Running title: Effects of BHT impregnated film on storage of crackers

Effects of butylated hydroxytoluene (BHT) impregnated film on storage of vegetable crackers (Kesan filem pembungkus berisi hidroksitoluena dibutilkan (BHT) ke atas penyimpanan keropok sayur)

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Abstract

Active packaging is a new approach in food industry. The incorporation of active substances such as antioxidant into packaging materials will protect oxygen sensitive food products. A storage study was conducted to evaluate the effectiveness of butylated hydroxytoluene (BHT) impregnated film for maintaining the quality of vegetable crackers. Samples of vegetable crackers were packed in high density polyethylene (HDPE) films with 60 μ m of thickness, impregnated with two levels of BHT (0.05% and 1.0% w/w). Normal HDPE film packaging was used as control. All packs were heat sealed and stored at 27 °C ± 5 °C with relative humidity of 70- 80%. Changes in quality during storage were determined by organoleptic evaluation and free fatty acids analysis as the indicator of rancidity. Vegetable crackers packed in HDPE film with 1.0% w/w of BHT remained acceptable up to 8 weeks storage. Those packed in film impregnated with 0.5% w/w BHT was acceptable at 7 weeks storage while crackers packed in normal HDPE was acceptable at 3 weeks storage.

Introduction

Most consumers are looking for food that have better fresh-like qualities, contain no preservatives but at the same time long lasting. The types of packaging and packaging materials used have a significant effect on the quality of food products. Thus, packaging itself has an important role in maintaining the quality and determining the shelf life of the food.

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As a response to consumer demands, active packaging concepts have been introduced. Active food packaging provides some additional functions in comparison to traditional passive food packaging materials which are limited to protect the food products against external influences only. Packaging is termed 'active' when it performs some role in the preservation of food other than providing an inert barrier to external conditions. It also involved in the interactions between food, packaging materials and the internal gaseous atmospheres (Labuza and Breene 1989). Therefore, active packaging not only provides protection but it can interact with food and respond to any changes (Rooney 1995).

The extra functions of active packaging may be obtained by the incorporation of active substances into the packaging materials or packaging system to improve its functionality and give new active properties (Han 2000). These active properties include antioxidant and antimicrobial, selective permeation, controlled and modified atmospheres, selective molecular absorption and controlled degradation. The additional active properties can give better stability, quality and preservation condition of packaged products as well as convenience during handling. Packaging materials containing antioxidants can release active compounds at controlled rates suitable for reducing the oxidation process in a wide range of food (LaCoste et al. 2005).

Rancidity of edible oils and fatty food due to lipid oxidation is a serious problem in some sectors of the food industry. The oxidation reactions are natural but critical since they occur due to free radical chain reactions. Therefore, oxidation inhibitors such as antioxidant may be added to the food or the packaging system in order to prevent the oxidation reactions. The antioxidants will react with the free radicals interrupting the propagation phase of the chain reactions.

Antioxidants are also incorporated into polyolefins used in packaging as a common practice to protect the polymer against degradation during processing (Vulic et al. 2002). The most common antioxidants in plastics are phenolics such as 3,5-di(tertiary-butyl) 4-hydroxytoluene. It is well established that antioxidants are lost from polymer films and sheets during storage (Calvert and Billingham 1979).

Studies of migration of butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) from monolayer polyolefin films have shown that these compounds possess high mobility towards fat, and this characteristic has led to their application as antioxidant active packaging (Wessling et al. 1999; Wessling et al. 2000; Van Aardt et al. 2007). The antioxidant concentrations in polymeric films decrease during storage not only due to oxidation but also due to diffusion of antioxidants through the bulk of polymer towards its surface followed by evaporation (Miltz et al.

2

1988). The diffusion of BHT from HDPE into oat flakes has been studied and the result found that only 55% of the original BHT remained in the package after 1 week storage (Han et al. 1987).

