Shelf life assessment of industrial durum wheat bread as a function of packaging system

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Abstract

This study compared the effect of different packaging systems on industrial durum wheat bread shelf-life, with regard to thermoformed packaging (TF) and flow-packaging (FP). Two TFs having different thickness and one FP were compared by assessing physico-chemical and sensorial properties and volatile compounds of sliced bread during 90 days of storage. Texture, a_w and bread moisture varied according to a first-order kinetic model, with FP samples ageing faster than TFs. Sensorial features such as consistency, stale odor, and sour odor, increased their intensity during storage. Furans decreased, whereas hexanal increased. The Principal Component Analysis of the whole dataset pointed out that the TF system at reduced thickness could be adopted up to 60 days, without compromising the standard commercial life of industrial bread and allowing to save packaging material. The FP system would allow further saving, but it should be preferred when the expected product turnover is within 30 days.

Key words: durum wheat bread; shelf life; packaging system; volatile compounds; textural properties; sensorial properties

1. Introduction

The shelf life of food, defined as the period of time during which quality loss does not exceed a tolerable level, can be decisively influenced by packaging. Bread shelf life is mainly affected by staling, a complex degradative phenomenon which, in turn, depends on starch retrogradation and moisture loss (Bollaìn, Angioloni, & Collar, 2005; Katina, Salmenkallio-Marttila, Partanen, Forssell, & Autio, 2006). Staling results in chemical and physical changes such as decrease of softness and cohesiveness, as well as loss of aroma and flavor (He & Hoseney, 1990).

It is consolidated that durum wheat bread, especially popular in the Mediterranean area due to its specific sensory and textural properties (Pasqualone, 2012; Quaglia, 1988), undergoes slower staling compared with soft wheat bread, due to high water-binding capacity of durum wheat semolina (Boyacioglou & D’Appolonia, 1994; Hareland & Puhr, 1998; Quaglia, 1988; Rinaldi et al., 2015). The addition of enzymes, such as lipase and amylase, to bread formulation (Bollaín et al., 2005; Giannone et al., 2016; Palacios, Schwarz, & D'Appolonia, 2004), or the use of sourdough (Pasqualone, Summo, Bilancia, & Caponio, 2007; Rinaldi et al., 2015), can further reduce durum wheat bread staling.

Bread staling results in a decrease of consumer acceptance and in great economic losses. As bakery products are becoming a major part of the international food market, the baking industry is undergoing a period of rapid change and modernization, involving the setup of bakery plants with improved technology and new products development (Byrne, 2000). In order to achieve longer shelf lives, refrigerating conditions have been applied to dough, prebaked or not (Rask, 1989; Selomulyo & Zhou, 2007). In addition, new packaging technologies have been investigated.

Packaging is the last step of production and food technologists have to select the most suitable type of packaging to ensure the longest shelf life. The success in the market is equally based on product intrinsic quality and packaging effectiveness in preserving, and communicating, this quality. The conventional packaging procedure applied in baking industry uses atmospheric air and approved lidding materials for foods. However, modern packaging is performed under modified atmosphere and with composite materials specifically formulated in order to retain the inert gases. Several studies evidenced the effectiveness of packaging in maintaining the quality characteristics of bread, slowing down moisture loss and molds growth, by using: i) suitable materials (Licciardello, Cipri, & Muratore, 2014; Pagani, Lucisano, Mariotti, & Limbo, 2006); ii) active packaging (Latou, Mexis, Badeka, & Kontominas, 2010; Mihaly Cozmuta et al., 2015); iii) modified atmosphere (Del Nobile, Martoriello, Cavella, Giudici, & Masi, 2003; Piergiovanni & Fava, 1997).

Nowadays, indeed, an essential issue is the selection of packaging systems which are not only effective, i.e. able to maintain quality characteristics, but also efficient, i.e. able to contain environmental impact and costs generated by packaging production and disposal. In a preliminary study, Licciardello et al. (2014) have assessed the feasibility of reducing the thickness of materials used in thermoformed packaging of durum wheat bread, finding that potential gains are possible without compromising the standard shelf life. However, no study has compared the effect of different packaging systems on bread shelf life, with special regard to thermoformed packaging and flow-packaging. Flow-packaging has the advantage of high working speed and could allow further saving of packaging material. The choice of packaging materials is often based on packaging performances, with special regards for gas barrier properties; however, in the case of thermoformed packages, the film properties in the finished product differ from those of the material as received due to thermal stretching, and need to be verified in the conditions of use. Hence, the comparison and choice cannot be made only on the basis of technical sheets available.

The objective of the present study was to evaluate the influence of different packaging systems (namely, one commonly used two-piece thermoformed packaging, a two-piece thermoformed packaging at reduced thickness, and flow-packaging by a very thin material), on quality variations of industrial durum wheat bread by monitoring physico-chemical and sensorial parameters during 90 days of storage.

2. Materials and methods

2.1 Sample preparation

Bread was prepared at a local bread-making company (Valle del Dittaino Società Cooperativa Agricola, Assoro, Italy), according to a consolidated industrial process based on the following formulation: durum wheat remilled semolina, water (66% on semolina basis), compressed yeast (0.47% on semolina basis), NaCl (2.2% on semolina basis), maltogenic α-amylase (0.05% on semolina basis). The ingredients were mixed and kneaded for 17 min by means of a diving arms kneader. The final dough temperature was 26±1 °C. The dough was rested in bulk for 15 min, scaled into 980±20 g portions (100 loaves, repeated for three production trials), proofed for 150 min (32±1 °C and 66±2% RH) and baked at 240 °C for 60 min, in industrial tunnel oven. The baked loaves, weighting approximately 800 g each, were automatically transported to a cooling chamber, set at 20±2 °C for 120 min. After cooling, the loaves were sliced by means of an automatic slicing machine to 11±1 mm thickness.

2.2 Packaging systems

After slicing, portions of 400 g of bread slices were packaged. Three packaging systems were compared; two of them consisted of two-piece packages made up of a thermoformed bottom and a lid. The first packaging system (‘thermoformed 1’ or TF1, commonly used by the baking industry were the trials were carried out) consisted of a 275 μm bottom film and a 125 μm lid; the second was similar to TF1, but with thinner films, 225 μm and 33 μm for bottom and lid, respectively (packaging system ‘thermoformed 2’ or TF2). The third system involved flow-packaging using a 62 μm coextruded film (‘flow-packaging’ or FP). All films were made of multilayered polyolefin materials. An automatic industrial thermoforming machine (MIX 9000, Tecnosistem snc, Coccaglio, Italy) shaped the bottom films for TF1 and TF2 before inserting the sliced bread and sealing with the corresponding lid film, whereas FP was filled and formed by a flow-packaging machine (Jaguar, Record spa, Garbagnate Monastero, Italy). All packaging systems included sprayed ethanol (1.6% on bread weight basis) and modified atmosphere composed of 30% CO_2 and 70% N_2.

