Whey Protein Isolate Edible Coatings: Effect on the Rancidity Process of Dry Roasted Peanuts

Juan I. Maté, E. N. Frankel, and J. M. Krochta*

Department of Food Science and Technology, University of California, Davis, California 95616

Dry-roasted peanuts were coated with whey protein isolate (WPI)/glycerol solutions. Accelerated rancidity tests of uncoated and coated nuts were performed. Coating thickness and environmental relative humidity were studied as factors that affected rancidity. In addition, the effect of limiting the amount of WPI solution absorbed by the nutmeat on the performance of the coating was evaluated. WPI/glycerol edible coatings delayed the oxidative deterioration of dry-roasted peanuts. Greater thickness and lower relative humidity resulted in more effective coatings. Therefore, the mechanism of protection of the coatings relies on its properties as an oxygen barrier. The continuity of the coating was shown to be critical for its effectiveness. In addition, limiting the WPI solution migration into the nutmeat did not improve the effectiveness of the WPI coating.

Keywords: *Whey protein; coatings; peanuts; rancidity*

INTRODUCTION

Roasted peanuts are susceptible to lipid oxidation, causing rancidity (Agbo et al., 1992; Yuki et al., 1978). Agronomic, processing, and storage conditions affect this chemical process. If lipid oxidation in roasted peanuts is not controlled, certain off-flavors develop that make the product unacceptable.

Oxygen concentration is one of the most important storage factors affecting lipid oxidation (Labuza, 1971). By reducing the O_2 concentration around the nuts, lipid oxidation can be reduced. Maté et al. (1996) quantified the dramatic effect of a low-O_2 environment on the lipid oxidation of dry-roasted peanuts at low and intermediate relative humidities. Nitrogen-flushing, vacuum packaging, metal cans, glass jars, and metallized films are all means used in industry to increase the shelf life of peanuts.

The use of edible coatings provides an alternative approach to the above packaging. Reduced O_2 content within each nut could be achieved by surrounding each nut with a continuous edible coating with a low O_2 permeability. Whey protein isolate (WPI)-based edible films have low O_2 permeability (McHugh and Krochta, 1994). Maté and Krochta (1996) coated peanuts by dipping them into an increased-viscosity WPI solution, followed by air-drying. They showed that WPI-based edible coatings are also good O_2 barriers on the nut surface and could delay considerably O_2 uptake of dry-roasted peanuts. The delay in O_2 uptake in coated peanuts is a good indication that these coatings could delay the rancidity process. These coatings could provide a simpler, cheaper, and/or more recyclable package and continued protection of nuts after opening.

The objective of this work was to evaluate how WPI-based edible coatings affect the development of rancidity. Products resulting from lipid oxidation were measured by two analyses. Peroxide value (PV) was measured as an indicator of the formation of hydroperoxide, the primary initial product of lipid oxidation (Nawar, 1985). Hexanal content by static headspace gas chromatography was performed as an indicator of the formation of breakdown products. Linoleic acid is a major component in the fatty acid composition of peanuts (Ahmed and Young, 1982), and hexanal is a major breakdown product of the oxidation of linoleic acid (Frankel, 1982).

The presence of the coating as an O_2 barrier would reduce O_2 diffusion into the nutmeat and limit the lipid oxidation rate. If this mechanism is correct, the better the barrier, the slower the rate of lipid oxidation. To check this hypothesis, the effect of coating thickness and environmental relative humidity on the behavior of the coatings was evaluated. Since a thicker coating is a better barrier, it would have a greater effect in delaying rancidity. Moreover, for the same WPI coating formulation and thickness, higher storage relative humidity, increases O_2 permeability (McHugh and Krochta, 1994), and therefore it would reduce its performance as an O_2 barrier coating.

