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Rapid communication

Quality changes in semi-hard cheese packaged in a poly(lactic acid) material

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Abstract

A study was performed in order to evaluate the influence of barrier properties of a poly(lactic acid) (PLA) relative to an amorphous poly(ethylene terephthalate)/polyethylene (APET/PE) packaging material on quality of Danbo cheese during light exposure and storage in the dark. Results showed that moisture loss from cheeses packaged in PLA was approximately 10 times higher than from the reference packages, but dry surface spots were not observed before 56 days of storage in the PLA packages. Secondary lipid oxidation products were primarily developed when both oxygen and light were present. During light exposure, lipid oxidation of cheeses packaged in PLA was rather limited for the first 56 days of storage, whereas lipid oxidation was almost negligible when the cheeses were protected from light during the 84 days of shelf life. The results indicate that the present PLA can be used for packaging of Danbo cheese for a shelf life maximum of 56 days in order to protect against both moisture loss and lipid oxidation.

Keywords: Poly(lactic acid) (PLA); Semi-hard cheese; Water vapour barrier; Oxygen barrier; Light barrier; Moisture loss; Headspace gas concentration; Secondary lipid oxidation products

1. Introduction

From a food quality point of view, poly(lactic acid) (PLA) has proved suitable for packaging of foods requiring low to medium gas and water vapour barriers and with relatively short shelf lives. The scarce literature shows the potential of using PLA for packaging of orange juice (Haugaard, Danielsen, & Bertelsen, 2003; Haugaard, Weber, Danielsen, & Bertelsen, 2002), yoghurt (Frederiksen, Haugaard, Poll, & Becker, 2003), salad dressing (Haugaard et al., 2003) and sour cream (Holm & Mortensen, 2004), which are conventionally packaged in either polyethylene or polystyrene. In all studies, the foods packaged in PLA were better protected against chemical quality changes, including loss of ascorbic acid in orange juice and lipid oxidation in the fat-containing foods, than were foods packaged in conventional materials.

At present, the water vapour barrier properties of PLA are inferior to those conventionally used for high-barrier packaging (van Tuil, Fowler, Lawther, & Weber, 2000). The impact of high water vapour transmission rates (WVTR) is moisture loss, as documented for mushrooms packaged in PLA, where moisture loss was approximately four times higher than products packaged in a conventional synthetic material (Holm & Mortensen, 2004). In the evaluations of fresh orange juice (Haugaard et al., 2002), yoghurt (Frederiksen et al., 2003), salad dressing (Haugaard et al., 2003) and sour cream (Holm & Mortensen, 2004), moisture loss was not investigated, but as the WVTR

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of the actual PLA packages was low (0.1 g/package × day) (Haugaard et al., 2002), moisture loss is not likely to be a problem.

In addition to the WVTR, the oxygen transmission rate (OTR) of PLA materials is generally higher than that of conventional packaging materials for cheese, a category which includes laminates based on, e.g., poly(ethylene terephthalate) (PET) and polyethylene (PE). However, such a comparison is based on WVTR and OTR measured under standard conditions, namely 37.8 °C and 90% relative humidity (RH) (ASTM F1249) for WVTR and 23 °C and 0% RH (ASTM D3985) for OTR. These temperatures and relative humidities are far from the actual storage conditions of cheeses. Hence, more realistic comparisons may be made by measuring the barrier characteristics of the packaging materials under actual food storage conditions.

The aim of this study was to evaluate PLA for packaging of semi-hard cheeses, which require modified atmosphere (MA) packaging and have a shelf life of 84 days, hence constituting a rather complex food and placing severe demands on the barrier properties of the packaging material. The study focussed on the impact of the water vapour, gas and light barriers on the quality of the cheeses in order to pinpoint needed barrier improvements. The reference packages and the PLA-based packages were characterised and compared by making a priori calculations on the package transmission rates using available information on standard film permeabilities and geometric properties of the packages. The effects on quality were monitored experimentally during storage by measurement of moisture loss from the packages, changes in the headspace gas composition, development of secondary lipid oxidation products, as well as odour and visible mould growth.The study was designed to simulate chilled retail storage (4 °C), where products were exposed to light or stored in the dark.