The packaging materials were kindly supplied by Cryovac Sealed Air S.r.l. (Passirana di Rho, Italy). Permeability properties, as from the technical sheets of the supplier, were as follows.

O_2 transmission rate (OTR): i) TF1 lid film < 3 g/m^2, 24 h, bar; bottom film = 1 g/m^2, 24 h, bar; ii) TF2 lid film = 4 g/m^2, 24 h, bar; bottom film = 1 g/m^2, 24 h, bar; iii) FP = 4.5 g/m^2, 24 h, bar.

Water vapor transmission rate (WVTR): i) TF1 lid film < 10 g/m^2 24 h; bottom film ≤ 10 g/m^2, 24 h; ii) TF2 lid and bottom films = not reported; iii) FP = 4 g/m^2, 24 h.

Packaged breads TF1, TF2, and FP were analyzed on the same day of baking (t_0) and after 7, 15, 30, 60, and 90 days of dark storage at 20±1 °C and 55% relative humidity. Three breads ($n = 3$) per each of three packaging systems considered and per each of six sampling times were analyzed, for a total of 54 samples.

2.3 Headspace gas composition analysis

The internal O_2 and CO_2 composition of packages was determined by means of Dansensor Checkpoint portable gas analyzer (Dansensor, Ringsted, Denmark). Ten mL of headspace were analyzed, with three replications.

2.4 Determination of moisture, water activity, alkaline water retention capacity

Moisture content of bread crumb and crust was determined by oven drying at 105 °C until constant weight. Two bread slices (11±1 mm thickness) for each of two repetitions were used, and moisture was determined on one square crumb sample (40 mm × 40 mm) taken from the center of each slice, and on approximately 3 g crust samples manually cut from the same slices. Crumb to crust ratio of breads was 3:1 (w/w). Water activity (a_w) was determined by Hygropalm 40 AW (Rotronic Instruments Ltd, Crawley, UK) according to manufacturers' instructions. Three bread slices (11±1 mm thickness) were used, after removal of the crust. For each set of determinations, separate loaves were considered. Alkaline water retention capacity (AWRC) was determined according to the method described by Yamazaki (1953), conveniently modified for the analysis of bread crumb (Licciardello et al., 2014). Briefly, 1 g of bread crumb, previously dried until constant weight and ground in a mortar, was put in 15-mL tubes (W1), added with 5 mL 0.1 N $NaHCO_3$ and vortexed for 30 s, then let at room temperature for 20 min. The slurry was centrifuged at 3000 rpm for 15 min, the supernatant was discarded and tubes were let drip for 10 min upside down inclined by 15°. Dried tubes were then weighed (W2). AWRC was calculated as $[(W2 - W1)/W1] \times 100$, where W1 is the weight of the tube containing the dry sample and W2 is the weight of the tube containing the dripped sample. Analyses were conducted in duplicate.

Experimental data were fitted to the following first-order kinetic model:

$$C\,(t) = C^{\infty} + \left(C^{0} - C^{\infty}\right) \cdot \exp\left(-k \cdot t\right)$$

where: $C\,(t)$ is the value of the descriptor at time t, C^{∞} is the value of the descriptor at equilibrium (infinite time), C^{0} is the initial value of the descriptor (time zero), k is the kinetic constant, t is the time.

2.5 Texture Profile Analysis

The Texture Profile Analysis (TPA) of bread was carried out by means of an Universal Testing machine (model 3344, Instron, Norwood, MA, USA), equipped with a 5.0 cm diameter cylindrical probe and a 2000 N load cell. Data were acquired through Bluehill® 2 software (Instron, Norwood, MA, USA). Cyclic compression tests (30s gap between first and second compression) were set up: trigger load and crosshead speed were 5 g and 3 mm/s respectively, the force required to compress the samples by 40% was recorded on 5-cm side square portions of 22-mm thick slices, and the average value of five replicates was taken.

Three primary TPA parameters (firmness, springiness, and resilience), and one derived parameter (chewiness) were calculated: firmness (N), defined as the peak force during the first compression cycle; springiness (mm), i.e. the elastic recovery that occurs when the compressive force is removed, defined as the height to which the food recovers during the time that elapses between the end of the first and the start of the second compression; resilience, defined as the adimensional ratio between the negative force input and the positive force input during the first compression, or Area 5/Area 4; chewiness (N mm), defined as the product of firmness, resilience and springiness.

With the aim of studying gradients of firmness during aging, crumb firmness was fitted to the modified Avrami equation (Armero & Collar, 1998):

$$\theta = (F_\infty - F_t) / (F_\infty - F_0) = \exp(-kt^n)$$

where θ is the fraction of the total change in the crumb firmness still to occur. F_0, F_t and F_∞ are experimental values of fitness at times zero, t, and infinite (or limiting value), k is the rate constant, and n is the Avrami exponent. All parameters were obtained from the modelling process.

Springiness, resilience and chewiness data were fitted to the first-order kinetic model previously described in paragraph 2.4.

2.6 Color parameters

Two slices of bread for each sample were scanned by a scanner Canoscan N650U (Canon Computer System, Inc., Costa Mesa, CA, U.S.A.). Four images (sized 2 × 2 cm) from different points of each replicate slice were acquired at 300 dpi resolution and processed by the software Image Color Summarizer v0.5 # 2006–2011 (Martin Krzywinski, http://mkweb.bcgsc.ca/color_summarizer/) obtaining the *r, g*, *b* (respectively: red, green and blue indexes) and *h*, *s*, *v* (respectively: hue, saturation and lightness) color indices.

2.7 Determination of volatile compounds

Volatile compounds of bread samples were determined by solid phase micro-extraction (SPME) coupled to gas-chromatography/mass spectrometry (GC/MS). Sample delivery from productive site to the laboratory for volatile determination accounted for about 10 h, therefore t_0 data of volatiles have to be intended as 10 h after baking and packing. Maintaining the crumb to crust ratio of 3:1 (w/w), an amount of 400 ± 0.05 mg of bread crust and crumb (cut in pieces of 2-3 mm, then mixed together) was added of 4 mL of a 20% NaCl (w/v) aqueous solution in a 20-mL vial. The SPME analysis was made by using an Agilent 6850 gas-chromatograph equipped with an Agilent 5975 mass-spectrometer (Agilent Technologies Inc., Santa Clara, CA, USA) as in Pasqualone et al. (2015) with the following modifications: time and temperature of fiber exposure to sample headspace = 40 min at 50 °C; desorption time = 2 min; GC injector temperature = 300 °C; flow = 2.0 mL/min. Peak identification was performed by computer matching with the reference mass spectra of National Institute of Standards and Technology (NIST) and Wiley libraries. The semi-quantitative data (peak areas expressed as total ion counts - TIC) were used to compare the samples. The analysis was carried out in triplicate.