Since peanuts are dry and porous, the coating solution could be absorbed by the nutmeat from the moment of the dipping until the end of the drying process, despite the high viscosity of the WPI solution and the hydrophobic nature of the nut surface. It is not known how the partial absorption of the coating solution could affect lipid oxidation of the coated product. If there is a layer of hydrophobic material between the nutmeat and the WPI coating, the WPI solution migration could be limited. Peanuts were coated with a thin layer of distilled acetylated monoglycerides (DAM) to form a protective coating to limit WPI solution migration. DAM was chosen because it is a stable hydrophobic material that does not provide protection against lipid oxidation in roasted peanuts (Hoover and Nathan, 1981). Those peanuts with a layer of DAM were coated with an additional layer of WPI solution, making a bilayer coating. The effect of the possible migration of the WPI solution into the nutmeat on the lipid oxidation was evaluated by comparing the behavior of nuts coated with a bilayer coating with that of nuts coated with only a WPI solution.

MATERIALS AND METHODS

Materials. Dry-roasted peanuts (extra large Virginia variety) were supplied by PERT Laboratories, Edenton, NC. The dry-roasting process was performed for 23 min at 141 °C

* Author to whom correspondence should be addressed [telephone (916) 752-2164; fax (916) 752-4759].

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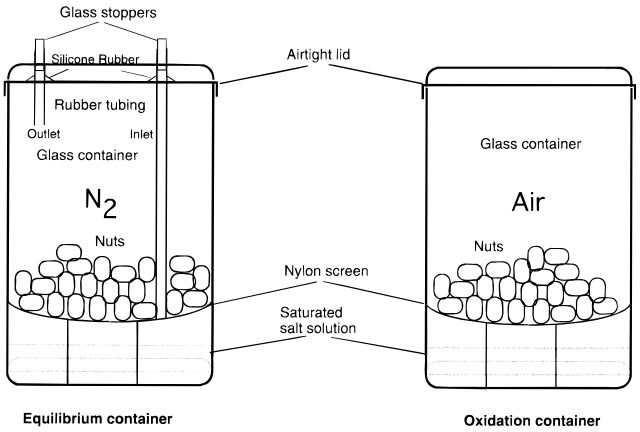

Figure 1. Containers used to equilibrate nuts at the required relative humidity under nitrogen (equilibrium container) and to maintain nuts at the required relative humidity under air (oxidation container).

(285 °F). Nuts were sent to UC Davis overnight and kept at 2 °C until used. WPI (>95% protein) was obtained from Le Sueur Isolates (Le Sueur, MN). Myvacet 5-07 (DAM) was supplied by Eastman Chemical Products, Inc. (Kingsport, TN). Glycerol (Gly), potassium acetate, and sodium bromide were obtained from Fisher Scientific, Inc. (Fair Lawn, NJ).

WPI Coating Procedure. The method described by Maté and Krochta (1996) to coat dry roasted peanuts with a WPI solution with increased viscosity was used. WPI solution was prepared according to the method described by McHugh and Krochta (1994) but with higher protein concentration. It was necessary to use 11.5% protein concentration in the solution to obtain similar viscosity in the same storage time as in the procedure described by Maté and Krochta (1996). Two coating formulations were examined: (i) WPI 60/Gly 40, in which there was a 60/40 (w:w) ratio of WPI and Gly in the formulation, and (ii) WPI 50/Gly 50, in which equal amounts of WPI and Gly were added in the solution.

Whole peanuts were placed in pins that were attached to a board. Then, the nuts were dipped into the solution maintained at 5 °C by an ice bath. Immediately after, the pin boards with nuts were placed in a drier (Maté and Krochta, 1996). The boards were automatically rotated to get an even distribution of the coating around the nuts. To study the effect of thickness on the behavior of the coated nuts, two different thicknesses were evaluated for each formulation. Nuts were coated with either three or five dippings of WPI 60/Gly 40 solution (W60/G40×3 coating and W60/G40×5 coating, respectively), and some other nuts were coated with either three or five dippings of WPI 50/Gly 50 solution (W50/G50×3 coating and W50/G50×5 coating, respectively). Once the final coating was dry, nuts were taken from the boards and the small hole made by the pin in each peanut was covered with a drop of solution.

DAM−WPI Bilayer Coating Procedure. Peanuts were first coated with a thin layer of DAM. Dry-roasted peanuts were placed on pins and dipped in liquid DAM for about 1 s. Liquid DAM was maintained at 87 ± 2 °C with a plate heater. After cooling, peanuts had a thin layer of solid DAM coating. This procedure is similar to the one described by the company that produces Myvacet 5-07 (K) (Eastman Chemical Products, 1987). DAM-coated peanuts were then coated with three dippings of WPI 50/Gly 50 solution, producing a bilayer coating composed of an inner layer of DAM and an external W50/G50×3 coating.