2. Materials and methods

2.1. Packaging and storage of cheese

Blocks of Danbo cheeses (approximately 170 g 45+ semi-hard cheeses) were obtained from Arla Foods amba (Viby J, Denmark). The blocks were packaged in thermoformed, transparent PLA trays with a film thickness of 500 μm, closed with a lid made of 500 μm PLA film (Hycail bv, Noordhorn, The Netherlands), or for comparison purposes, a conventional reference package, consisting of a 420 μm amorphous APET/PE (380 μm APET/40 μm PE) tray (Amcor Flexibles, Lund, Sweden) closed with a lid made of 102 μm PET/PE film (36 μm PET/hot melt/40 μm PE) (Amcor Flexibles, Argentan, France). The dimensions of the trays were 17.5 × 8 × 2.5 cm. The surface area of the lids was 0.014 m^2 and the area of the formed trays was 0.0268 m^2. The cheeses were packaged in a MA consisting of 30% carbon dioxide and 70% nitrogen at Multivac (Vejle, Denmark). The packages were stored in a display cabinet under conditions similar to those in retail stores. The average temperature and relative humidity during storage were determined by temperature and relative humidity loggers (Testo logger 174 NTC Sensor) to be 4 ± 2 °C and 50 ± 10%, respectively. Samples were exposed, 24 h per day, to Philips TLD 18W/830 New Generation fluorescent light tubes (Philips, Eindhoven, The Netherlands) with an average light intensity of 1500 lx at the surface of the cheese measured with a Digital Light Meter (Model YF-172). Half of the packages were covered with black plastic, which resulted in a total light protection. The samples were rotated regularly to minimise possible temperature and exposure differences in the display cabinets.

2.2. Characterisation of the product

Characterisation of the cheeses was carried out using standard methods to include: total fat (IDF Standard 5B, 1986), total protein (IDF Standard 20B, 1993), total solids (IDF Standard 4A, 1982), salt (IDF Standard 88A, 1988) and pH.

Determinations of moisture loss, headspace gas composition, secondary lipid oxidation products, and evaluation of odour, surface-drying, and visible mould growth, were carried out after 0, 7, 14, 28, 56, 84 and 133 days of storage. Three PLA and three reference packages stored in the dark or exposed to fluorescent light were withdrawn at the respective times of analysis. A 4 mm thick slice was cut off the cheese surface facing the light source and used for further analysis, thereby illustrating a worst-case scenario.

2.3. Moisture loss

Moisture loss of the entire package, to include cheese, tray and lid, was measured as weight loss from the package, hence assuming that moisture loss was the main cause of weight loss from the cheese. Moisture loss at each time of sampling was calculated relative to weight at the time of packaging.

2.4. Headspace gas composition

Prior to opening the cheese packages, headspace gas composition, expressed as % oxygen and % carbon dioxide was determined using a CheckMate 9000 gas analyzer (FBI Dansensor, Ringsted, Denmark) and a needle inserted through a septum placed on the packages.

2.5. Odour and visual changes

At each time of sampling, odour, surface-drying and mould growth were qualitatively evaluated by two analysts.

2.6. Secondary lipid oxidation products

The content of secondary lipid oxidation products was determined by solid-phase microextraction gas chromatography–mass spectrometry (SPME GC/MS). The quantification was based on the addition of 20 μl of internal standard (0.0373 g of 5-methyl-2-hexanone/ml of rapeseed oil). The following method was used: 2 g chopped cheese and the internal standard were weighed in a 10 ml vial and frozen until analysis. Prior to analysis, the samples were thawed at 60 °C for 30 min. Subsequently, the SPME fibre (75 μm Carboxen/PDMS, Supelco, Bellefonte, PA) was inserted into the headspace of the vial for 20 min at 60 °C. The fibre was inserted into an HP GC 6890 series 11 gas GC equipped with an MS detector 5973 series (Hewlett-Packard). Desorption time was 10 min. The analysis included the following parameters: HP FFAP 25 m × 0.2 mm × 0.30 μm (Hewlett-Packard) column; injection temperature, 250 °C; helium carrier gas flow, 0.4 ml/min; splitless; purge time, 2 min; temperature programme, initial temperature of 50 °C for 5 min, increased to 80 °C at 6 °C/min, followed by an increase to 210 °C at 10 °C/min. The following MS parameters were applied: 0–1.6 min, scan *m*/*z* 45–300 (2.84 scan/s); 1.6–31 min; scan *m*/*z* 30–300 (5.24 scan/s) (Mortensen, Sørensen, & Stapelfeldt, 2002a).

2.7. Light transmission

The light transmission of the PLA and reference lids were determined in the range of 800–200 nm on a Cintra 40 UV/visible spectrophotometer (GBC Scientific Equipment, Victoria, Australia) equipped with a barium sulphate-coated integrating sphere detector. The data interval was 4.5 nm, the scan speed 400.0 nm/min and the slit width 2.0 nm.

2.8. Statistical analysis

Statistical analysis of the effect of the packages, storage time and light exposure was conducted by three-way analysis of variance by the general linear model (GLM) procedure (SAS, version 8.2) (SAS, 1999). The analysis was performed for the response variables: moisture loss, oxygen and carbon dioxide in the package headspace and finally secondary lipid oxidation products. Values for day 0 were not included in the analysis as they were obtained prior to packaging and do hence not reflect the effect of packaging. Significant effects were further classified by least significance of difference (LSD) ($p \leqslant 0.05$).