2.8 Sensory evaluation

As for volatiles determination, sensory determinations on fresh bread (t_0) were performed 10 h after baking and packing. Quantitative Descriptive Sensory Analysis of bread samples was performed by a panel consisting of 8 trained members in the conditions described in a previous work (Pasqualone et al., 2007). The list of sensory terms included descriptors of appearance (crumb color), textural characteristics (crumb cohesiveness, crumb consistency), and odor (semolina, sour, toast, stale). The descriptors were rated on an anchored line scale that provided a 0-9 score range (0 = minimum; 9 = maximum intensity). The definitions of each descriptor and the scale anchors are reported in Pasqualone et al. (2007).

2.9 Statistical analyses

The data were analysed with package IBM® SPSS® Statistics 13.0 (Armonk, NY, USA) for Windows. One-way analysis of variance (ANOVA) was performed to understand the effects of different packaging on physico-chemical attributes of durum wheat bread. Tukey HSD test ($P < 0.05$) was used for post hoc comparison of means. The Principal Component Analysis (PCA) was performed with XLStat (Addinsoft SARL, New York, NY, USA) for Windows.

3. Results and discussion

3.1 Headspace gas composition analysis

Figure 1 shows the variations of O_2 and CO_2 level inside bread packages during 90 days of storage. The initial modified atmosphere composition, i.e. 70% N_2 and 30% CO_2, underwent significant changes during storage as a function of the packaging system.

In particular, the CO_2 decrease can be attributed both to the dissolution of the gas into the food matrix and to permeability through the packaging material. Overall, the observed CO_2 permeability of the tested materials followed the order TF1<TF2<FP. Until 30 days, CO_2 values were not significantly different ($P < 0.05$) between TF1 and TF2, while FP scored significantly ($P < 0.05$) lower values compared to the thermoformed packages already after 15 days. A similar trend was observed for the O_2 level: in the TF1 samples it practically did not change during storage; slight increases were observed in TF2, not exceeding 1.0% after 90 days, and more marked increases were detected in the FP system, that allowed to reach 2.3% O_2 after 90 days. No significant differences in the O_2 level were observed between TF1 and TF2 headspaces after 60 and 90 days. These results allowed to point out the real behaviour of TF1 and TF2 materials, that could not be fully foreseen by the permeability properties reported in the technical sheets due to modifications involved by stretching and thermoforming.

3.2 Bread moisture, a_w and AWRC

Table 1 shows the changes in moisture content of crumb and crust, a_w, and AWRC of differently packed durum wheat bread samples, as well as the kinetic parameters resulting from the best-fit of the experimental data to a first-order kinetic model.

The initial crumb moisture content was within the typical range of fresh durum wheat bread obtained from semolina with high protein content (Pasqualone et al., 2007; Raffo et al., 2003), and tended to decrease during storage with significant variations ($P < 0.05$) until 30 days for TF2 and FP, and until 60 days for TF1. The latter showed significantly higher crumb moisture than FP, but without significant differences with TF2 from 60 days onwards. An opposite trend was observed for crust moisture content, whose values increased dramatically in the first 7 days, with no significant increases during the rest of the storage period. The experimental data fit well the first-order kinetic model, with C^{∞} values very similar to experimental data at 90 days. Moisture variations were faster in FP than in TF1 samples, especially for crust moisture gain, as testified by higher k value for FP than for TF1. Moisture values of TF1 and TF2 moisture, instead, changed at similar rates. Water migration from crumb to crust and, then, to the ambient, is one of the main events occurring just after baking. As a consequence, crumb hardens while crust first acquires a leathery consistence, then hardens itself with detrimental effects on bread quality. One of the objectives of a packaging system is to limit water loss, and this can be achieved by materials with suitable barrier to water vapor. The observed results were therefore imputable to high WVTR value of the FP film, as reported in the technical sheet.

Paralleling crumb moisture loss, also crumb a_w decreased in all samples during storage. This phenomenon was more evident for FP, again in agreement with higher vapor permeability of FP film: the a_w decrease followed a first-order kinetics and FP showed dramatically higher kinetic constant compared to TF1 and TF2 (Table 1). The differences between the three packaging systems were significant after 7 days, while TF1 exhibited a_w values significantly ($P < 0.05$) higher than those of the other samples at 30 and 60 days of conservation. At the end of the storage period all of the samples showed similar values of a_w, below 0.900 and very close to the calculated C^∞ values, irrespective of the packaging system.

The AWRC values significantly ($P < 0.05$) decreased until the end of the storage period for each of the packaging solutions considered, with significantly lower values for FP than for TF2 starting from 30 days. This parameter was effective in differentiating fresh bread from aged one, in agreement with previous studies (Sidhu, Al-Saqer, & Al-Zenki, 2007; Licciardello et al., 2014). AWRC is correlated with the degree of starch crystallization, since gelatinized starch has a higher capacity to bind water, compared to retrograded starch (Indrani, Rao, Sankar, & Rao, 2000). The observed trend suggests that starch retrogradation was especially involved in bread quality loss during the initial phase of ageing (15 days), when the rate of variation was faster. The variation of AWRC, however, could not be satisfactorily described by the first-order kinetic model.

3.3 Bread textural features

Table 2 shows the changes in textural features of differently packed durum wheat bread samples, as well as the kinetic parameters resulting from the best-fit of the experimental data to the Avrami equation (for firmness) or to a first-order kinetic model (for springiness, resilience, and chewiness).

Texture is an important characteristic in consumer's perception of food and influences the purchasing decisions. Firming of bread crumb is one of the most evident events in bread ageing and one of the most common parameters used to evaluate staling. A significant increase in crumb firmness was observed for all samples during storage. In particular, firmness increased faster in FP samples than in TF2 and TF1. This result was in agreement with the AWRC measures that evidenced a greater extent of starch retrogradation in FP samples. TF1 generally retained softer crumb than TF2 samples, but at the end of the storage period the difference with TF2 disappeared. Bread hardening was particularly fast during the first 15 days, then progressively tended to a steady state, corresponding to the maximum firming. Firmness data were modeled using Avrami equation, demonstrating that FP was associated with a higher firming rate (higher k) compared with TF2. The model parameter F_∞ was very close to experimental values observed at 90 days, indicating that bread had reached the maximum firmness by that time. The n term varied from 0.88 for TF2 to 1.16 for FP: other authors who have modeled bread firming kinetic data by the Avrami equation have indicated that the Avrami exponent n is close to 1 (Kim & D'Appolonia, 1977). Nevertheless, other publications state that the exponent n can take different values; however, the determination of the n exponent is often drawn for very few data points and is questionable. Le-Bail, Boumali, Jury, Ben-Aissa, & Zuniga (2009) used a simple first order model ($n = 1$) which fitted very well the experimental results obtained during staling of bread samples baked in a miniaturized baking system.

The other textural parameters were modeled using a first-order kinetic model. Springiness significantly increased during storage, well fitting the kinetic of first order. TF1 showed significantly ($P < 0.05$) lower springiness than TF2 and FP at 7 and 15 days of storage, whereas no significant differences were observed among the three packaging systems at 30 days and 60 days. At the end of the storage period FP samples showed the highest springiness, with C^∞ values similar to the experimental data. Overall, the kinetic model of springiness variations highlighted two different behaviors: one, which is relative to TF1, characterized by lower kinetic constant ($k = 0.040$), the other faster, with $k = 0.153$ and $k = 0.195$ for samples TF2 and FP, respectively.