Equilibration Procedure. Coated nuts were placed in individual glass containers (equilibrium container, Figure 1) and equilibrated at different relative humidities. Nuts coated with higher Gly content formulation (WPI 50/Gly 50) were equilibrated at 21% relative humidity. Nuts coated with lower Gly content formulation (WPI 60/Gly 40) were equilibrated at 53% relative humidity. Uncoated nuts were equilibrated at both 21% and 53% relative humidity. Furthermore, to study the effect of relative humidity on the performance of the coatings, some nuts with W50/G50×3 coating were also equilibrated at 53% relative humidity and some nuts with W60/G40×5 coating were also equilibrated at 21% relative humidity.

Constant relative humidities were maintained by saturated salt solutions in the bottom of glass containers (1.5 L) with airtight lids (Figure 1). Potassium acetate (CH_3COOK) was used to provide a relative humidity of about 21% at 37 °C (ASTM, 1985) and sodium bromide (NaBr) to provide a relative humidity of about 53% at 37 °C (Kitic et al., 1986). Preparation of the solutions was done according to standards (ASTM, 1985).

The glass containers with the nuts were placed into a controlled-temperature room at 37 °C. All glass containers (equilibrium containers, Figure 1) were flushed with nitrogen weekly to prevent lipid oxidation during the equilibration period. Aluminum foil was used to cover all containers to exclude light. Preliminary experiments showed that after 3 weeks, nuts could be considered at equilibrium at the selected relative humidity (Maté and Krochta, 1996). The amount of coating added to the nuts was calculated by measuring the difference in weight between 10 nuts before coating and after the equilibrium period, taking into account the change in weight of uncoated nuts because of the relative humidity.

Storage Test. After the equilibrium period, nuts were transferred from individual equilibrium containers to individual oxidation containers (Figure 1) with the same saturated solution. The oxidation containers had air in the headspace to cause lipid oxidation. A sample containing 20 nuts (≈15 g) was collected from each container to determine the initial oxidation level. Samples were then collected every 2 weeks for 10 weeks to follow the progression of the rancidity process. Static headspace analysis and PV were performed in triplicate with all samples.

Peroxide Value. PV of peanut oil was determined by the method described according to Chapman and Mackay (1949). Oil for analysis was extracted from the nuts by cold-pressing. Nuts were first chopped and then wrapped in filter paper. They were then placed in a special cell to be pressed. A Carver laminating press (Model 126, Carver Hydraulic Equipment, New York, NY) was used to provide 55 000 kPa of pressure on the cell. Clean oil was collected as it was coming out of the cell.

Static Headspace Gas Chromatography. The method described by Frankel and Huang (1994) was used. Nut samples were ground with a coffee grinder for 30 s. Samples of ground uncoated nuts weighing 0.55 g were placed into 6 mL vials together with 1 mL of deionized water. For ground coated nuts the sample weighed 0.65 g to account for the coating (approximately 15% of the sample). The vials were then sealed with silicone rubber Teflon caps and heated to 65 °C for 15 min. The headspace was analyzed using a Perkin-Elmer Sigma 3B gas chromatograph with an H-6 headspace sampler (Norwalk, CT) and a capillary DB-1701 column (30 m × 0.32 mm, 1 μm thickness; J&W, Folsom, CA) heated isothermally at 65 °C. The gas chromatograph conditions were as follows: helium linear gas velocity, 20 cm/s (helium head column pressure, 30 psi); splitless injector temperature, 180 °C; and detector temperature, 200 °C. Hexanal was identified by comparison with the retention time of reference compound. Peak areas were integrated electronically (C-R3A Chromatopac; Simatzu Co., Kyoto, Japan). For quantitative determination of hexanal, an internal standard curve, based on known amounts of hexanal added to fresh nut samples, was used for each type of nut.

Coating Thickness. After the experiment, thicknesses of the coatings of five remaining coated peanuts were measured. Coatings were peeled off from the peanut surface and thickness was measured in six different places with a caliper micrometer (No. 7326, Mitutoyo Manufacturing Co. Ltd., Tokyo, Japan).

