Effect of Oxygen-Absorbing Packaging on the Shelf Life of a Liquid-Based Component of Military Operational Rations

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ABSTRACT: Oxygen within the sealed package can reduce the quality of liquid-based food products with high oil content such as hot-filled meal-ready-to-eat (MRE) cheese spread, a component of military operational rations. The aim of this study was to test a novel oxygen absorber-containing laminate material and its ability to maintain and/or extend shelf life of a cheese-spread MRE item. An iron-based oxygen absorber (ABSO₂RB®) activated by moisture was incorporated into the laminate and used to pack hot-filled cheese spread MREs. The kinetics of oxygen absorption due to humidity and temperature were characterized and peel tests performed to ensure pouch seal integrity. Accelerated shelf-life tests of ABSO₂RB and regular MRE pouches without the O₂-absorber were conducted for 3 mo at 51.7 °C (125 °F), and 6 mo at 37.8 °C (100 °F) by measuring oxygen concentration (Mocon O₂-analyzer), microbiological, and physicochemical quality characteristics, including color, texture, moisture, free fatty acid (FFA), pH, water activity, and vitamins and A. Pouches stored at 26.7 °C (80 °F) for 12 mo served as calibrated controls. Consumer tests were conducted in-house and a confirmatory sensory test was conducted at Natick by a trained panel using a 9-point hedonic scale. ABSO₂RB-laminates maintain the same seal integrity and strength as those of the control samples. The headspace oxygen concentrations in these pouches reached ($P < 0.05$) $0.5\%$ in 11 d of storage at 26.7 °C (80 °F) and remained below this level throughout the storage period (1 y). No microbial growth (aerobic, coliforms, yeast, and molds) was detected ($P < 0.05$) for both packages. Overall, the ABSO₂RB-pouches indicate an improved reduction in oxygen and vitamin C retention compared with MRE controls and maintained product quality (physicochemical and organoleptic). ABSO₂RB-laminates met the accelerated shelf-life requirement of 1 mo at 51.7 °C (125 °F), and 6 mo at 37.8 °C (100 °F). This study clearly shows the benefits of using active packaging technology in retaining nutrition and prolonging shelf life of high-fat, liquid content MRE items.

Keywords: active packaging, headspace, laminate, oxygen absorber, rancidity

Introduction

High levels of oxygen present in food packages may facilitate the growth of yeast, molds, and aerobic bacteria, off-flavors and off-odors development, color change, and nutritional losses, thereby causing significant reductions in the shelf life of foods. Therefore, the control of oxygen levels in food packages is important to limit the rate of these deteriorative and spoilage reactions in foods. Rancidity is caused when oxygen combines with unsaturated fatty acids. In addition, several moist food items in MREs are subject to nonenzymatic browning reactions. This type of degradation is facilitated by the presence of oxygen within the package and it could be reduced by packaging sensitive food items in oxygen-absorbing packaging material. Active packaging technologies provide a means to address this problem with those designed to scavenge oxygen being the most used for food applications (Charles and others 2006).

Oxygen-absorbing systems provide an alternative to vacuum and gas flushing packaging to improve product quality and shelf life. Furthermore, they are economically viable in reducing packaging costs and increasing profitability (Ozdemir and Floros 2004). Such technology has been successfully applied to a wide variety of foods including meat products, fresh pasta, fruits, dairy and nuts, among others (Rooney 1995; Vermeiren and others 1999; Coma 2008). The purpose of an oxygen scavenger is to create a low oxygen atmosphere in sealed packs of the product, thereby slowing or preventing deterioration through oxidation and/or growth of microorganisms. It allows the reduction of oxygen concentration to values lower than 0.01%, and since it simplifies the process and reduces the cost of equipment; it could be advantageous compared with modified atmosphere packaging including vacuum packaging (Alvarez 2000).

Most oxygen scavengers in commercial use today are iron-based systems, but they can also be based on catechol, ascorbic acid, and its analogues, or unsaturated hydrocarbons and polyamides, mostly in the form of sachets inserted into the package (Smith and others 1990; Vermeiren and others 1999, 2003; Brady and others 2001). The incorporation of scavengers in packaging films is a better way of resolving sachet-related problems. Oxygen-absorbing sachets are commonly used in dry bakery products but are impractical in liquid suspensions where the sachet may become immersed into the food product. This complication is eliminated by imbedding the oxygen-absorbing material within the structure of the packaging material. By incorporating an oxygen-absorbing material in the product contact layer, contamination of a product by...
leakage from a sachet will not occur. This approach also eliminates the risk of ingestion by consumer (Graff 1998). However, it is possible for the active agent to migrate from the film into the product. Oxygen-scavenging films also offer potential cost savings due to increased production efficiency and convenience. Scavengers may either be imbedded into a solid, dispersed in the plastic, or introduced into various layers of the package, including adhesive, lacquer, or enamel layers (Rooney 1995; De Kruijf and others 2002).

Shelf stability is critical because the military requires that MRE foods be stable for a minimum of 3 y without refrigeration at 26.7 °C (80 °F). The unitized group ration (UGR) requirement is at least 18 mo at 26.7 °C. When a change in food formulation or in packaging occurs, further studies on shelf life and stability have to be carried out. In fact, these changes could affect chemical, physical, and nutritional characteristics of the considered food. Hence the present study was undertaken to evaluate the effect of the oxygen-absorbing laminate on the shelf life of MRE cheese spread in terms of microbiological, physical, chemical, and sensory characteristics during storage. Cheese spread is particularly sensitive to this type of degradation and it was chosen as the food item to test this preservation technique.