Resilience, that shows how well a product 'fights to regain its original position after a stress' (Abdelghafor, Mustafa, Ibrahim, & Krishnan, 2011), decreased significantly with storage time, indicating a marked tendency of bread to become crumblier, with a less cohesive structure. Similarly to springiness, a higher kinetic constant was observed for TF2 and FP ($k = 0.093$ and 0.088, respectively), while FP1 showed $k =$ as low as 0.034. The resilience value at infinite time of TF1 and TF2 were similar to each other; FP scored the lowest value ($C^\infty = 0.66$).

The trends of variation of the derived parameter chewiness (firmness * resilience * springiness) paralleled those of firmness and springiness, increasing significantly ($P < 0.05$) during storage. Although the estimated k value was the lowest for FP, the chewiness value at infinite time was significantly higher (almost double) for this sample compared with the two thermoformed systems, which were assigned similar C^{∞} values.

3.4 Bread volatile compounds

Figure 2 reports the variations of the most abundant volatile compounds of bread samples during storage. Furan-derivatives and aldehydes, arising from Maillard reaction and lipid oxidation, respectively, characterized the volatile profile of breads. An overall comparison of the three packaging types points out that they had a similar effect towards the volatile compounds, apart few sampling points. With the only exception of hexanal, the volatiles decreased during time, but keeping quite high amounts during the first 15 days. A more evident depletion affected the volatile compounds as storage went on.

More specifically, the levels of 2-furanmethanol, derived from Maillard reaction and responsible for burnt note (Chang, Seitz, & Chambers, 1995), were different in the last stages of storage, with FP samples showing lower amounts than TF1 and TF2. Furfural, typically present in bread (Makhoul et al., 2015) and contributing a ‘brown’ note (Chang et al., 1995), significantly decreased since from 15 days, due to permeation through the films, with no differences among packaging types. Benzaldehyde, derived from aminoacid degradation, also through Strecker thermal reaction (Beleggia, Platani, Spano, Monteleone, & Cattivelli, 2009), decreased faster in TF2 than in TF1 and FP. Benzaldehyde has been already observed in durum wheat bread by other authors (Bianchi, Careri, Chiavaro, Musci, & Vittadini, 2008). Overall, the Maillard reaction volatiles positively contribute to fresh bread aroma and their decrease during storage was detrimental. This decrease was imputable to packaging permeability, allowing these compounds to escape, as well as to the possible formation of inclusion complexes with amylose (Martínez-Anaya, 1996). The differences among packaging types, when observed, were possibly due to differences in packaging selectivity and scalping phenomena.

As regards lipid oxidation volatiles, hexanal and nonanal were detected, deriving from the oxidation of linoleic and oleic acids, respectively (Frankel, 1983). Hexanal and nonanal have been already reported in bread (Chang et al., 1995; Chiavaro, Vittadini, Musci, Bianchi, & Curti, 2008), as well as in other cereal-based foods such as semolina, pasta, and biscuits (Pasqualone et al., 2014; 2015). Hexanal is responsible for a green, cut grass note, which has no obvious relationship to the typical bread flavor, although in total may have some influence (Chang et al., 1995), whereas nonanal is related to a rubbery, beany note (Chang et al., 1995). The formulation of bread samples did not include fat or oil, but the lipid fraction of semolina, although scarce, is mainly polyunsaturated (Pasqualone, Caponio, & Simeone, 2004; Pasqualone, Paradiso, Summo, Caponio, & Gomes, 2014) and very susceptible to lipoxygenase activity, leading to unstable fatty acid hydroperoxides which, in turn, decompose to carbonyl compounds. The latter can be responsible for off flavors in bread (Martínez-Anaya et al., 1996).

Hexanal, being originated during processing, mainly in the kneading step (Caponio, Summo, Pasqualone, & Bilancia, 2008), was present in freshly packed bread and increased after long storage, due to further oxidative phenomena involving linoleic acid, without differences among packaging types. Therefore, packaging permeability allowed hexanal to escape, but at longer times the raise of this volatile due to oxidation overcome the loss throughout the films.

Nonanal, instead, already originated during processing as well, did not show further increase after long storage because derived from the less oxidizable oleic acid. On the contrary, nonanal even decreased during storage. In fact, having a longer carbon chain than hexanal, nonanal is more hydrophobic (the octanol/water partition coefficients are 3.56 and 1.97 for nonanal and hexanal, respectively) and, therefore, has greater affinity towards olefins constituting the packaging materials, with a consequent higher scalping potential. The decrease of nonanal during storage was greater for TF2 samples than TF1 and FP. Nonanal showed significant differences among packaging systems also at t_0. This difference was imputable to the time, accounting for approximately 10 h, elapsed from production and packaging to the analytical determination of volatiles.

3.5 Bread color parameters

Among the color parameters instrumentally determined by image analysis, hue (Figure 3) significantly decreased during storage: hue values observed after 30 day were significantly lower than in freshly packed breads, irrespective of packaging system. The other parameters showed slight variations, which however could not be correlated with storage time (data not shown). Hue is a parameter derived from RGB coordinates, however it is interesting to notice that the single primary parameters are not correlated with ageing, while their derived index, hue, contains more information and is able to represent the color change which occurs during storage. Color changes during durum wheat bread ageing could be due to the oxidation of carotenoids which characterize durum wheat (Pasqualone et al., 2007), however this hypothesis needs to be investigated more in depth.

3.6 Bread sensory features

Bread sensory features were monitored during storage (Figure 3), with special regard to descriptors related to color, odor notes, and textural characteristics. Freshly packed bread were characterized by brilliant yellowish, highly cohesive and quite consistent crumb, with moderately intense pleasant odor notes of semolina, toast, and slight sour. Yellow crumb color was due to carotenoid pigments, while high consistency was imputable to tenacious gluten, both usually present in durum wheat remilled semolina (Pasqualone, Caponio, & Simeone, 2004).

During storage, the intensity of the sensory descriptors decreased, with the exception of consistency, stale odor, and sour odor. Overall, but with lower statistical significance, the results of sensory evaluation confirmed the trends evidenced by instrumental measures of crumb textural properties, moisture, color hue, and volatile compounds. In particular, a progressive color decrease was observed during time, though not significant in TF1 (P = 0.119), with no difference among packaging types. In a previous work, carried out in unpackaged durum wheat bread, yellowish crumb shifted to a paler tone due to the increase of opacity related to starch retrogradation and moisture loss, with a significant correlation between sensory and colorimetric data (Pasqualone et al., 2007).

A decrease of crumb cohesiveness, leading to a marked tendency to crumble, and an increase of consistency, were observed in all breads. The decrease of cohesiveness was faster than the consistency increase, as already reported (Pasqualone et al., 2007). TF1 samples tended to present lower crumb consistency than FP samples, with a significant difference ($P < 0.05$) at 7 days.