RESULTS AND DISCUSSION

Coating Characteristics. WPI coatings, regardless of composition or thickness, provided a glossy appearance that distinguished the coated nuts from the

Table 1. Coating Characteristics and Storage Relative Humidity of Various Coated Peanuts

coating formulation	storage relative humidity (%)	coating wt[a] (%)*	coating thickness (μm) av[b]	coating thickness (μm) s_p[c]
WPI 50/Gly 50				
3 dippings	21	14.8	285	108
5 dippings	21	20.4	436	148
3 dippings	53	13.8	216	51
WPI 60/Gly 40				
3 dippings	53	10.7	197	55
5 dippings	53	23.5	427	93
5 dippings	21	21.7	484	190
myvacet	21	2.5	n/m[d]	n/m
bilayer	21	16.23	304	54

[a] Coating weight based on amount of coating in final weight of coated nut [b] Average coating thickness of all tested nuts. [c] s_p is the pool standard deviation. [d] Not measured.

uncoated ones. The coated nuts were also slightly darker than the uncoated ones. This darkening effect was much less prominent in the case of the bilayer coating. Since with the bilayer coating WPI solution migration into the nutmeat is limited, the darkening effect was likely related to this migration.

During the equilibrium period, part of the water, which acted as plasticizer, left the coating, which became more brittle and shrank, resulting in increased mechanical stresses. As a consequence, cracks appeared in most of the W60/G40×3 coatings stored at 53% relative humidity during the equilibrium period. The rest of the coatings did not develop cracks and appeared continuous around the nuts.

As previously observed (Maté and Krochta, 1996) coating thickness was not uniform within each treatment. For each coating treatment, there were two sources of thickness variation. First, there was variation of the coating thickness for each nut. This was quantified by the pooled standard deviation (Table 1). Second, there was variation of the average coating thickness among nuts. Results of ANOVA indicated that the average coating thickness was not significantly different among nuts ($p < 0.01$) in all coatings but W50/G50×3 stored at 53% relative humidity. Therefore, coating thickness variation among nuts was relatively smaller than coating thickness variation within each nut. Therefore, the coating technique was relatively consistent in coating thickness.

Coating thickness increased with increased number of dippings and also with greater coating weight (Table 1). Coating thickness averages ranged between 215 and 435 μm for the WPI 50/Gly 50 formulation and between 197 and 427 μm for the WPI 60/Gly 40 formulation. This shows that thicknesses were similar for both formulations with the same number of dippings.

During the peeling of the coated nuts to measure coating thickness, it was observed that there were small amounts of oil between the coating and the nutmeat. Probably, the oil came out of the peanut tissue as a consequence of the pressure exerted on the nutmeat by the coating during the shrinking that happened in the drying process. The amount of oil in each coating was not quantified.

Effect of Thickness on Oxidative Stability. Nuts with W50/G50×3 coating (285 μm average thickness) took about twice as much time to reach the same PV value as the uncoated peanuts (Figure 2) at 37 °C and 21% relative humidity. The limiting PV critical for acceptability of roasted peanuts is 20−30 mequiv/Kg