Materials and Methods

Food material

MRE cheese spread was packaged by the PortionPac plant in Stone Mountain, Ga., U.S.A. with samples in ABSO2RB®-laminates and controls in regular MRE packaging film. Pouch dimensions were 35.56 × 15.24 cm (14 × 6 in) with an area of 542 cm² (84 in²). This product was hot filled at 76.7 to 82.2 °C (170° to 180 °F). A total of 600 samples (42.5 g each) were shipped to Texas A&M Univ. for testing based on the performance requirements following the specifications of the Packaging Requirements and Quality Assurance Provisions documents for plain cheese spread, Performance-Based Contract Requirements or PCRs: (1) shelf life of 36 mo (UGRs and MRES) at 26.7 °C (80 °F) (PCR-C-039) and (2) palatability and general acceptance must meet approved product standard characteristics (PCR-C-039).

Oxygen-absorbing packaging material

The laminate was purchased from Cadillac Products Packaging Co. (Troy, Mich.) who then manufactured the pouches for packaging of the MRES. The structure consisted of 48 gauge PET/10 lbs per ream PE/0.35 mil-inch aluminum foil per 3 mil ABSO2RB sealant. The ABSO2RB sealant is a blend of low-density polyethylene (LDPE) and linear LLDPE (polyolefins) with an iron-based oxygen absorber that is water activated. Water reacts with the oxygen to create hydroxide ions that react with the ferrous ions to produce iron (II) hydroxide. The iron (II) hydroxide quickly oxidizes into iron (III) oxide-hydroxide in the presence of oxygen (Vermeiren and others 1999). In short, it is a trilayer coextrusion that contains both PE and iron-based oxygen absorber. However, the food contact layer consists entirely of PE. The structure of the laminate film is illustrated in Figure 1. The laminate was opaque.

A series of analyses were performed on the new oxygen absorber material in pellet form and its influence on food microbial and physichochemical quality to confirm that the material could indeed help maintain MRE cheese spread shelf life.

Optical microscopy investigation of laminate material

Transmitted optical microscopy (TOM) was used to characterize the laminate structure of the oxygen-absorbing packaging films. The film was cut, cleaned, and embedded in an epoxy resin. After curing at room temperature, the epoxy block with the films embedded in the middle was sectioned using an Ultracut E microtome and a Microstar diamond knife. A thin section (approximately 40 μm in thickness) was then collected in a medium of immersion oil and secured between 2 glass slides. The thin section was examined using an Olympus BX60 optical microscope (Olympus America Inc., Center Valley, Pa., U.S.A.) under transmission mode.

Pouch peel testing

Peel testing was performed on the seam of the reference pouch and oxygen absorber-containing pouches stored at room temperature and those aged at 51.7 °C (125 °F) for 60 h, respectively. An aging time of 60 h at elevated temperature was chosen to assess the integrity of the pouch films. It has been shown that the oxygen absorber will complete its reaction within 60 h. The tests were conducted using an Instron machine (Model 4411) at room temperature. The testing rate was 5.08 mm/min. Peel strength was obtained based on at least 4 specimens per sample. The T-peel tests were done on the actual pouches that have a typical sealed width of 0.254 cm (0.1 in). As a result, the test was done on a sealed area of 2.54 × 0.254 cm (1 × 0.1 in). The rest of the testing condition and preparation follow that of the ASTM standard F-88 (ASTM 2007). Average values and standard deviations have been reported.

Shelf-life studies

The content of each sample unit (1 pouch) was evaluated for appearance, odor, flavor, texture, film integrity, chemistry, microbiological, and overall quality (sensory) for the duration of the 3 different storage studies, which consisted of (1) 3 mo at 51.7 °C (125 °F), (2) 6 mo at 37.8 °C (100 °F), and (3) 12 mo at 26.7 °C (80 °F) with constant relative humidity (65% to 75%). Sampling intervals consisted of (1) 1, 2, 3, 4, and 6 wk at 51.7 °C (125 °F), (2) 1, 3, and 6 mo at 37.8 °C (100 °F), and (3) 1, 6, and 12 mo at 26.7 °C (80 °F). Each test performed consisted of 3 replications with 3 replicates per treatment (that is, storage temperature and time).

Headspace analysis. Oxygen concentration inside the pouches was measured throughout storage using a Mocon Toray oxygen analyzer model LC700F (Toray Engineering Co., Chuo-ku, Tokyo, Japan). The pouches were centrifuged at 1000 × g for 10 min (Alleg- gra 25R centrifuge, Beckman Coulter Inc., Fullerton, Calif., U.S.A.). Next, internal gases were withdrawn throughout a rubber septa placed in 1 side of the pouch using a 1-mL syringe. The withdrawn gases (1 mL) were immediately injected into the O₂ analyzer. Prior to sample injection, the O₂ analyzer was calibrated with air samples. Determinations were made in quintuplicate. Gas headspace samples were collected from new pouches on a daily basis from the day the pouches arrived until oxygen concentrations stabilized. After that, data points were collected on a monthly basis depending on the shelf-life study.

