos, *Textural attributes of commercial biscuits. Effect of relative humidity on their quality.* International Journal of Food Science & Technology, 2006. **41**(7): p. 782-789.
16. Sakač, M., et al., *Shelf-life prediction of gluten-free rice-buckwheat cookies.* Journal of Cereal Science, 2016. **69**: p. 336-343.
17. Lu, L.-X. and F. Xu, *Effect of light-barrier property of packaging film on the photo-oxidation and shelf life of cookies based on accelerated tests.* Packaging Technology and Science, 2009. **22**(2): p. 107-113.

18. Calligaris, S., et al., *Shelf-life Modeling of Bakery Products by Using Oxidation Indices.* Journal of Agricultural and Food Chemistry, 2007. **55**(5): p. 2004-2009.
19. Bialek, M., et al., *Oxidative Stability of Lipid Fraction of Cookies Enriched with Chokeberry Polyphenols Extract*, in *Polish Journal of Food and Nutrition Sciences*. 2016. p. 77.
20. Jensen, P.N. and J. Risbo, *Oxidative stability of snack and cereal products in relation to moisture sorption.* Food Chemistry, 2007. **103**(3): p. 717-724.
21. Romeo, F.V., et al., *Shelf-life of Almond Pastry Cookies with Different Types of Packaging and Levels of Temperature.* Food Science and Technology International, 2010. **16**(3): p. 233-240.
22. Nagi, H.P.S., et al., *Effect of Storage Period and Packaging on the Shelf Life of Cereal Bran Incorporated Biscuits.* American Journal of Food Technology, 2012. **7**: p. 301-310.
23. Foster, K.D., J.E. Bronlund, and A.H.J. Paterson, *The contribution of milk fat towards the caking of dairy powders.* International Dairy Journal, 2005. **15**(1): p. 85-91.
24. Thomsen, M.K., et al., *Two Types of Radicals in Whole Milk Powder. Effect of Lactose Crystallization, Lipid Oxidation, and Browning Reactions.* Journal of Agricultural and Food Chemistry, 2005. **53**(5): p. 1805-1811.
25. Thomas, M.E.C., et al., *Milk Powders Ageing: Effect on Physical and Functional Properties.* Critical Reviews in Food Science and Nutrition, 2004. **44**(5): p. 297-322.
26. Schuck, P., et al., *Keeping quality of dairy ingredients.* Lait, 2007. **87**(4-5): p. 481-488.
27. Fitzpatrick, J.J., et al., *Glass transition and the flowability and caking of powders containing amorphous lactose.* Powder Technology, 2007. **178**(2): p. 119-128.
28. Jouppila, K. and Y.H. Roos, *Glass Transitions and Crystallization in Milk Powders.* Journal of Dairy Science, 1994. **77**(10): p. 2907-2915.
29. Cao, J., et al., *Novel Approach To Evaluate the Oxidation State of Vegetable Oils Using Characteristic Oxidation Indicators.* Journal of agricultural and food chemistry, 2014. **62**.
30. Azarbad, M.H. and H. Jeleń, *Determination of Hexanal—an Indicator of Lipid Oxidation by Static Headspace Gas Chromatography (SHS-GC) in Fat-Rich Food Matrices.* Food Analytical Methods, 2015. **8**(7): p. 1727-1733.
31. Fenaille, F., et al., *Comparison of Mass Spectrometry-Based Electronic Nose and Solid Phase MicroExtraction Gas ChromatographyMass Spectrometry Technique to Assess Infant Formula Oxidation.* Journal of Agricultural and Food Chemistry, 2003. **51**(9): p. 2790-2796.
32. Lloyd, M.A., S.J. Hess, and M.A. Drake, *Effect of nitrogen flushing and storage temperature on flavor and shelf-life of whole milk powder.* Journal of Dairy Science, 2009. **92**(6): p. 2409-2422.
33. Romeu-Nadal, M., et al., *Oxidation stability of the lipid fraction in milk powder formulas.* Food Chemistry, 2007. **100**(2): p. 756-763.
34. Lim, S.D., et al., *Effect of packaging conditions on the quality of whole milk powder (2). The shelf-life prediction of whole milk powder by packaging conditions.* Korean Journal of Animal Science, 1994. **36**(1): p. 100-107.
35. Camargo Novaes, S.S., et al., *Stability of omega-3 enriched milk powder in different commercial packages stored under accelerated conditions of temperature and relative humidity.* International Dairy Journal, 2019. **88**: p. 1-9.
36. An, D.S., J.H. Lee, and D.S. Lee, *Water vapor and oxygen barrier estimation in designing a single-serve package of powdered infant formula for required shelf life.* Journal of Food Process Engineering, 2018. **41**(1): p. e12592.