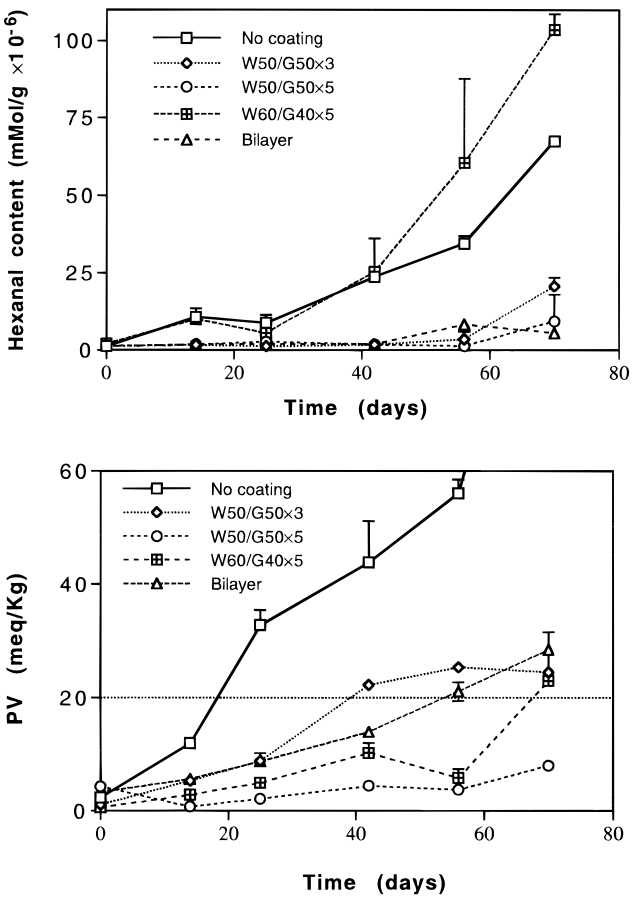

Figure 2. Effect of time on the peroxide value and hexanal content (static head space analysis) of uncoated nuts and nuts coated with different formulations stored at 37 °C and 21% relative humidity environment. Bars indicate standard deviations.

(Evranuz, 1993). If we assume that the acceptable limit is 20 mequiv/Kg, uncoated nuts took 20 days to become unacceptable, whereas nuts with W50/G50×3 coating took about 40 days. Similar delays in O_2 uptake were observed previously with the same coating, similar thickness, and same storage conditions (Maté and Krochta, 1996).

A thicker coating of the same formulation (W50/G50×5, 436 μm) and the same storage conditions (37 °C and 21% relative humidity) delayed further the formation of peroxides (Figure 2). This stability effect was also reflected in hexanal content. The hexanal content corresponding to the uncoated nuts started to increase from day 0. For coated nuts (both W50/G50×3 and W50/G50×5), it took almost 60 days to start the hexanal content increase. This increase was greater for nuts with the thinner coating than for nuts with the thicker coating. Since the thicker the coating, the better the O_2 barrier, these results confirm the hypothesis that the delay of the rancidity process was due to reduced O_2 availability within the nutmeat.

Similar thickness effect was expected for nuts with WPI 60/Gly 40 coatings stored at 53% relative humidity and 37 °C. However, data obtained for nuts coated with W60/G40×3 could not be used to study the thickness effect because of cracking that occurred during the equilibration period. These cracks reduced drastically the effect of the coating as an O_2 barrier. As a result, the productions of PVs in nuts with W60/G40×3 coating and uncoated nuts were similar (Figure 3). PVs were higher for uncoated nuts at any time probably because

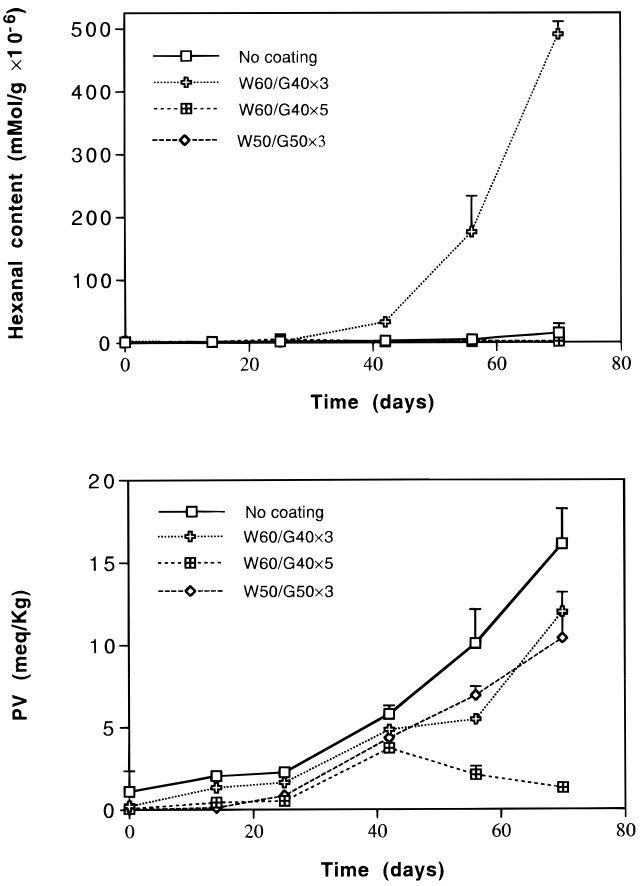

Figure 3. Effect of time on the peroxide value and hexanal content (static head space analysis) of uncoated nuts and nuts coated with different formulations stored at 37 °C and at 53% relative humidity environment. Bars indicate standard deviations.