2.9. Estimation of transmission rates and moisture loss

Estimates of the transmission rate, TR, (oxygen or water vapour) of the formed trays were calculated by assuming that the reduction in thickness during thermoforming was evenly distributed and that the permeability coefficient of the material, P, was unchanged by the deformation of the material. With these assumptions, TR of the drawn films, TR_{film}, was calculated as:

$$TR_{Foil}^{Formed} = TR_{Foil}^{Unformed} \frac{A^{Formed}}{A^{Unformed}}, \quad (1)$$

where the As denote the areas of formed and unformed films, respectively.

Assuming that the sealing procedure does not affect the overall permeability, the TR pertinent to a package consisting of different films can be calculated as:

$$TR_{Package} = \sum A\, TR_{Foil}, \quad (2)$$

where A is the area of the individual film piece.

Estimates of the moisture loss rate $\left(\frac{dm_w}{dt}\right)$ was calculated from the WVTR measured under standard conditions by adjusting to the actual difference in humidity, ΔRH, from the one corresponding to standard conditions, $\Delta RH_{standard}$:

$$\frac{dm_w}{dt} = WVTR_{Foil} A \frac{\Delta RH}{\Delta RH_{standard}} = WVTR_{Package} \frac{\Delta RH}{\Delta RH_{standard}}. \quad (3)$$

The moisture loss rate relative to the initial product mass, m_0 can be calculated as:

$$\frac{d(m_w/m_0)}{dt} = WVTR_{Foil} \frac{A}{m_0} \frac{\Delta RH}{\Delta RH_{standard}}. \quad (4)$$

3. Results and discussion

3.1. Characterisation of the cheeses

The Danbo cheeses contained 27.0% fat. Protein and dry matter contents were determined to be 25.6% and 57.6%, respectively, resulting in a fat in dry matter content amounting to 46.9%. Salt content totalled 1.6% and the pH was 5.2. The characterisation indicated that the products were well within the expected gross composition range.

3.2. Characterisation of packaging materials and packages under standard conditions

As quality of the cheese stored in PLA packages was to be compared to that of conventional reference packages, the two types of packages were characterised and compared based on estimates made from standard measurements. The OTR and WVTR (measured under standard conditions) of the packaging films involved are provided in Table 1. Comparisons of PLA and the reference materials reveal that the reference tray material (APET/PE) had a 2.5 and 30.6 times lower OTR and WVTR than PLA, respectively. Although the reference lid material (PET/PE) was very thin (102 μm), it provided six times lower WVTR but 1.5 times higher OTR than did the PLA film. Hence, the reference tray and lid films provided better barrier properties although they were thinner than the PLA film. This is caused by the combination of the APET and PE materials, whereas the PLA film consists of only one material with low barrier properties.

$OTR_{Package}$(ml/day × atm) and $WVTR_{Package}$(g/day) for the thermoformed packages may be estimated taking the lid and tray areas into account as well as the reduced material thickness due to the thermoforming process (calculated by Eqs. (1) and (2)). The transmission rates are given in Table 2. The combination of the thin and quite oxygen-permeable reference lid film and the thicker reference tray gives an OTR that is only a factor of 1.6 lower than the corresponding OTR for the PLA package. With respect to WVTR, the PLA package provided a 16 times lower protection than did the reference package. Although the barrier properties of the reference package were better than that of the PLA package, the differences are smaller than those of the tray films in Table 1. Hence, PLA packages may provide a better protection against water vapour and oxygen permeation than that expected from the permeability data of the films. It should be noted that these estimates are not corrected for differences between the temperatures for standard measurements and the storage temperature. Hence, the actual transmission rates may be somewhat affected by the process of sealing the packages. However, the estimates serve as "nominal" standard transmission rates in order to facilitate comparison of the reference with the PLA package.

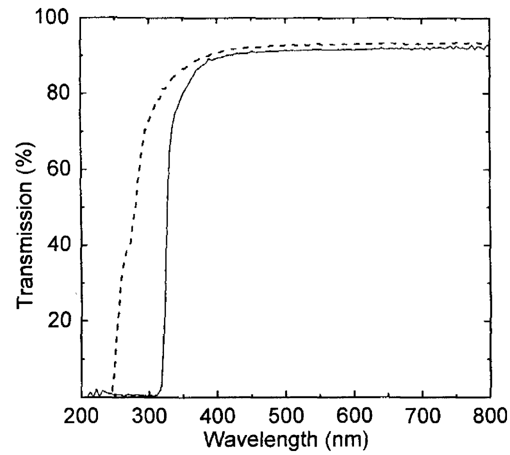

Fig. 1. Light transmission spectra of PLA (dashed line) and reference lids (straight line).