Irrespective of packaging system, significant decreases of semolina and toast odor were evidenced in all breads at 60 days, compared with freshly packed samples, whereas stale and sour odor increased. No statistical differences were observed at the end of storage, due to high data variability. The decrease of certain odor notes was probably imputable, besides volatilization through packaging films, to interactions between aroma components and amylose (Martínez-Anaya, 1996). The increase, instead, was due to oxidative phenomena, mainly involving carbonyl compounds and carotenoid pigments (Kulp & Ponte, 1981; Martínez-Anaya, 1996), that led to the formation of off-flavors at an extent exceeding the permeability of packaging or amylose interactions. Although perceivable, however, stale odor never reached an excessively high score: it was scored around 3 (scale 0-9) after 30 days storage, and remained on similar levels also after 60 days.

3.7 Principal Component Analysis of the whole dataset

The Principal Component Analysis (PCA) of the whole dataset pointed out that the first two principal components, PC1 and PC2, explained together about 79% of total variability. The loading plot (Figure 4 a) shows that PC1, in particular, accounted for 70% of variability and was positively correlated with all the appreciable characteristics, such as crumb moisture, color and cohesiveness, semolina odor, toast odor, water activity, crumb resilience and all the volatile compounds except hexanal, whereas it was negatively correlated with undesired stale odor, crumb consistency, crust moisture, crumb hardness, chewiness, and springiness. Therefore, PC1 allowed to discriminate bread samples in the score plot (Fig. 4 b) according to storage time: longer storage times corresponded to worse sensory and textural features. The PC2, accounting for about 9% of variability, showed a negative correlation with AWRC and sour odor, while a positive correlation with all volatile compounds except hexanal, as well as with hue, crust moisture, and springiness.

This variability was mainly due, as pointed out by the score plot, to the changes occurring in breads in the initial stages of storage. As a consequence, three clearly distinct groups of breads could be observed in the score plot. The first included fresh breads (t_0), together with the TF1 bread stored for 7 days: this would mean that TF1 was the only packaging system able to keep almost unaltered bread characteristics in the first week of storage. The second group includes TF2 and FP breads stored for 7 days, together with all samples stored for 15 days: these breads were involved in changes regarding loss of AWRC, and slight variations of volatile compounds and textural properties. Nevertheless, the properties of these breads remained clearly different respect to those of long-term stored breads (30-90 days, third group), which all showed the typical features of staling, although with some differentiations. In particular, at long storage times the two thermoformed packaging systems were comparable, with only a slight differentiation between them, and only the FP system was more distant. The latter, at 30 days, was similar to TF1 at 60 days. So, while in the short-term storage TF1 was by far the most effective packaging system, considering that the standard shelf-life of industrial durum wheat bread reaches 60 days, TF1 could be effectively substituted by TF2 up to this time, whereas FP could be used up to 30 days.

4. Conclusions

Based on the whole data set, and results of the PCA analysis, an overall comparison of the three packaging systems points out a significant influence on bread characteristics in the initial phase of storage, when the conventional system TF1 showed the best performance, allowing only slight changes compared to the fresh product. Data elaboration for textural parameters, crumb and crust moisture and a_w changes by a first-order kinetic model allowed to highlight slower kinetic constants for TF1 and faster for TF2 and FP. However, storage times longer than 15 days, which correspond to the period when the majority of product is generally purchased, tended to smooth the differences induced by packaging. Both TF2 – thermoformed package with lower thickness – and FP could be valid alternatives to TF1: while the former would not jeopardize the standard shelf life of 60 days, the latter could be adopted when the expected product turnover is within 30 days. The adoption of TF2 or FP systems would carry a significant reduction of packaging consumption which, in turn, results in environmental and economic improvements.

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Figure captions

Figure 1. Variations of headspace CO_2 and O_2 composition (mean ± standard deviation) of durum wheat bread package during 90 days of storage, as a function of packaging system (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack).

Figure 2. Variations of volatile compounds of durum wheat bread during 90 days of storage, as a function of packaging system (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack). Different letters indicate significant differences due to the effect of packaging type (at $P < 0.05$, based on Tukey HSD test).

Figure 3. Variations of color (instrumentally determined) and sensory properties of durum wheat bread during 90 days of storage, as a function of packaging system (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack). Different letters indicate significant differences due to the effect of packaging type (at $P < 0.05$, based on Tukey HSD test).

Figure 4. Loading plot (a) and score plot (b) of the principal components analysis carried out on the analytical data of durum wheat bread during storage, under three different packaging systems (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack). Data labels in the score plot indicate the days of storage.

Table 1. Changes in moisture content of crumb and crust, a_w, and alkaline water retention capacity (AWRC) of differently packed durum wheat bread samples (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack) during 90 days of storage, and kinetic parameters resulting from the best-fit of the experimental data to a first-order kinetic model (k = kinetic constant; C^0 = initial value of the parameter; C^∞ = value of the parameter at infinite time).

Storage time (days)	TF1	TF2	FP	TF1	TF2	FP
	a_w			*AWRC (%)*		
0	0.917±0.004^{c}	0.917±0.002^{d}	0.917±0.006^{c}	315.3±2.3^{d}	315.3±2.3^{d}	315.3±2.3^{e}
7	0.916±0.003^{cC}	0.911±0.001^{cB}	0.906±0.003^{bA}	313.0±5.2^{e}	319.3±3.2^{e}	307.6±5.1^{e}
15	0.910±0.001^{bB}	0.910±0.002^{cB}	0.905±0.002^{bA}	300.0±5.6^{cd}	301.4±4.1^{d}	291.8±2.4^{d}
30	0.910±0.001^{bB}	0.905±0.002^{bA}	0.903±0.002^{bA}	292.4±0.1^{cB}	289.0±1.1^{cB}	277.0±3.7^{cA}
60	0.908±0.002^{bB}	0.903±0.002^{abA}	0.903±0.002^{bA}	265.1±3.8^{bAB}	275.3±2.0^{bB}	263.9±3.6^{bA}
90	0.899±0.004^{a}	0.899±0.002^{a}	0.897±0.003^{a}	250.6±2.1^{aA}	264.8±5.5^{aB}	239.4±3.9^{aA}
k ($\times 10^{-2}$)	2.81±1.35	3.43±0.99	13.40±4.13	-	-	-
C^0	0.917±0.001	0.915±0.001	0.916±0.002	-	-	-
C^∞	0.903±0.003	0.899±0.002	0.900±0.001	-	-	-
	Crumb moisture (g/100 g)			*Crust moisture (g/100 g)*		
0	45.4±0.2^{e}	45.4±0.2^{c}	45.4±0.2^{c}	22.3±4.0^{a}	22.3±4.0^{a}	22.3±4.0^{a}
7	43.8±0.7^{d}	42.9±1.0^{b}	40.6±2.0^{b}	30.2±0.3^{b}	29.6±1.0^{b}	31.5±0.1^{b}
15	40.5±0.5^{cA}	42.3±0.1^{bB}	40.7±0.1^{bA}	30.4±0.7^{b}	30.7±0.3^{b}	33.4±2.2^{b}
30	39.1±0.4^{bB}	36.8±0.7^{aAB}	35.5±1.5^{aA}	33.2±2.2^{b}	30.7±1.3^{b}	32.8±0.6^{b}
60	38.1±0.4^{abB}	37.3±0.5^{aB}	36.0±0.3^{aA}	34.9±0.9^{b}	31.9±1.6^{b}	33.3±0.1^{b}
90	37.6±1.0^{a}	37.7±1.4^{a}	36.2±0.1^{a}	34.5±1.4^{b}	32.3±0.9^{b}	33.4±0.2^{b}
k ($\times 10^{-2}$)	5.68±0.98	5.64±1.76	7.26±2.09	8.52±3.30	18.29±9.37	24.79±11.81
C^0	45.7±0.4	45.8±0.8	45.4±0.9	24.0±1.4	23.6±1.3	23.6±1.3
C^∞	37.6±0.4	37.0±0.7	35.7±0.7	34.4±1.0	31.6±0.7	33.3±0.7