Microbial analysis. Total aerobic count, coliform count, Escherichia coli, yeast and molds, and Lactobacillus spp. were carried out using standard procedures (AOAC 1998c,d,e,f,g,h). Briefly,
the contents of 3 cheese spread pouches for each treatment were placed in sterile stomacher bags and mixed thoroughly. Ten grams of sample were transferred to a new sterile stomacher bag and 90 mL of buffered peptone water were added. The mixture was homogenized for 1 min. Serial dilutions were made using buffered peptone water. Total aerobic count, coliform count and Escherichia coli, and yeast and mold populations were determined using microbiologic plate count plates, yeast and mold count plates, E. coli/coliform count plates petrifilm plates (3M Petrifilm, 3M Microbiology Products, St. Paul, Minn., U.S.A.) in duplicate, respectively. Plates were incubated at 35 °C for 48 h for aerobic plate counts, for 24 h for coliform, for 48 h for E. coli, and at 25 °C for 5 d for yeast and molds. Lactobacilli spp. populations were determined using procedures recommended in the APHA Compendium (Smittle and Cirigliano 1992) using Lactobacillus-selective MRS agar (Man, Rogosa, and Sharp) plates and incubating at 25 °C in a CO2 enriched atmosphere for 7 d, in duplicate. Microbial counts were expressed as the number of viable bacterial colonies per gram (CFU/g).

Product quality attributes

Color. Changes in cheese spread color were assessed using a Labscan XE (16437) colorimeter (HunterLab, Inc., Reston, Va., U.S.A.) with the CIELAB system with measuring aperture diameter of 56 mm, and illuminant/viewing geometry of D65/10°. The colorimeter was calibrated using the standard white and black plates. Three pouches were used for each treatment and 3 readings were made on each pouch content. The mean values were used to determine the color coordinates L* (lightness – darkness), a* (redness – greenness), and b* (yellowness – blueness).

Texture (spreadability). Sample spreadability was measured with a texture analyzer (TA.XT2i, Texture Technologies Corp., Scardale, N.Y., U.S.A.) equipped with a spreadability rig (TA-425 TTC) consisting of a set of precisely matched male and female acrylic 90° cones. The cheese spread was filled into the lower cones, flattened with a spatula, and then positioned in the base holder for testing. The test involved traveling 24 mm from a fixed position 25 mm over the bottom of the lower cone. The final gap between the 2 cones was precisely 1 mm. Test speed was 3 mm/s. The Texture Expert software program recorded the maximum force (N) to spread the samples. Fifteen measurements were performed for each treatment (ABSO2RB and regular MRE pouches) under different temperatures. Samples were allowed to equilibrate to room temperature (approximately 21 °C) prior to testing.

Product weight. The average net weight of the cheese spread samples was measured throughout the entire shelf-life study to ensure the samples would meet weight product requirements. No individual pouch shall have a net weight of less than 39.69 g (PCR-C-039 2006). The cheese spread pouches from each treatment (ABSO;RB and regular MRE pouches) were weighed in an analytical balance (Sartorius analytic AC 210s, Sartorius Corp., N.Y., U.S.A., ± 0.0001 g). The average weight of the packaging film alone was subtracted to get the net weight of the pouches. Readings were done in quintuplicate.

Moisture content and water activity. To meet specifications, moisture content of cheese spread cannot be less than 38% and not greater than 42% (PCR-C-039 2006). Approximately 5 g of samples were weighed and dried at 60 to 65 °C (≤ 13.3 kPa) to a constant weight (for about 10 to 12 h) in a vacuum oven (Squared Lab Line Instruments, Melrose Park, Ill., U.S.A.) following the AOAC method 930.04 (AOAC 1990a). After comparison and standardization with the AOAC method (standard), moisture content was determined by microwave drying using the CEM SMART TRAC™ System 5 moisture analyzer (CEM Corp., Matthews, N.C., U.S.A.). Water activity monitoring is important since the O2-absorbing compounds are activated by moisture present in the packaging headspace. Water activity was monitored using a Rotronic Hygroskop DT (model DT-2, Rotronic Instruments Corp., Huntington, N.Y., U.S.A.) connected to a water bath (Haake F3 Fisons, Thermo Fisher Scientific, Newington, N.H., U.S.A.) at 20 °C. Samples were placed in a plastic sample holder and loaded into the equipment. Readings were recorded after the system reached equilibrium (approximately 30 min). Measurements were made in triplicates.

Fat content. The fat content (%) of the cheese spread samples was determined by microwave drying using the CEM SMART TRAC™ System 5 moisture analyzer (CEM Corp., Matthews, N.C., U.S.A.) followed by NMR reading of the dried samples (Smart system 5 ProFat™ analyzer, CEM Corp.). Three cheese spread pouches per treatment were analyzed throughout storage time.

pH. The AOAC method 981.12 (AOAC 1998a) was followed to record the pH using a digital pH meter (Corning model 350 pH/ion analyzer Corning, Inc., N.Y., U.S.A.) standardized to pH of 4, 7, and 10 buffers. Samples consisted of the content of 1 cheese spread pouch. Three measurements were performed for each treatment (ABSO;RB and regular MRE pouches under different temperatures) and the analysis was performed in triplicate throughout storage time.