The light transmission spectra of the lid films are given in Fig. 1. Both the PLA and reference lid allow approximately 90% transmission in the visual region of the spectrum in accordance with the transparent and colourless appearance of both films. As normally noted for transparent packaging films, a "cut-off" was observed in the UV-region below which transmission of light becomes negligible (Robertson, 1993). For the reference lid, the "cut-off" wavelength was at slightly higher wavelengths than that of the PLA lid.

3.3. Time development of moisture loss

The changes in cheese quality over time attributable to loss of moisture and formation of secondary lipid oxidation products are, in general, influenced by the permeabilities and light transmission of the package and storage characteristics, including temperature, humidity and light intensity.

Table 1
Barrier properties of PLA and the reference tray (APET/PE) and lid films (PET/PE)

Tray material	Usage	Thickness (μm)	OTR[a] (ml O_2/m^2 × day × atm)	WVTR[b] (g H_2O/m^2 × day)
PLA[c]	Tray and lid	500	22.8	30.6
APET/PE	Tray	420	9	1
PET/PE	Lid	102	33	5

[a] Measured at 23 °C and 0% RH (ASTM D3985).
[b] Measured at 37.8 °C and 90% RH (ASTM F1249).
[c] Scaled linearly from measurements on films with a thickness of 150 μm.

Table 2
Barrier properties of PLA and reference packages together with estimated and observed moisture losses from Danbo cheeses

Package	$OTR_{Package}$ (ml O_2/day × atm)	$WVTR_{Package}$ (g H_2O/day)	Moisture loss (estimated) (g/day)	Moisture loss (observed) (g/day)
PLA	1.49	2.00	1.11	0.056
Reference	0.923	0.121	0.0674	0.0064

Semi-hard cheeses generally have water activities close to 1. Depending on WVTR of the packaging materials and the external humidity (RH_e), a thermodynamic driving force exists for transportation of water out of the package. Hence, if the WVTR is high and RH_e low, large amounts of moisture may be drawn out of the packages resulting in loss of quality and products not meeting the weight requirements.

Fig. 2 depicts moisture loss from the cheeses during storage. No significant differences were observed between storage in light or in darkness for any of the packaging types, and the data were subsequently pooled. The moisture loss could be described by a linear relationship ($R^2 = 0.997$ and 0.899 for PLA and reference packages, respectively) that increased as a function of storage time ($p \leqslant 0.0454$). The linear relationship between moisture loss and time is an indication of a constant moisture loss rate and is consistent with the fact that the moist cheese was able to maintain a high and constant water activity, and that the packages were stored under constant humidity. When storing under these conditions, the moisture loss rate will be constant according to Eq. (3).

Significantly more moisture was lost from the cheeses packaged in PLA than in the reference packages ($p \leqslant 0.0008$). The moisture loss rates from the PLA and the reference packages, as determined from linear regression, amounted to 0.056 and 0.006 g/day, respectively. Hence, almost 10 times better protection against moisture loss was provided by the reference package than the PLA package. The corresponding moisture loss rates, estimated theoretically from WVTRs measured under standard conditions (37.8 °C), are given in Table 2, together with the observed rates. The estimated moisture loss rates are about 20 and 10 times greater than the observed rates for PLA and reference packages, respectively. When evaluating the moisture loss of the PLA-packaged cheeses relative to the reference material-packaged, the PLA packages performed better than expected, based on the "nominal" standard package WVTR.

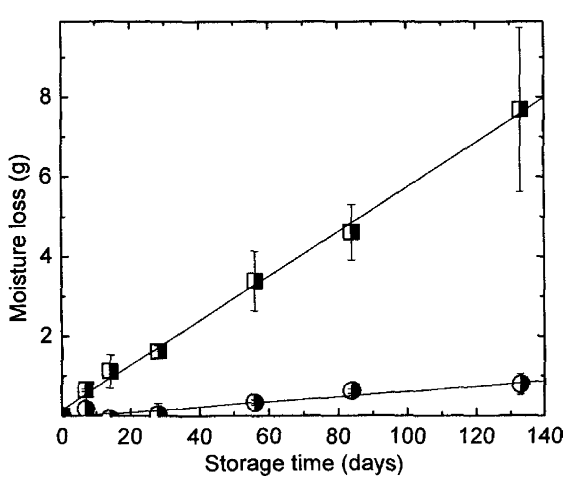

Fig. 2. Moisture loss from Danbo cheese packages relative to weight at time of packaging stored for 0–133 days at 4 °C in PLA (square) and the reference (circle). R^2 was 0.997 for the PLA package and 0.899 for the reference package.