BHT is also widely used in dried products and oxygen sensitive food. It was incorporated directly into food which has proven to be a very successful and inexpensive method for protecting oxygen sensitive food (Hoojat et al. 1987). The volatility of BHT turned into an advantage when it was discovered that it could be added to the packaging materials from which the antioxidant evaporates to protect the enclosed food by its vapour. The addition of 0.1% BHT to polymer packaging has been shown to be effective in preventing oxidation of meat pigments to maintain fresh meat colour (Finkle et al. 2000; Dawson 2001). The release of antioxidants from an active multilayer co-extruded film to whole milk powder was determined during 30 days storage at 30 °C (Granda-Restrepo et al. 2009).

The main objectives of this study were to evaluate the effectiveness of BHT impregnated high density polyethylene (HDPE) film in preventing the oxidation of vegetable crackers and to determine the shelf life of the products.

Materials and methods

Preparation of BHT impregnated films

HDPE resin grade Marlex[®] HHM TR-144 supplied by Marlex Polyethylene was impregnated with BHT (supplied by Sigma Aldrich) as the antioxidant cum the active component in the package. A pellet form of compounded material was produced through a process of mixing (between HDPE resin and BHT) and extrusion using a Brabender twin-screw compounder (model PL-2000 Plasticorder, Germany). The processing temperatures were at 165°C/180°C/190°C which were hot enough to melt the resin and 25 °C below the boiling point of BHT which prevents the tendency of the BHT to evaporate (Yanidis 1996).

The compounded pellets containing two levels of BHT, 0.5% w/w and 1.0% w/w were formed into plastic films with 60 µm thickness using a pilot plant scale extrusion blown film line (model Tai King, Taiwan). The normal HDPE films with the same thickness were produced without the addition of any additives or active components using the same extrusion blown film machine. The films were produced at Plastic Technology Centre, SIRIM Berhad. They were made into pouches as packaging materials for the vegetable crackers used in the study.

Preparation and packaging of vegetable crackers

Vegetable crackers (Panda, Indonesia) were purchased from the local market. The crackers were fried using palm oil in a deep fryer (BERJAYA Electrical Deep Fryer Model DF13) for about 2 min?? at $120^{\circ}C \pm 5^{\circ}C$. The crackers were removed and allowed to cool. Ten pieces of crackers at approximately 5 g were put in a 12.5 cm x 10.0 cm pouch and were heat sealed. The samples were packed in three types of packaging materials with 60 µm of thickness. The packaging materials were normal HDPE film (control), HDPE + 0.5% BHT film and HDPE + 1.0% BHT film.

Storage of crackers

All packages were arranged in a wire meshed cabinet and stored in the laboratory with temperature at 27 °C \pm 5 °C and relative humidity of 70-80%. Two parameters were used to predict the shelf-life of a product, i.e. organoleptic evaluation and free fatty acid analysis. The samples were drawn at 2 weeks intervals and the study was carried out for more than 2 months. Termination of the experiment was based on the organoleptic evaluation results.

Organoleptic evaluation

A total of 20 untrained panellists were selected to evaluate the taste, odour, texture and overall acceptability of the crackers using a 5-point hedonic rating scale. A score of 5 indicated 'most acceptable', and a score of 1 'totally unacceptable' while a score of 3 meant 'neither acceptable nor unacceptable'. Score under 3 was considered the cut off point for unacceptable products.

Free fatty acids analysis

Free fatty acids (FFA) as lauric acid percentages in oil samples were determined using an alkali titration according to Pearson's method (1976). A volume of 25 ml diethyl ether was mixed with 25 ml alcohol and 1 ml of 1% phenolphthalein solution (as an indicator) and carefully neutralized with 0.1M sodium hydroxide. Then, 5 g of oil was dissolved (extracted from the vegetable crackers, how?) in the mixed neutral solvent and titrated with aqueous 0.1M sodium hydroxide until a pink colour which persists for 15 s is obtained. FFA value (mg/g) was calculated according to the equation:

$$FFA = \frac{V \times C \times 56.11}{M}$$

Where, V = Volume of sodium hydroxide

C = Concentration of sodium hydroxide m = Mass of oil (g)

Experimental design and statistical analysis

A completely randomised design was used for the experiments. For the storage study, data were presented as mean values of two separate determinations for each treatment. For organoleptic evaluation data presented were mean values of 20 taste panellists. Statistical analyses were performed with analysis of variance (ANOVA) using SAS software package (SAS Inst. 1985) and the differences among mean were processed by Duncan Multiple Range Test. Significance was defined at level of p < 0.05.