37. Galić, K., D. Ćurić, and D. Gabrić, *Shelf Life of Packaged Bakery Goods—A Review*. Critical Reviews in Food Science and Nutrition, 2009. **49**(5): p. 405-426.
38. Fontana, A.J., *Water activity of saturated salt solutions*, in *Water Activity in Foods: Fundamentals and Applications*, V.G. Barbosa-Cánovas, et al., Editors. 2007, Blackwell Publishing - IFT Press.
39. Bligh, E.G. and W.J. Dyer, *A rapid method of total lipid extraction and purification.* Canadian Journal of Biochemistry and Physiology, 1959. **37**(8): p. 911-917.
40. Jellema, A., et al., *Determination of free fatty acids in milk and milk products*. Bulletin of the International Dairy Federation : 265. 1991, Brussels: IDF.
41. American Oil Chemists Society and D. Firestone, *Official methods and recommended practices of the AOCS*. 2009, Urbana, Ill: AOCS.
42. Mestdagh, F., et al., *Interaction between whey proteins and lipids during light-induced oxidation.* Food Chemistry, 2011. **126**(3): p. 1190-1197.
43. *Food Analysis - Fourth Edition*. Food Analysis, ed. S.S. Nielsen. 2010, West Lafayette, IN, USA: Springer.
44. Romani, S., et al., *Physico-Chemical and electronic nose measurements on the study of biscuit baking kinetics.* Italian Journal of Food Science, 2012. **24**(1): p. 32-40.
45. Szczesniak, A.S., *Texture is a sensory property.* Food Quality and Preference, 2002. **13**(4): p. 215-225.
46. Bree, I., et al., *Modelling the degradation kinetics of vitamin C in fruit juice in relation to the initial headspace oxygen concentration.* Food Chemistry, 2012. **134**: p. 207–214.
47. Mestdagh, F., et al., *Protective Influence of Several Packaging Materials on Light Oxidation of Milk.* Journal of Dairy Science, 2005. **88**(2): p. 499-510.
48. R Development Core Team, *R: A language and environment for statistical computing*. 2018, R Foundation for Statistical Computing: Vienna, Austria.
49. Brunauer, S., et al., *On a Theory of the van der Waals Adsorption of Gases.* Journal of the American Chemical Society, 1940. **62**(7): p. 1723-1732.
50. Hao, F., L. Lu, and J. Wang, *Finite Element Simulation of Shelf Life Prediction of Moisture-Sensitive Crackers in Permeable Packaging under Different Storage Conditions.* Journal of Food Processing and Preservation, 2016. **40**(1): p. 37-47.
51. Palou, E., A. López-Malo, and A. Argaiz, *Effect of temperature on the moisture sorption isotherms of some cookies and corn snacks.* Journal of Food Engineering, 1997. **31**(1): p. 85-93.
52. McMinn, W.A.M., D.J. McKee, and T.R.A. Magee, *Moisture adsorption behaviour of oatmeal biscuit and oat flakes.* Journal of Food Engineering, 2007. **79**(2): p. 481-493.
53. Guiné, R.P.F., et al., *Adsorption Isotherms of Maria Biscuits from Different Brands.* Journal of Food Process Engineering, 2014. **37**(3): p. 329-337.
54. Lewicki, P.P., *The applicability of the GAB model to food water sorption isotherms.* International Journal of Food Science & Technology, 1997. **32**(6): p. 553-557.
55. Mir, M.A. and N. Nath, *Sorption isotherms of fortified mango bars.* Journal of Food Engineering, 1995. **25**(1): p. 141-150.
56. Karrila, S. and T. Karrila, *Effect of powdering on critical water activity estimate from dynamic dewpoint isotherm of a crispy starch-based snack: a case study with fish cracker.* Journal of Food Science and Technology, 2020: p. 1-10.
57. Woody, A.L., *Probing and Three-Point Bend Methods Compared to Sensory Scales as Measurements for Cookie Texture*, in *Food Science and Technology*. 2003, University of Tennessee.
58. Chen, L. and U.L. Opara, *Texture measurement approaches in fresh and processed foods — A review.* Food Research International, 2013. **51**(2): p. 823-835.

59. Maes, C., et al., *Recent Updates on the Barrier Properties of Ethylene Vinyl Alcohol Copolymer (EVOH): A Review*. Polymer Reviews, 2017: p. 1-38.
60. Zhou, Y. and Y.H. Roos, *Stability and Plasticizing and Crystallization Effects of Vitamins in Amorphous Sugar Systems.* Journal of Agricultural and Food Chemistry, 2012. **60**(4): p. 1075-1083.
61. Langová, J. and J. Stencl, *Moisture sorption isotherms of whole milk powder in the temperature range of 5–35 °C and critical values of water activity prediction*. Vol. 83. 2015. S35-S40.
62. Day, E.A., D.A. Lillard, and M.W. Montgomery, *Autoxidation of Milk Lipids. III. Effect on Flavor of the Additive Interactions of Carbonyl Compounds at Subthreshold Concentrations1*. Journal of Dairy Science, 1963. **46**(4): p. 291-294.
63. Celestino, E.L., M. Iyer, and H. Roginski, *Reconstituted UHT-treated milk: Effects of raw milk, powder quality and storage conditions of UHT milk on its physico-hemical attributes and flavour.* International Dairy Journal, 1997. **7**(2): p. 129-140.
64. Schmidt, S.J., *Water and Solids Mobility in Foods*, in *Advances in Food and Nutrition Research*. 2004, Academic Press. p. 1-101.