The discrepancy between the observed and estimated moisture loss rates may be ascribable to the assumption behind the estimates. First of all, the ASTM standard WVTR measurements are performed at an elevated temperature that is much higher than the relevant storage temperature for cheese. The water vapour barrier property of the reference film is mainly attributable to the PE portion of the film. By lowering the temperature from the standard temperature (37.8 °C) to the actual storage temperature (4 °C), an approximately fivefold decrease in permeability is expected for PE (Robertson, 1993), which could partly explain the differences between the estimated and observed moisture losses. Furthermore, thermoforming the trays may result, not only in a reduction in material thickness, but also in changes of the material properties due to process-induced changes in polymer orientation (Pettersen, Gällstedt, & Eie, 2004). In this case, the permeability coefficients, P, characterizing the materials, are not identical, and Eq. (1) is not expected to be strictly valid. In the case of PLA, knowledge of temperature-dependence of permeabilities and behaviour during thermoforming is almost nonexistent. The temperature-dependence of WVTR of PLA is said to be characterised by a negative activation energy, which means that WVTR increases with a decrease in the temperature (Auras, Harte, Selke, & Hernandez, 2003). However, such behaviour is not consistent with the factor 20 reduction in WVTR, which was found in this study. Hence, should the WVTR be used to estimate moisture loss, it should be measured on the entire package (i.e., tray and lid) under realistic temperature and moisture conditions. However, within the food packaging industry, the choice of packaging material is primarily based on the properties of the films measured under standard conditions, such as those provided in Tables 1 and 2, and would, with respect to PLA, be estimated to give a lower degree of protection than was actually observed.

The observations of visible dry spots on the cheese surface were related to the moisture loss. Few dry spots were observed after 56 days of storage in the PLA packages, whereas no spots were observed for the cheese stored in the reference packages. From the perspective of the cheese producer, the actual PLA package under investigation did not offer sufficient protection for the cheese to be acceptable throughout the storage period of 84 days. In order to estimate how changes in material and package geometry properties affect the shelf life, the observation of the first dry spots (on day 56) was assigned to a critical relative moisture loss. After 56 days, the moisture loss from the PLA packages amounted to 3.1 g, and hence a critical moisture loss limit of 3.1 g/170 g = 1.8% of the initial weight, may be defined. With respect to usage of the present PLA material for packaging of cheese, a reduction in the WVTR or the desired shelf life would be required. However, it may not be necessary to reduce the WVTR to that of the reference material in order to avoid surface-drying. As the observed moisture loss rate was 0.056 g/day, the critical loss limit was 3.1 g, and the desired shelf-life was 84 days, a lowering of the WVTR of the PLA material by a factor of $84 \times 0.056/3.1 = 1.5$ would be adequate. However, it would also be worth considering changing the geometry of the packages, as the relative moisture loss rate is expected to be proportional to the package area and inversely proportional to the initial weight of the cheese. Doubling the amount of cheese and the depth of the package will give an A/m_0-ratio (Eq. (4)), which is a factor of 1.5 lower than the corresponding ratio for the package used in the storage experiments, and consequently adequate moisture loss protection should be obtainable using the here applied PLA film.

3.4. Headspace gas composition

The headspace gas composition of a cheese package changes dynamically as the dominant gases, oxygen and carbon dioxide, can be produced or removed through respiration, oxidation, solubilization and permeation processes.

Throughout the storage period, the headspace of the packages was analysed for oxygen and carbon dioxide, and the results are shown in Fig. 3(a) and (b). Danbo cheeses are packaged in a MA consisting of 30% carbon dioxide and 70% nitrogen and with a targeted maximum residual oxygen level of 0.5% at the time of packaging. Oxygen accumulated in all the packages as a function of storage time, but more rapidly and to a greater extent in the PLA than in the reference packages ($p \leqslant 0.0001$). When considering the concentration gradient from surroundings to package, the observed increase is due to a permeation of oxygen into the package. The higher rate of oxygen permeation for PLA packages must be attributed to the higher OTR of this type of package compared to the reference (Table 2). In the PLA package headspace, the rate of oxygen accumulation was identical in packages stored in light as well as in the dark until approximately 56 days of storage. Thereafter, oxygen accumulation continued in the dark-stored packages until 84 days of storage, followed by a slight, however, non-significant decrease. In the light-exposed packages, oxygen decreased significantly after 56 days of storage. This difference in the light-stored packages is a result of a larger consumption of oxygen due to oxidative reactions compared to the influx of oxygen through the packaging material. The difference in oxygen accumulation rate was smaller for dark and light-exposed cheeses, when packaged in the reference material, than when packaged in PLA. This may be ascribed to a lower rate of oxidation for the reference system due to the lower oxygen contents.