Free fatty acid (FFA). This value was used as an indicator of lipid rancidity though there are other factors responsible for the occurrence of rancidity in cheese, including the action of enzymes. FFA was measured according to AOAC official method 940.28 (AOAC 1990b). Fat was extracted from cheese spread samples by first drying them under vacuum. The content of a pouch was distributed in an aluminum cup (approximately 5 g in each cup), weighed and dried at 60 to 65 °C (≤ 13.3 kPa) for about 10 to 12 h in a vacuum oven (Squared Lab Line Instruments, Melrose Park, Ill., U.S.A.). After drying, the samples were transferred to 250 mL Erlenmeyer and 50 mL of petroleum ether were added. Samples were stored for 6 h at room temperature in the dark. The petroleum ether was removed using a rotavapor (Heidolph Laborota 4001; Methrom U.S.A., Inc., Riverview, Fla., U.S.A.) at 40 °C. Subsequently, the extracted fat was weighed (approximately 3.5 g) and 50 mL of ethanol (previously neutralized) were added and the solution was mixed thoroughly. The mixture was then titrated with 0.01 N NaOH with vigorous shaking until permanent faint pink (2 mL phenolphthalein solution as indicator) appears and persisted for > 1 min. Results were reported as percent free fatty acids expressed as oleic acid, as this is the predominant fatty acid in cheese (Pearson 1971).

Vitamin C (ascorbic acid) content. Vitamin C content was monitored according to AOAC official method 985.33 (AOAC 1998b). Twenty grams (20 g) of cheese spread were homogenized with an immersion blender (400 Watt Immersion blender—kitchen selectives, Lenexa, Kans., U.S.A.) for 1 min with 100 mL of extracting solution (metaphosphoric acid–acetic acid solution). The homogenate was vacuum filtered (vacuum pump–KNF Neuberger, Trenton, N.J., U.S.A.) with qualitative paper (Whatman Nr 4; Whatman, Inc., Clifton, N.J., U.S.A.) and 10 mL of the filtered solution were titrated with 2,6-dichloroindophenol standard solution. The volume of titration was recorded and used to quantify vitamin C content of the sample. The indophenol solution was standardized by titrating an ascorbic acid standard solution (1 mg/mL) and sample blanks. Vitamin C content was expressed in milligrams of ascorbic acid per gram of sample on wet basis. Three repetitions with duplicates were performed throughout the shelf-life study.

Vitamin A content. Vitamin A content was determined according to the standard methods for the examination of dairy products.
method 15.160 (Hooi and others 2004). Briefly, 2 to 3 g of cheese spread sample were weighed and transferred to test tubes. After the samples were dissolved with 5 mL of 1% (w/v) pyrogallol (Sigma-Aldrich, St. Louis, Mo., U.S.A.) in ethanol, 2 mL of 50% (w/v) KOH (Sigma-Aldrich) in water were added, tubes were closed and mixed vigorously. Subsequently, the test tubes were placed in a water bath (S/P water bath, Baxter Healthcare Corp, Miami, Fla., U.S.A.) at 80 °C for 20 min with constant agitation to allow saponification. The saponified samples were placed in an ice-water bath to quickly cool down (approximately 30 min). Twenty milliliters of diethyl ether/petroleum ether (1:1) were added to the test tubes and mixed vigorously following the addition of 15 mL of cold distilled water.

To complete vitamin A extraction, the samples were centrifuged at 1000 × g for 10 min (Allegra 25R centrifuge, Beckman Coulter Inc.). Ten milliliters of the upper organic layer were collected and transferred to conical flasks. The solvents were evaporated to dryness using a rotavapor (Heidolph Laborator 4001, Brinkmann) and redissolved in 5 mL HPLC grade methanol and filtered through 0.2-μm PTFE filter (Acradisc CR 13-mm syringe filter, Pall Life Sciences, East Hill, N.Y., U.S.A.). An aliquot of 100 μL of this solution was injected into the HPLC system. The HPLC system and HPLC conditions were a high performance liquid chromatograph (Dionex, Germering, Germany) equipped with a P800 pump, FDA-100 photodiode array detector set up at 325 nm, an ASI-100 automated sample injector, and Chromeleon 6.5 software (Dionex). The column was a Supelcosil LC-18, 250 × 4.6 mm, C18, 5 μm particle size (Supelco, Bellefonte, Pa., U.S.A.) with a C18 guard column, 5 μm, 20 × 4 mm, LC-18 SupelGuard (Supelco). The mobile phase consisted of methanol:water (95:5), isocratic with a flow rate of 1 mL/min. All-trans-retinol (Sigma) was used as standard (2 μg injected into the column, retention time: 7.30 min) following the same procedures used to prepare the samples. Throughout the whole procedure samples were protected from light exposure. Analysis was made with 3 repetitions and 2 replicates.

Sensory analysis

The cheese spread samples (ABSO2RB and regular MRE pouches) stored at 26.7 and 37.8 °C were evaluated in terms of color, odor, texture, flavor, and overall quality throughout storage. Two pouches from each treatment were placed in covered glass containers labeled with a random 3-digit number and presented to each panelist at once for a total of 4 samples. A minimum of 30 panelists, consisting of students, staff and faculty at Texas A&M Univ. formed the untrained, consumer test panel. Evaluation was conducted in a well-equipped taste panel booth. Panelists were asked to evaluate the samples and indicate their preferences using a 9-point hedonic scale as described by Meilgaard and others (1999). A score of 1 represented attributes most disliked and a score of 9 represented attributes most liked. Scores higher than or equal to 5 were considered acceptable.