Results and discussion

Organoleptic evaluation

The vegetable crackers' quality was evaluated organoleptically based on taste, odour, texture and overall acceptability (*Table 1*). Deterioration in organoleptic qualities was mainly due to the softening of product, loss of crispness and development of rancidity (Jainudin and Hasnah 1991). The organoleptic results of the samples in different types of HDPE films were compared by taking a mean score of 3 as the lowest limit of overall acceptability.

Crackers packed in normal HDPE film showed significant changes (p < 0.05) in taste and odour after 2 weeks storage. Significant differences in taste and odour (p < 0.05) for crackers in HDPE + 0.5% BHT film occurred after 6 weeks storage as compared to HDPE + 1.0% BHT film which was still acceptable after 8 weeks storage (*Tables 1*).

There were no significant differences (p > 0.05) in texture of vegetable crackers packed in normal HDPE film during the storage period. On the other hand, there were significant differences in texture of crackers packed in HDPE + 0.5% BHT film and HDPE + 1.0% BHT film after 6 and 4 weeks storage respectively (*Table 1*).

The loss of quality during storage of vegetable crackers can be attributed to rancidity which is due to lipid oxidation which can transform food flavour, dull the colour of food products and change the nutritional value of the food. The use of palm oil might contribute to lipid oxidation. A high proportion of short- and medium- chain fatty acids in the oil were more susceptible to breakdown (Smith et al. 1986). Crackers were detected rancid due to changes in taste and odour. Rancidity was detected in crackers packed in normal HDPE film at 4 weeks storage while crackers in HDPE + 1.0% BHT film were still acceptable after 8 weeks storage. The panellists detected changes in taste and odour of crackers in HDPE + 0.5% BHT film at 6 weeks storage. These results indicated that vegetable crackers packaged with normal HDPE film have a shelf life of about 3 weeks. Those packed in HDPE + 1.0% BHT film have a shelf life of more than 8 weeks. The shelf life of crackers packed in HDPE + 0.5% BHT film remained acceptable up to 6 weeks.

Formation of free fatty acid

Formation of free fatty acid (FFA) is an important measure of rancidity of food. Generally, the FFA values of all samples increased throughout the storage period (*Figure 1*). The FFA value of vegetable crackers in antioxidant impregnated films (HDPE + 0.5% BHT and HDPE + 1.0% BHT) and normal HDPE film showed significant differences (p < 0.05) after 2 weeks storage (*Figure 1*). The FFA values for crackers in HDPE film, HDPE + 0.5% BHT film and HDPE + 1.0% BHT film were subsequently increased to 0.14, 0.18 and 0.15% respectively after 8 weeks storage. There was a tendency for oxidation to occur since palm oil was used to fry the crackers. Edible fats, oils and fatty food will oxidize slowly during storage and form various oxidation products.

These oxidation products will cause rancidity and deterioration of the sensory properties (Pokorny 1991). The impregnated BHT in HDPE films maybe lost due to diffusion into the space area inside the films during storage (Calvert and Billingham 1979; Miltz et al 1988). The evaporation of BHT from the films will give protection to the enclosed crackers by its vapour. The BHT will react with free radicals interrupting the propagation phase of the chain reaction during oxidation reaction.