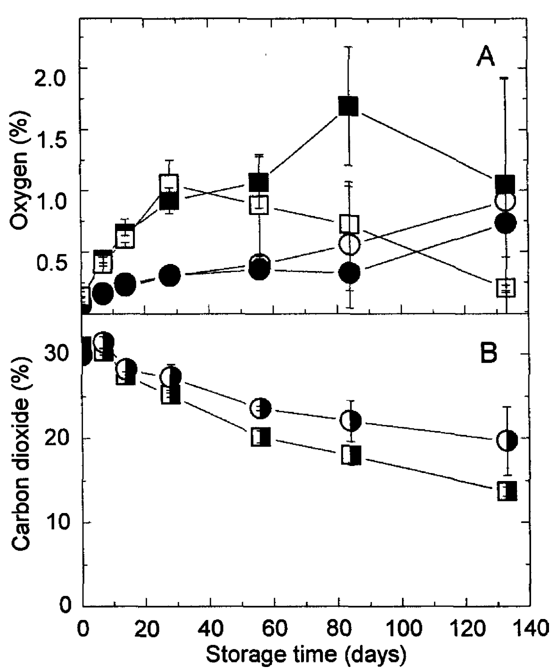

Fig. 3. A Oxygen and B carbon dioxide concentrations in the headspace of Danbo cheese packages stored for 0–133 days at 4 °C in PLA (square) and the reference (circle) stored in the dark (closed symbols) or at 1500 lx (open symbols).

Mortensen, Sørensen, and Stapelfeldt (2002b) found that the headspace oxygen content decreased to almost zero immediately after packaging of Havarti cheese, as that type of cheese was acting as an "oxygen absorber". Such a phenomenon was not observed in the present study, which may be explained by differences in product composition and processing.

In general, the high rate of oxygen accumulation in the PLA packages is not compatible with the desired MA with a low oxygen concentration of maximally 0.5%. Hence, the critical limit of oxygen was exceeded by using the PLA material with a too high oxygen permeability coefficient.

Headspace carbon dioxide concentrations (Fig. 3b) decreased as a function of storage time ($p \leqslant 0.0001$) for both the PLA and the reference package, regardless of exposure conditions. The loss of carbon dioxide was significantly higher for the PLA packages than for the reference packages ($p \leqslant 0.0001$). Generally, carbon dioxide is generated through respiration and reduced when being dissolved in the cheese or when permeating through the packaging material to the external atmosphere. The observed differences in carbon dioxide loss must be attributed to the permeation process as solubilisation into the product is generally a much faster process, which typically proceeds over a timescale of 1–2 days. The rate of change of the carbon dioxide concentration was higher in the beginning than later in the storage experiment. Initially, the driving force for carbon dioxide permeation out of the system is high, due to a high internal concentration of the permeant and a low external concentration in the atmosphere. Therefore, the driving force, and consequently the permeation are diminishing at later stages of the storage experiment. At the end of storage, the PLA system had reached an internal concentration of 20% carbon dioxide, whereas the concentration in the reference system was 14% carbon dioxide.

Carbon dioxide protects the cheeses against microbial growth and may contribute to the overall flavour (Juric, Bertelsen, Mortensen, & Petersen, 2003). The minor differences in carbon dioxide concentration in PLA and reference packages are not expected to cause any differences in the protection against microbial growth and flavour or the ability to obtain the required carbon dioxide atmosphere of the two products. However, the reduced carbon dioxide level in the packages may affect mould growth, which is an important factor when determining the shelf life of packaged cheese. However, specific microbiological investigations were out of the scope of the present study, and no visual mould growth was observed in non-leaking packages.

3.5. Secondary lipid oxidation products

SPME GC is a simple method for concentrating and detecting volatile components from foods (Zhang, Yang, & Pawliszyn, 1994; Steffen & Paeliszyn, 1996). The method has proved suitable for the detection of volatile secondary lipid oxidation products and for differentiating between Havarti cheeses exposed to fluorescent light or stored in the dark (Mortensen et al., 2002a).