A parallel sensory study was conducted at U.S. Army Natick Soldier Center by a trained panel (12 panelists) using a 9-point hedonic scale. The trained panelists evaluated the same parameters as the consumer panelists with the addition of samples stored at 4.4 °C (shelf life), and their interaction were evaluated. Differences between variables were tested for significance by one-way analysis of variance (ANOVA). Significant different means (P ≤ 0.05) were separated by the Tukey test.

Statistical analysis

Data analysis was performed using SPSS software for Windows, v. 11.5.1 (SPSS 2002). The effect of packaging type, length of storage (shelf life), and their interaction were evaluated. Differences between variables were tested for significance by one-way analysis of variance (ANOVA). Significant different means (P ≤ 0.05) were separated by the Tukey test.

Results and Discussion

Film oxygen-absorbing capability

Prior to the testing of the oxygen-absorbing capability of ABSO2RB film, the oxygen absorption kinetics of the oxygen absorber-containing material in pellet form was first characterized at temperatures ranging from 25 to 65 °C (77 to 149 °F) and relative humidity (RH) from 75% to 100%. The results show that both temperature and relative humidity can significantly affect the oxygen absorption rates. At temperatures ranging from 25 to 45 °C (77 to 113 °F), the oxygen absorption rates increase as temperatures increased at fixed RH (0.184 O2/h for 25 °C, 0.534% O2/h for 35 °C, and 0.948% O2/h for 45 °C under 100% RH; 0.711% O2/h for 25 °C, 0.890% O2/h for 35 °C, and 0.990% O2/h for 45 °C under 75% RH). At RH ranging from 75% to 100%, the oxygen absorption rates decrease as the RH is increased at a fixed temperature. Further increase in temperature to 65 °C (149 °F) will dramatically inhibit the oxygen absorption rates. It is hypothesized that high temperature leads to high vapor pressure, thus limiting the oxygen absorption reaction.

The activation energy for the oxygen absorption was also estimated at different RH using the Arrhenius equation \( \ln(k) = \ln(k_0) - \frac{E_a}{R T} \), where \( k \) is the oxygen absorption rate, \( k_0 \) is the preexponential factor, \( E_a \) is activation energy, \( R \) is gas constant, and \( T \) is absolute temperature. The results show that for 75% and 100% RH, the \( E_a \) are 13.1 and 64.8 J/mol, respectively. The above data clearly indicate that lower RH leads to lower activation energy and high absorption rate. Therefore, the oxygen-absorbing materials chosen in this study would perform better at lower temperature and lower RH. The optimal condition is found to be at 45 °C (113 °F) and 75% RH. The above findings are useful as guidance for better understanding and design of the ABSO2RB for pouch laminate applications.

Figure 2 shows the change in O2 concentration for the 2 types of packages, ABSO2RB and regular MRE pouches. Both packaging materials showed an exponential decay of oxygen concentration with time. Major changes in headspace gas composition occurred in the pouches containing the O2 scavenger (ABSO2RB) in the first days of storage at room temperature with these pouches reaching equilibration of the atmosphere at a faster rate. Within 11 d of storage, the oxygen concentration in the headspace of the ABSO2RB laminate was below 1% and remained below this level throughout the whole storage period (1 y). Oxygen concentration in the regular MRE pouches decreased by 50% during the first 15 d and remained stable down to a concentration of 5%. The oxygen decreased in the regular packaging because the oxygen reacted with the food. Thus the purpose of the oxygen-absorbing packaging is to remove the oxygen before degrading reactions occur. This result supports the effectiveness of the O2-absorbing laminated evaluated in this study since we had data that demonstrated that oxygen depletion in the ABSO2RB pouches occurred considerably faster than in regular pouches. That is solid evidence that the laminate effectively absorbed oxygen. Such a trend was also observed with other foodstuffs (that is, fish) packed with O2 scavenger with iron-based system (Mohan and others 2008).

Film properties

Laminate structure. A TOM image of the cross section of the oxygen absorber-containing film is shown in Figure 3. A total of 6 layers can be clearly identified (PE, oxygen absorber-containing sealant, tie-layer, aluminum foil, pigment layer, and PET). The dark particles dispersed in the sealant layer are oxygen absorbers.
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Pouch peel testing. The T-peel testing reveals that aging at 51.7 °C (125 °F) does not deteriorate the integrity of the pouch that contains oxygen absorbers. The samples stored at room temperature and aged at 51.7 °C for 60 h have almost the same T-peel strength values (16 ± 0.6 and 16 ± 0.8 lbs, respectively). These T-peel strength values are the same as the reference sample that does not contain any oxygen absorbers.

Shelf-life studies

Microbial analysis. Results from microbial tests confirmed that all samples tested were commercially sterilized. Neither bacterial nor yeast and mold growth was observed throughout the shelf-life studies. The colony counts were below detection limit with EPC (estimated plate counts) less than 10 (data not shown). Thus, the cheese spread packed using the ABSO2RB-laminates meet the requirements of commercial sterility for operational rations (PCR-C-039 2006).

Product weight, moisture content, water activity, fat content, and pH. Both packaging materials (regular MRE and ABSO2RB) met the weight requirement during the storage period with average of 45.5 g. Similarly, both packaging materials met the moisture content specifications throughout storage time. Actually, no difference (P > 0.05) of moisture content was observed between packages for all shelf-life studies (average values of 40.53% and 40.27%, respectively). Although the samples stored at 51.7 °C had slightly increased values of water activity within time (final values of 0.925 ± 0.93 and 0.92 ± 0.68 for regular and ABSO2RB pouches, respectively), probably due to the exposure to high temperature, although there were no significant differences (P > 0.05) between the 2 types of packaging. The water activity of pouches stored at 37.8 °C for 6 mo was 0.925 ± 0.93 for regular MRE and 0.922 ± 0.93 for ABSO2RB pouches and for samples stored at 80 °F for 1 y was 0.9687 ± 0.93 for regular MRE and 0.9623 ± 0.98 for ABSO2RB pouches, respectively.