Conclusion

The results of this study demonstrated the effectiveness of BHT in HDPE films which was transferred from package to product via the evaporation mechanism to retard lipid oxidation of vegetable crackers. The use of antioxidants cannot maintain the oxidative stability indefinitely but it can slow down the rancidity process significantly. The antioxidant impregnated HDPE films were able to maintain the quality of vegetable crackers and at the same time extend the shelf life of the product. Vegetable crackers packed in HDPE + 1.0% BHT and HDPE + 0.5% BHT films had a shelf life of 8 and 6 weeks respectively. Those packed in normal HDPE had a shelf life of only 3

6

weeks. The use of antioxidant impregnated films as a packaging material helped to reduce oxidation, maintain the quality and prolong the shelf life of vegetable crackers.

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*not in the list

- Pearson 1976

- SAS Institute 1985

Abstrak

Pembungkusan aktif merupakan satu pendekatan baru dalam industri makanan. Gabungan bahan aktif seperti antioksidan ke dalam bahan pembungkus dapat memberi perlindungan kepada produk yang sensitif terhadap oksigen. Satu kajian penyimpanan keropok sayur yang dibungkus dengan filem pembungkus berisi hidroksitoluena dibutilkan (BHT) telah dijalankan untuk menilai keberkesanan filem pembungkus tersebut bagi mengekalkan kualiti produk. Keropok sayur dibungkus di dalam filem polietilena berketumpatan tinggi (HDPE) dengan ketebalan 60 μm, diisi tepu dengan dua aras BHT (0.5% dan 1.0% w/w). Filem HDPE biasa yang bertindak sebagai kawalan. Kesemua bungkusan dipateri dengan haba dan disimpan pada suhu 27 °C± 5 °C dengan kelembapan relative 70-80%. Perubahan kualiti semasa penyimpanan ditentukan melalui penilaian organoleptik dan analisis asid lemak bebas sebagai penanda ketengikan. Keropok sayur yang dibungkus di dalam filem HDPE dengan 1.0% BHT masih boleh diterima sehingga 8 minggu penyimpanan berbanding dengan 3 minggu bagi keropok sayur yang dibungkus di dalam filem HDPE biasa.

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Table 1. Sensory scores of organoleptic properties of vegetable crackers during storage at 27 $^{\circ}\text{C} \pm 5$ $^{\circ}\text{C}$

| Storage period | HDPE | HDPE + 0.5% BHT | HDPE + 1.0% BHT |
|----------------------|--------|-----------------|-----------------|
| (week) | | | |
| Taste | | | |
| 0 | 3.70 a | 3.70 a | 3.70 ab |
| 2 | 3.25 b | 3.75 a | 4.10 a |
| 4 | 2.65 c | 3.75 a | 3.80 a |
| 6 | 2.70 c | 3.20 b | 3.55 b |
| 8 | 2.95 c | 2.90 c | 3.15 c |
| Odour | | | |
| 0 | 3.75 a | 3.75 a | 3.75 ab |
| 2 | 3.20 b | 3.55 a | 3.95 a |
| 4 | 2.50 c | 3.55 a | 3.85 a |
| 6 | 2.60 c | 2.85 b | 3.20 bc |
| 8 | 2.80 c | 2.85 b | 3.0 c |
| Texture | | | |
| 0 | 3.95 a | 3.95 a | 3.95 a |
| 2 | 3.80 a | 3.95 a | 4.15 a |
| 4 | 3.60 a | 3.80 a | 3.65 b |
| 6 | 3.45 a | 3.35 b | 3.45 b |
| 8 | 3.65 a | 3.25 b | 3.35 b |
| verall acceptability | | | |
| 0 | 3.65 a | 3.65 a | 3.65 ab |
| 2 | 3.15 b | 3.65 a | 3.95 a |
| 4 | 2.35 c | 3.75 a | 3.65 ab |
| 6 | 2.10 c | 3.05 b | 3.50 b |
| 8 | 2.35 c | 2.95 b | 3.15 c |

Means within a column with the same letters are not significantly different at p < 0.05 (n = 20) Scores 1= Totally unacceptable, 3 = Neither acceptable nor unacceptable, 5 = Most acceptable



Figure 1. Changes in free fatty acid values of vegetable crackers in different packaging films during storage at 27 $^{\circ}C \pm 5 \,^{\circ}C (n = 2)$