Table 3 depicts the volatile compounds identified from the chromatograms by their mass spectra after 84 days of storage, together with their respective odour threshold values and sensory characteristics. The thresholds originate from water samples and may be different for cheeses due to synergistic and antagonistic effects of volatiles in food systems. In addition, different thresholds for some of the volatile compounds are found in various studies as is apparent from Table 3, with the consequence that threshold values are not always well-defined. Nevertheless, these threshold values can give a rough overview of the impact of the volatiles on the quality of the cheeses. In general, the odour threshold values of alcohols are higher than those of aldehydes and of most ketones. By comparing the threshold values

Table 3
Significant volatile compounds identified by gas chromatography–mass spectrometry (GC/MS) in top slices of Danbo cheeses stored for 84 days

Group of compounds	Volatile compound	Concentration (ppm)				Odour threshold values in water (ppm)	Sensory characteristics[a,b]
		Light storage		Dark storage			
		PLA	Reference	PLA	Reference		
Alcohols	2-Butanol	0.035	0.556	0	1.835	0.525[c]	Alcoholic
	1-Hexanol	0.091	0	0	0.005	2.5[d]	Fruity
	1-Pentanol	0.273	0.009	0.006	0.009	4[e]	Fusel-like
Aldehydes	Heptanal	1.01	0	0	0.011	0.003–0.02[c,f]	Fatty, harsh, pungent
	2-Heptenal	0.077	0.001	0	0	0.013–0.051[c]	Fatty, pungent, green
	Benzaldehyde	0.483	0.251	0.512	0.181	0.003–0.35[c,e,f]	Almond, bitter
	Hexanal	1.93	0.01	0	0	0.006–0.6[g]	Green, grass
	2-Hexenal	0.011	0	0	0.025	0.017[e]	Green, leafy
	Octanal	0.073	0	0	0.03	0.0007–0.007[c,f]	Fatty, soapy
	2-Octenal	0.007	0.011	0.01	0.006	0.003–0.004[c]	Green-leafy, orange, honey, cognac
	Nonanal	0.171	0	0	0.003	0.001[c]	Fatty, green, grass
Ketones	2-Butanone	1.83	2.325	4.099	1.49	50[f]	Ethereal, acetone-like
	2-Heptanone	0	0.178	0.111	0.104	0.001–3[c,h,i,j]	Blue cheese, musty
	2-Pentanone	0.11	0.14	0.462	1.333	0.3[i]	Blue cheese, musty, fatty
	2-Octanone	0	0	0.008	0.006	0.0145[j]	Fruity, musty
	2-Nonanone	0.016	0.213	0.134	0.068	0.0109[j]	Blue cheese, musty, fatty
Sulphur compounds	Dimethyl disulphide	0.021	0	0.001	0	0.00002–0.012[c,f]	Corn, sharp, sulphurous
	Acetic acid	3.77	2.05	2.65	1.74	0.007–24.3[c]	Acidic

[a] Sigma Aldrich (2003–2004).
[b] Burdock (1995).
[c] van Gemert and Nettenbreijer (1977).
[d] Hansen et al. (1992).
[e] Fazzalari (1978).
[f] Kochar (1996).
[g] Larsen and Poll (1992).
[h] Rothe et al. (1972).
[i] Aoki and Koizumi (1986).
[j] Belitz and Grosch (1999).

with the concentration of each component, it was noted that the levels of most volatile compounds exceeded the threshold values. Consequently, these may have an impact on the resulting cheese flavour and odour.

Exposure to light had a major impact on the formation of the volatile compounds, hexanal, heptanal, nonanal and 1-pentanol. Hexanal and heptanal are formed by photosensitised oxidation of linoleic and linoleneic acids, respectively. Nonanal is formed by free radical oxidation or photosensitised oxidation of oleic acid, and 1-pentanol is formed by reduction of the aldehyde counterpart, pentanal, which, like the other alcohols presented in Table 3, originates from photosensitized oxidation of linoleic acid (Przybylski & Eskin, 1994). The development of these compounds over time is depicted in Fig. 4. These four chemical species were found in significantly higher amounts in systems exposed to light, and larger amounts were also noted in PLA-packaged products compared to products packaged in the reference material ($p \leqslant 0.0001$). This is in contrast to the systems stored in the dark, where almost identical and low concentrations were observed.

Development of the secondary lipid oxidation products in Fig. 4 had a ''lag phase'' of varying lengths. Such a lag phase is expected due to the conversion of primary oxidation products into secondary oxidation products. After 84 days of storage, the amounts of heptanal and