Fat content of cheese spread samples did not significantly (P > 0.05) change throughout the whole shelf-life study for either packaging material (regular MRE and ABSO2RB). Furthermore, the average fat content of cheese spread samples (40.84% ± 0.17) was in accordance to product requirements of fat content not less than 38% and not greater than 43% (PCR-C-039 2006). There was some variation on pH values during storage time, with no clear trend, possibly due to the effect of temperature than the packaging type. Overall, values of pH final for pouches stored at 51.7 °C changed from 5.66 to 5.518 ± 0.03 by the end of shelf life and from 5.62 to 5.57 ± 0.02 for regular and ABSO2RB pouches, respectively; the values for pouches stored at 37.8 °C for 6 mo ranged from 5.62 to 5.45 ± 0.05 for regular MRE and 5.64 to 5.52 ± 0.03 for ABSO2RB pouches.
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pouches. For samples stored at 26.7 °C for 1 y the pH ranged from 5.66 to 5.57 ± 0.03 for regular MRE and 5.66 to 5.59 ± 0.01 for ABSO2RB pouches, respectively. All samples were in accordance with product requirement during the whole storage period, where pH-value shall be not less than 5.5 and not greater than 5.9 (PCR-030:2006) (average values of 5.57 and 5.59 for control and ABSO2RB, respectively).

Color. The effect of packaging type and storage temperature on the color parameters (L*, a*, b*) of cheese spread is shown in Table 1. For samples stored at 51.7 °C, changes in color due to packaging were minimal, with time and storage temperature having the most significant effect. The L* values significantly decreased (darker samples) throughout storage for both packages. A similar trend was observed for samples stored at 37.8 °C, where changes were more due to the temperature and time than packaging type. The a* value showed the most variation (P < 0.05), though by the end of 6 mo these changes were not significant. After 1 y storage at 26.7 °C, the samples in pouches containing the O2-absorbing material were more yellowish and darker (P < 0.05) than those packed in the regular MRE pouches (average values of L*: 66.07 and 68.00; a*: 11.43 and 12.41; b*: 35.97 and 38.02, for regular MRE and ABSO2RB-laminates, respectively). These differences may be attributed to the inherent variability of samples during processing and packaging and were not perceived by the consumer panelists who gave the samples acceptable scores. Overall color values are in good agreement with consumer preferences (see Sensory Analysis section).

Texture. The changes in product spreadability due to packaging type and storage temperature are shown in Table 2. In general, the maximum force needed to spread the sample decreased throughout storage for both types of packages. However, differences among packaged samples were only pronounced in the pouches stored at 51.7 °C (P < 0.05). Within 1 y of storage at 26.7 °C, the spreadability of cheese spread packed in both regular MRE and ABSO2RB-laminates did not change (P > 0.05). Thus, storage temperature had a more drastic effect (P < 0.05) on cheese spreadability, as expected. These results are in good agreement with consumer preferences (see Sensory Analysis section).

Free fatty acid. For pouches stored at 51.7 and 38.8 °C, the FFA increased linearly (R² range of 0.971 to 0.985) with storage time (Figure 4). We can say that the samples packed in control MRE pouches had higher (P < 0.05) values of FFA than those packed in ABSO2RB laminates. After 1 y at 26.7 °C, the FFA content was approximately 0.70, still in the lower limit perceptible by consumers (objectionable odor or taste) of about 0.5% to 1.5% (Pearson 1971). This result was supported by the sensory evaluation scores (see Sensory Analysis section), indicating that oxidation, a well-established spoilage problem in fatty foods, can be controlled in some fashion by using the O2-absorbing laminate.

Vitamin C (ascorbic acid) content. For all storage temperatures, vitamin C content of the samples packed in O2-absorbing laminate was higher (P < 0.05) than for the controls throughout storage time (Figure 5). As expected, the lower the storage temperature, the slower the degradation rate. By the end of 1 y storage at 26.7 °C, and 6 mo at 37.8 °C, samples packed in ABSO2RB laminates had almost 1.5 times (47%) the amount of vitamin C content than the controls, respectively, indicating once again the effectiveness of the O2-absorbing laminate. It should be noticed that by the end of shelf life (week 4) at 51.7 °C, the vitamin C content in the samples packed in ABSO2RB laminates was still much higher. Samples were tested 2 wk later (week 6), and by that time degradation occurred with the concentration being the same as in with the regular MRE