^{a,A} Different lower case letters in column, for each parameter, indicate significant differences due to the effect of storage time (at $P < 0.05$, based on Tukey HSD test); different upper case letters in row, for each parameter, indicate significant differences due to the effect of packaging type (at $P < 0.05$, based on Tukey HSD test). Absence of letters indicates absence of significant differences.

Table 2. Changes in textural parameters of differently packed durum wheat bread samples (TF1 = thermoformed 1; TF2 = thermoformed 2; FP = flow-pack) during 90 days of storage. The table also reports the parameters (k = kinetic constant; n = Avrami exponent; F_∞ = limiting value of firmness at infinite time) resulting from the best-fit of Avrami equation to firmness data, as well as the parameters (k = kinetic constant; C^0 = initial value of the descriptor; C^∞ = value of the descriptor at infinite time) resulting from the best fit of a first-order kinetic model to resilience, springiness and chewiness data.

Storage time (days)	**TF1**	**TF2**	**FP**	**TF1**	**TF2**	**FP**
	Firmness (N)			*Resilience*		
0	22.17±1.30^{a}	22.17±1.30^{a}	22.17±1.30^{a}	0.91±0.02^{c}	0.91±0.04^{c}	0.91±0.03^{c}
7	31.47±2.28^{bA}	46.46±2.95^{bB}	49.08±3.07^{bB}	0.89±0.01^{cB}	0.80±0.02^{bA}	0.78±0.06^{bA}
15	58.96±4.68^{c}	60.51±2.76^{c}	63.62±0.17^{c}	0.79±0.02^{b}	0.75±0.06^{ab}	0.74±0.02^{b}
30	74.88±4.72^{dA}	82.98±2.04^{dB}	90.69±3.51^{dC}	0.77±0.04^{bB}	0.75±0.01^{abAB}	0.70±0.04^{abA}
60	79.28±3.18^{dA}	85.99±0.63^{dB}	113.02±4.28^{eC}	0.77±0.04^{b}	0.72±0.06^{ab}	0.68±0.05^{ab}
90	97.05±4.21^{eA}	99.91±4.00^{eA}	114.69±4.14^{eB}	0.68±0.03^{a}	0.68±0.01^{a}	0.64±0.05^{a}
k ($\times 10^{-2}$)	3.38±1.96	6.44±2.01	2.32±0.63	3.40±1.22	9.35±2.47	8.82±2.18
n or C^0	1.07±0.20	0.88±0.12	1.16±0.09	0.91±0.02	0.90±0.02	0.90±0.02
F_∞ or C^∞	92.34±4.31	99.36±4.24	117.17±2.21	0.70±0.03	0.71±0.01	0.66±0.01
	Springiness (mm)			*Chewiness (N mm)*		
0	4.53±0.90^{a}	4.53±0.91^{a}	4.53±0.20^{a}	91.38±5.41^{a}	91.38±4.79^{a}	91.38±7.81^{a}
7	4.68±0.54^{aA}	6.46±0.22^{bB}	6.77±0.80^{bB}	98.97±3.46^{aA}	178.42±5.78^{bB}	255.67±7.69^{bC}
15	5.73±0.52^{abA}	6.80±0.17^{bB}	7.28±0.12^{bB}	207.72±7.73^{bA}	231.42±3.78^{cB}	257.05±5.43^{bC}
30	6.43±0.18^{b}	6.98±0.92^{b}	7.40±0.61^{b}	276.22±5.95^{cA}	353.71±7.84^{dB}	466.89±5.62^{cC}
60	6.73±0.74^{b}	7.23±0.10^{b}	7.47±0.32^{b}	305.23±6.17^{dA}	333.85±5.55^{eB}	574.56±6.82^{dC}
90	7.05±0.40^{bA}	7.55±0.36^{bAB}	7.64±0.21^{bB}	352.62±6.32^{eA}	383.93±2.24^{fB}	620.89±2.21^{eC}
k ($\times 10^{-2}$)	4.01±1.48	15.30±4.50	19.50±5.60	3.56±0.54	5.65±0.65	3.19±0.38
C^0	4.37±0.26	4.56±0.28	4.53±0.27	74.88±10.27	87.11±10.52	101.32±14.56
C^∞	7.10±0.32	7.24±0.16	7.49±0.15	356.62±14.42	372.93±9.30	655.91±23.86

^{a,A} Different lower case letters in column, for each parameter, indicate significant differences due to the effect of storage time (at $P < 0.05$, based on Tukey HSD test); different upper case letters in row, for each parameter, indicate significant differences due to the effect of packaging type (at $P < 0.05$, based on Tukey HSD test). Absence of letters indicates absence of significant differences.