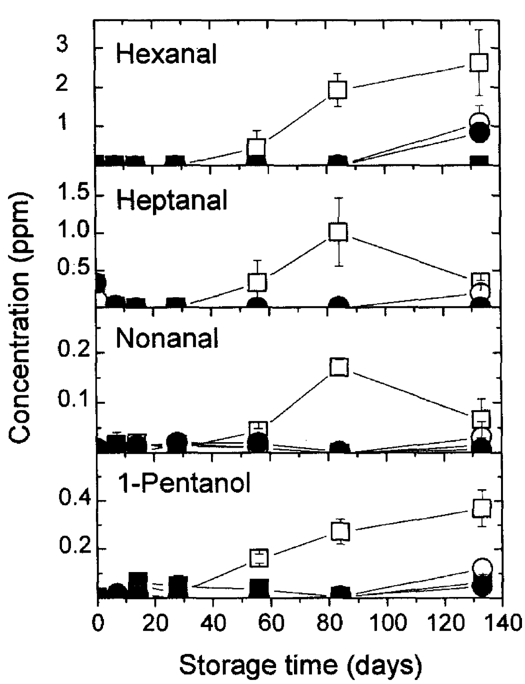

Fig. 4. Formation of hexanal, heptanal, nonanal and 1-pentanol in Danbo cheeses stored for 0–133 days at 4 °C in PLA (square) and the reference (circle) stored in the dark (closed symbols) or at 1500 lx (open symbols). Values are semi-quantitative and are based on internal standard equivalents.

nonanal decreased, suggesting that the two compounds were degraded into tertiary lipid oxidation products faster than their rate of generation. Nonanal, among other aliphatic aldehydes, is one of the most important secondary lipid oxidation products, because it is a major contributor to unpleasant odours and flavours in foods (Kochar, 1996). Nonanal has previously been detected in Danbo (Sørensen & Benfeldt, 2001) and Havarti cheeses (Lund, Sørensen, Hansen, & Hølmer, 2002; Mortensen et al., 2002a). Lund et al. (2002) and Mortensen et al. (2002a) observed that the formation of nonanal was dependent on light exposure to the same extent, as shown in Fig. 4.

In contrast to heptanal and nonanal, the development of hexanal and 1-pentanol continued to increase during the extent of the storage period. 1-Pentanol has previously been reported in light-exposed dairy products (Behnke, 1980; Day & Libbey, 1964; Lund et al., 2002; Mortensen et al., 2002a; Mortensen, Sørensen, & Stapelfeldt, 2002c; Mortensen, Sørensen, Danielsen, & Stapelfeldt, 2003a; Mortensen, Sørensen, & Stapelfeldt, 2003b, 2003c). 1-Pentanol, among other primary alcohols, makes only a minor contribution to the off-flavours produced by oxidation due to significantly higher flavour thresholds (see Table 3) than those of the corresponding aldehydes (Kochar, 1996). Hexanal has previously been reported in light-exposed dairy products (Lund & Hølmer, 2001; Mortensen et al., 2002a, 2002c; Mortensen et al., 2003a, 2003b, Mortensen, Sørensen, & Stapelfeldt, 2003c). The threshold value of hexanal is in the range of 0.03–0.6 ppm (Kochar, 1996), which was exceeded after 56 days of storage in cheeses packaged in PLA and exposed to light. The threshold was not exceeded in the reference-packaged cheeses until the sell-by date (84 days). Hence, the PLA packages did not protect the light-exposed cheeses from development of significant lipid oxidation and unpleasant odours during the whole shelf life of 84 days, but during the first 56 days of storage only limited lipid oxidation was observed as is apparent from Fig. 4. Although the cheeses developed differently according to the chemical analysis, it was not possible for the analysts to smell the differences between packaging types and light exposure conditions. Only loss of fresh smell during storage was detected.

The two materials studied are not expected to provide different protection against light-initiated lipid oxidation as the important wavelengths for this phenomenon (365, 405 and 435 nm (Lennersten & Lingnert, 2000)) are situated in the part of the spectrum, in which the transmittances of the two films are identical (Fig. 1). Hence, the difference in development of secondary lipid oxidation products cannot be ascribed solely to differences in light transmission but rather to a combined action of light and oxygen. Oxygen is present at much higher levels in the PLA packages than in the reference packages (Fig. 3a) due to the more permeable nature of the PLA material, thereby triggering the development of secondary oxidation products. Mortensen et al. (2002c) also found that oxidations in Havarti cheeses were more pronounced in transparent materials with a high OTR than in those with a low OTR.

4. Conclusions

The results of the storage experiment indicate that the present PLA packages can be used for storage of Danbo cheese for a period of 56 days where moisture loss and lipid oxidation were limited. At longer storage times, PLA did not provide a sufficient protection against moisture loss and lipid oxidation, and a lower WVTR and OTR are hence required, before PLA can be used for packaging of Danbo cheeses with a shelf life of 84 days. However, when light was excluded, the PLA packages provided a sufficient protection against lipid oxidation during the entire storage period. Furthermore, estimates of moisture loss indicated that PLA may provide adequate protection for 84 days, when doubling the amounts of cheese and depths of the package (amount of cheese compared to the surface area of the package). However, such estimations should be evaluated experimentally before firm conclusions can be drawn.

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