| Table 1 — Effect of package type on color parameters (L*, a*, b*) of MRE cheese spread packed in control MRE and ABSO2RB® pouches during accelerated shelf-life studies (125 °F [51.7 °C] for 6 wk and 100 °F [37.8 °C] for 6 mo). Calibrated controls at 80 °C (26.7 °C) for 1 y. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| L*              | a*              | b*              | L*              | a*              | b*              | L*              | a*              | b*              |
| 51.7 °C time (wk) |                 |                 | 11.5* (0.15)    | 12.4* (0.05)    | 37.2* (0.29)    | 38.90* (0.23)   |
| 0               | 68.50 (0.19)    | 68.01 (0.23)    | 68.05 (0.19)    | 68.56 (0.28)    | 11.88* (0.106)  | 13.82* (0.49)   |
| 1               | 67.05 (0.94)    | 66.87 (0.84)    | 63.69 (0.30)    | 62.79 (1.47)    | 12.70* (0.16)   | 13.25* (1.12)   |
| 2               | 63.99 (1.05)    | 62.98 (0.026)   | 61.39 (0.42)    | 60.48* (0.70)   | 13.42* (0.16)   | 14.71* (0.87)   |
| 3               | 61.79 (1.72)    | 62.32* (0.26)   | 61.00 (1.19)    | 60.25 (0.09)    | 12.97* (0.13)   | 13.62* (0.94)   |
| 4               | 61.38 (1.37)    | 61.16* (1.08)   | 60.31 (0.15)    | 60.01 (0.12)    | 13.85* (0.01)   | 14.32* (0.11)   |
| 5               | 60.74 (1.72)    | 60.39* (0.06)   | 60.38 (0.30)    | 60.81* (0.23)   | 12.30* (0.14)   | 13.31* (0.04)   |
| 6               | 59.24 (1.72)    | 58.99* (0.06)   | 59.50 (0.19)    | 59.01* (0.12)   | 11.49* (0.07)   | 12.33* (0.04)   |
| 37.8 °C time (mo) |                 |                 | 11.5* (0.15)    | 12.4* (0.12)    | 37.2* (0.29)    | 38.90* (0.23)   |
| 0               | 68.50 (0.19)    | 68.01 (0.23)    | 68.67* (0.37)   | 69.38* (0.12)   | 11.49* (0.14)   | 12.33* (0.13)   |
| 1               | 64.24* (1.72)   | 65.39* (2.96)   | 64.24* (1.72)   | 65.39* (2.96)   | 11.79* (0.18)   | 13.99* (0.04)   |
| 3               | 61.38 (1.37)    | 61.16* (1.08)   | 61.38 (1.37)    | 61.16* (1.08)   | 12.34* (0.76)   | 13.51* (1.53)   |
| 6               | 60.74 (1.72)    | 60.39* (0.06)   | 60.38 (0.30)    | 60.81* (0.23)   | 12.30* (0.14)   | 13.31* (0.13)   |
| 26.7 °C time (mo) |                 |                 | 11.5* (0.15)    | 12.4* (0.12)    | 37.2* (0.29)    | 38.90* (0.23)   |
| 0               | 68.50* (0.19)   | 68.01 (0.23)    | 66.07* (0.62)   | 68.00* (0.67)   | 11.49* (0.17)   | 12.41* (0.11)   |
| 12              | 66.07* (0.62)   | 68.00* (0.67)   | 64.24* (1.72)   | 65.39* (2.96)   | 11.79* (0.18)   | 13.99* (0.04)   |

a,b Means within a column which are not followed by a common superscript letter are significantly different (P < 0.05). Numbers in parentheses are the standard deviation.
pouches. This may be attributed to the longer exposure to extreme storage temperatures.

Vitamin A content. Vitamin A content was maintained well during storage in control MRE and O₂-absorbing laminates. Only samples tested at 26.7 °C, for both types of packaging, showed reductions at the end of 1-y storage (from 6.16 ± 0.69 μg/g to 3.07 ± 0.46 μg/g for the control MRE pouches and from 5.68 ± 0.86 μg/g to 3.58 ± 0.08 μg/g for the O₂-absorbing pouches). Despite that, no differences in vitamin A content were found between packages throughout the whole storage period for all the temperatures tested.

Sensory analysis

Consumer testing. Color scores slightly changed throughout storage for samples stored at 26.7 and 37.8 °C, with samples from both packages showing high acceptance levels (scores ≥ 5) (Figure 6). These results are similar to the study conducted by Ross and others (1997) when investigating color measurements as a method of assessing ration quality during storage. They found out that color parameters varied consistently for cheese spread samples under different storage conditions, and that L-values showed the highest correlation with consumer scores.

Odor scores had high acceptance levels throughout storage and no differences (P < 0.05) were found between packages and storage temperature during the entire shelf-life study (Figure 6). This result suggests that the consumers were not able to detect differences in cheese spread odor among treatments. For texture scores, a slight decrease in acceptance was observed for samples stored at 37.8 °C during storage for both types of packages, although the acceptability was well above 5 for control and ABSO₂RB samples (Figure 6). Results are in good agreement with measurements of spreadability

| Table 2 — Effect of package type on texture (spreadability force in Newton) of MRE cheese spread packed in control MRE and ABSO₂RB pouches during accelerated shelf-life studies [125 F (51.7 °C) for 6 wk and 100 F (37.8 °C) for 6 mo [24 wk]]. Calibrated controls at 80 °C (26.7 °C) for 1 y [24 mo]. |
|---|---|---|---|---|---|---|
| Time (wk) | MRE @ 51.7 °C | ABSO₂RB @ 51.7 °C | MRE @ 37.8 °C | ABSO₂RB @ 37.8 °C | MRE @ 26.7 °C | ABSO₂RB @ 26.7 °C |
| 0 | 422.82a | 430.51a | 422.82a | 430.51a | 422.82a | 430.51a |
| 1 | 415.67a | 368.43a | 405.71a | 398.53a | 422.82a | 430.51a |
| 2 | 251.10b | 252.82b | 13.40b | 18.36b | 11.40a | 12.52a |
| 3 | 263.45b | 243.53b | 251.79b | 246.70b | 414.32c | 421.41c |
| 6 | 81.10d | 52.82d | (3.83) | (8.34) | (15.50) | (19.81) |
| 12 | 285.78c | 199.18c | (21.08) | (65.08) | (33.25) | (45.78) |
| 24 | 236.62c | 238.69c | (1.08) | (4.45) | |
| 48 | 401.43c | 463.78c | |

Means within a column which are not followed by a common superscript letter are significantly different (P < 0.05). Numbers in parentheses are the standard deviation.