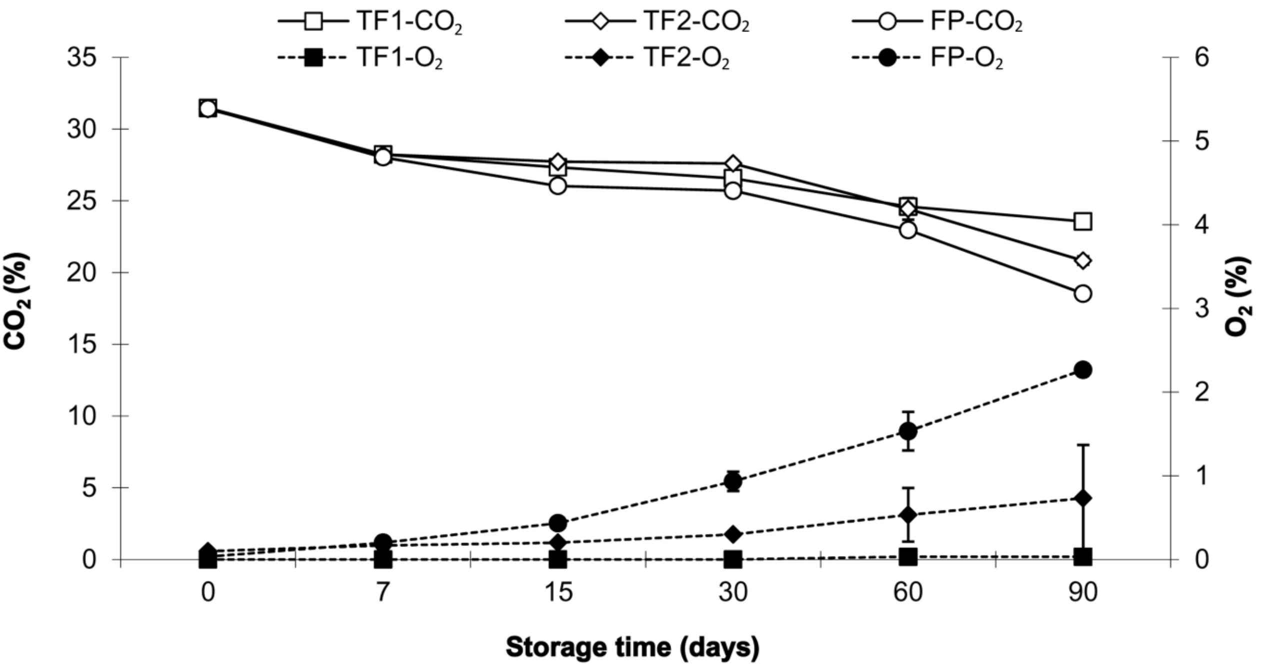

Figure 1

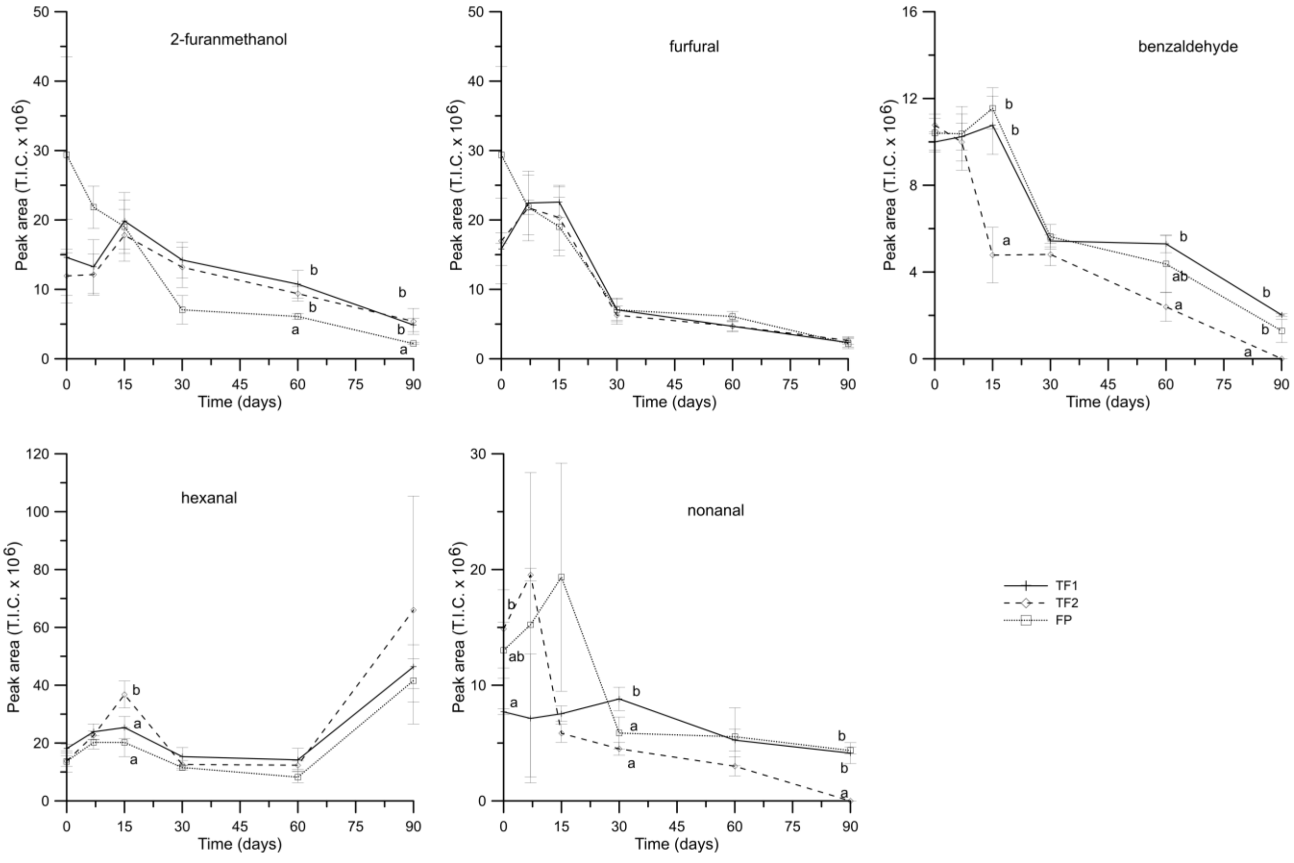

Figure 2

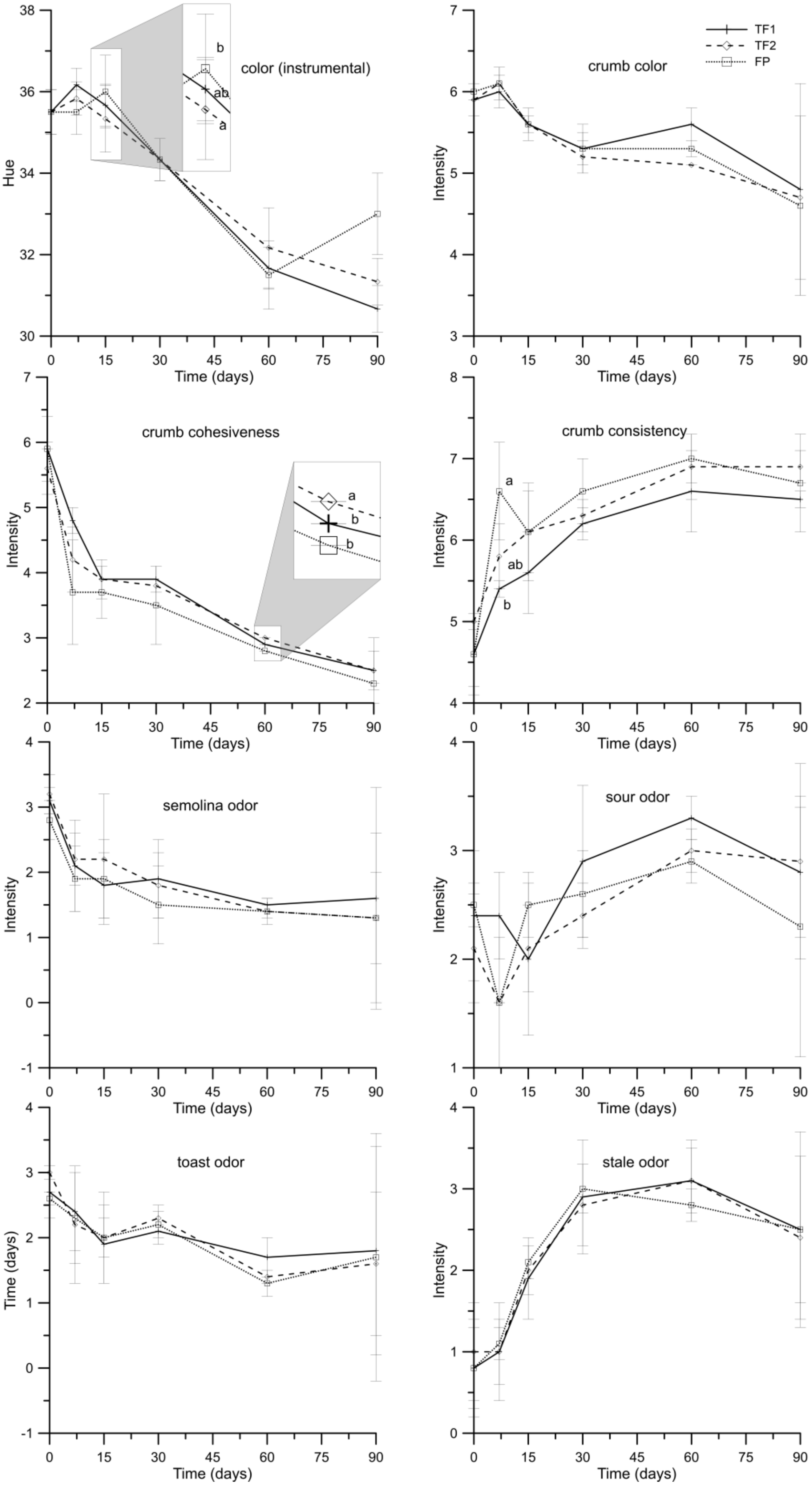
color (instrumental)
Hue
Time (days)
b
ab
a
crumb color
Intensity
TF1
TF2
FP
crumb cohesiveness
a
b
b
crumb consistency
a
ab
b
semolina odor
sour odor
toast odor
Time (days)
stale odor
0
15
30
45
60
75
90

Figure 3

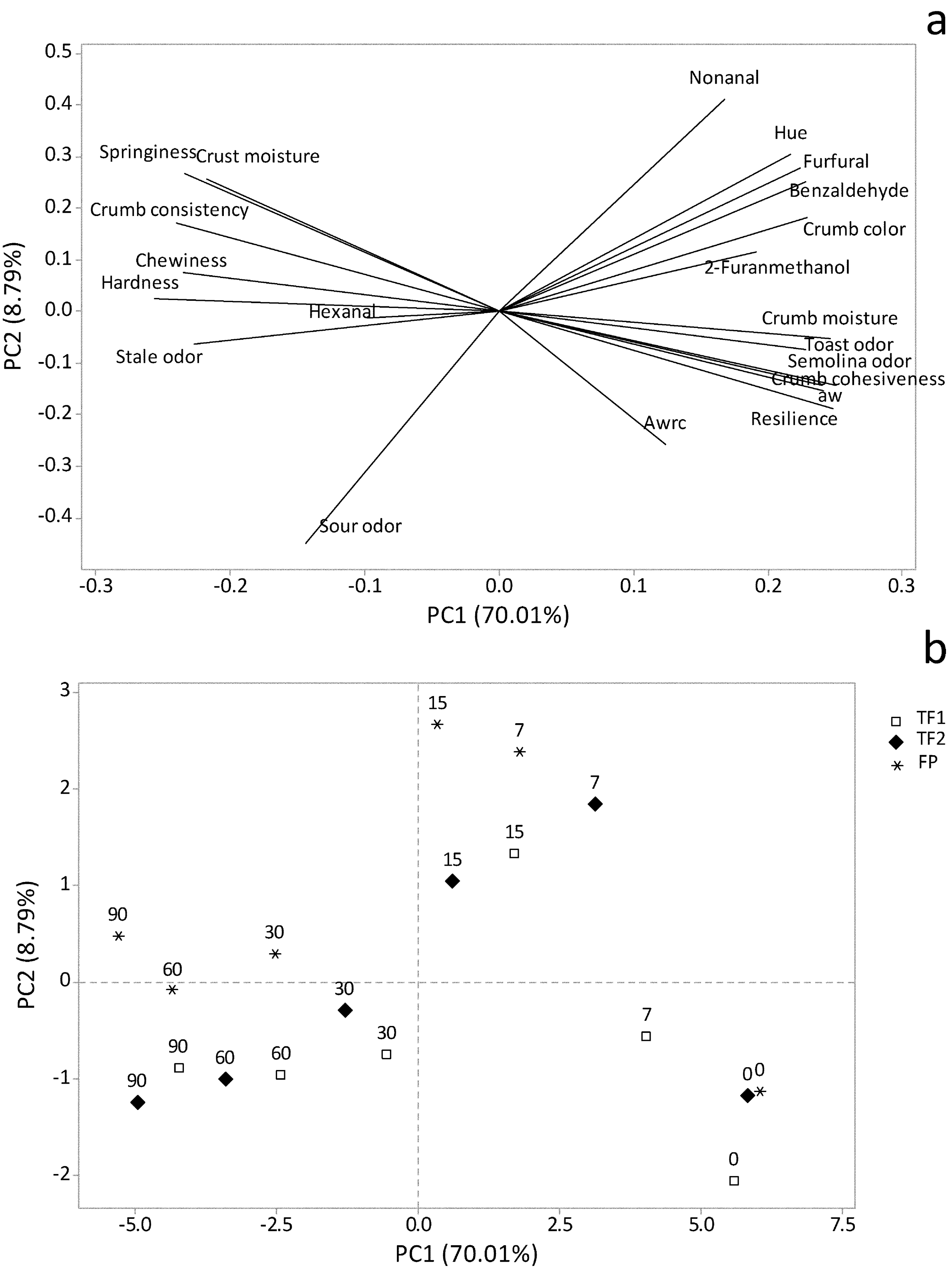
a
Nonanal
Hue
Furfural
Benzaldehyde
Crumb color
2-Furanmethanol
Springiness
Crust moisture
Crumb consistency
Chewiness
Hardness
Hexanal
Stale odor
Crumb moisture
Toast odor
Semolina odor
Crumb cohesiveness
aw
Resilience
Awrc
Sour odor
PC2 (8.79%)
PC1 (70.01%)
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
b
TF1
TF2
FP
15
7
7
15
15
90
30
60
30
30
90
60
60
90
7
0
0
0
PC2 (8.79%)
PC1 (70.01%)
3
2
1
0
-1
-2
-5.0
-2.5
0.0
2.5
5.0
7.5

Figure 4