Figure 4 — Effect of package type on development of rancidity (free fatty acid as percent oleic acid) of MRE cheese spread packed in control MRE and ABSO₂RB pouches during accelerated shelf-life studies [51.7 °C (125 F) for 6 wk; □ MRE, ○ ABSO₂RB; 37.8 °C (100 F) for 6 mo; ♦ MRE, ▼ ABSO₂RB; calibrated controls at 26.7 °C (80 F) for 1 y; ♦ MRE, ○ ABSO₂RB].
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with no significant difference in acceptability between treatments at 26.7 and 37.8 °C and a slight decrease ($P > 0.05$) in acceptance within time for samples stored at 37.8 °F. After the end of storage for samples at 26.7 and 37.8 °C the texture was still under specifications (smooth, homogenous, and easily spreadable) (PCR-C-039 2006).

When flavor was scored, all treatments were highly acceptable and only slight changes were observed throughout time. No significant difference ($P > 0.05$) in flavor was detected by the panelists. Similar trend was observed for overall quality scores (Figure 6). For samples stored at 26.7 °C, odor, flavor, and overall quality sensory attributes did not show ($P > 0.05$) significant changes between treatments (control and ABSO2RB) throughout the 12-mo storage period. These consumer acceptability results indicate that cheese spread samples packed in ABSO2RB pouches were rated at par with those packed in control MRE pouches and for most of the study length consumers could not detect significant differences among treatments.

Sensory test using a trained panel. Results of the sensory analysis conducted at the U.S. Army Natick Soldier Center are summarized in Figure 7. These results confirmed the acceptance of the products packaged in ABSO2RB pouches with all samples with scores above acceptability (> 5) and only a slight difference among treatments throughout storage.

**Figure 5** — Effect of package type on vitamin C (mg ascorbic acid/g) retention in MRE cheese spread packed in control MRE and ABSO2RB® pouches during accelerated shelf-life studies. (51.7 °C [125 °F] for 6 wk: •MRE, ○ABSO2RB; 37.8 °C [100 °F] for 6 mo: ▼MRE, ▽ABSO2RB; calibrated controls at 26.7 °C [80 °F] for 1 y: ♦MRE, ♠ABSO2RB).

**Figure 6** — Sensory test results for MRE cheese spread stored at 26.7 °C (80 °F) and 37.8 °C (100 °F) for 6 mo. There were a total of 30 consumer panelists. Scores were given based on a 9-point hedonic scale. Error bars represent standard deviation. Calibrated controls at 26.7 °C (80 °F) for 1 y. **Means with different superscript letters are significantly different ($P < 0.05$).**
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Conclusions

This study showed that the proposed O₂-absorbing laminate was efficient in reducing headspace oxygen concentration by 67.44% (from 20.4% to 6.82%) within 24 h. This active packaging material significantly reduced rancidity in cheese spread samples. In addition, the laminate helped delay the vitamin C decay, samples had high acceptable sensory characteristics throughout the whole shelf-life study and rated at par when not above with standard sample with respect to the sensory, physical, chemical, and microbiological characteristics. Samples also met shelf life the requirement of 6 mo at 37.8 °C (100 °F). Therefore, pouches containing O₂ scavenger in the laminate can help retain nutrition and extend shelf life of high-fat, liquid-like products.

Future research is recommended in other types of food products where oxygen could induce detrimental characteristics on the food. This study may be expanded to include other MRE and UGR items including retorted products.

Acknowledgments

The authors wish to thank Dr. C. Meyer and Ayal Shahar, Cadillac Products Packaging Co., for manufacturing the pouches and providing technical information regarding the laminate material. The authors also thank Dr. Z. Nikolov, Biological and Agricultural Engineering, and Drs. J. Keeton and R. Miller, Dept. of Animal Science, Texas A&M Univ., for allowing us to use their lab facilities and equipment to conduct HPLC analysis (vitamin A), fat and moisture content and sensory analysis, respectively. Thanks are also due to Dr. Susan Woodrad, Biological and Agricultural Engineering, for her assistance with procedures for nutrient analysis. Our deepest gratitude also goes to those who volunteered to carry out the sensory analysis and the students of the Food Engineering laboratory for their help with the experiments. We also thank Mr. Bob Ripp, PortionPac, for production and packaging of the samples. This study was funded by CORANET II (Combat Ration Network for Technology Implementation) as Short Term Project STP2021.

References


Figure 7 – Sensory analysis test results for MRE cheese spreads after 1 y of storage at 26.7 °C (80 °F) conducted at the U.S. Army Natick Soldier Center. There were a total of 12 trained panelists. Scores were given based on a 9-point hedonic scale. *Means with different superscript letters are significantly different (P < 0.05).
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