their initial values were higher. The hexanal value for peanuts coated with W60/G40×3 increased after 40 days, reflecting a breakdown of peroxides. This increase in hexanal content was not observed in uncoated nuts. This difference could be explained by assuming that a small amount of oil was pressed out during the drying due to the coating shrinkage. This oil, exposed to air in the cracks, could be much more susceptible to oxidation than the oil remaining in the tissue, and that could be responsible for the observed increase in hexanal value.

Nuts coated with W60/G40×5 and stored at 53% relative humidity did not develop cracks. The PV was always lower than the control, and no hexanal was detected throughout the storage experiment (Figure 3). This result showed that if the coating is continuous, W60/G4 coatings could provide protection for lipid oxidation at 53% relative humidity.

Effect of Relative Humidity on Oxidative Stability. W50/G50×3 coating was more effective in delaying lipid oxidation at 21% relative humidity than at 53% relative humidity. This is clearly illustrated by comparing PVs of coated and uncoated nuts at both relative humidities (Figures 2 and 3). After 70 days, nuts coated with W50/G50×3 and stored at 21% relative humidity had a PV about 22% of the PV of uncoated nuts. This percentage was 65% for nuts with the same coating but stored at 53% relative humidity. Hexanal content could not be used for this comparison, because at 53% relative humidity the formation of hexanal was small in both coated and uncoated nuts.

McHugh and Krochta (1994) showed an exponential relation between O_2 permeability of WPI films and the relative humidity to which they were exposed. Therefore, W50/G50×3 coatings were much poorer O_2 barriers at 53% relative humidity than at 21% relative humidity. Our results confirm that the mechanism of protection of the coatings can be attributed to their properties as a physical barrier against O_2 transport.

Previous results (Maté et al., 1996) showing that lipid oxidation of dry-roasted peanuts was greater at 21% relative humidity than at 53% relative humidity were confirmed in the present work. PV and hexanal content of uncoated nuts stored at 21% relative humidity were much higher than those stored at 53% relative humidity (Figures 2 and 3). As a consequence, a restriction of O_2 availability in the nutmeat will always be more effective in delaying lipid oxidation at 21% relative humidity than at 53% relative humidity. This fact results in a more dramatic coating effect at 21% relative humidity than at 53% relative humidity.

The effect of relative humidity on the performance of W60/G40×5 coatings was expected to be similar to that on W50/G50×3 coatings, previously described. On the basis of PV, the difference between uncoated and coated nuts was greater at 21% relative humidity than at 53% relative humidity at any time (Figures 2 and 3). However, hexanal content of coated nuts at 21% relative humidity increased after 24 days, showing a behavior similar to that of uncoated nuts (Figure 2). At 53% relative humidity coated and uncoated nuts did not develop significant amounts of hexanal, but after 70 days, the hexanal content was higher in the uncoated ones. Therefore, W60/G40×5 coating is not more effective in delaying the rancidity at 21% relative humidity than at 53% relative humidity.

At 21% relative humidity, W60/G40×5 is a brittle coating subject to high mechanical stress because of the low amount of plasticizer. Probably, there were small cracks in the coating that have not been detected. Similar to the case of W60/G40×3 at 53% relative humidity, oil in cracks could have been susceptible to oxidation that led to an increase in hexanal content. However, this did not happen at 53% relative humidity, because the coating had higher plasticizer content.

Effect of Bilayer Coating on Oxidative Stability. Bilayer and W50/G50×3 coatings were equally effective in delaying the formation of peroxides as well as the formation of hexanal (Figure 2). This showed that the reduction of the WPI migration into the nutmeat did not change the effectiveness of the WPI coating on development of rancidity. The difference in PV of the nuts coated with bilayer or W50/G50×3 was relatively small compared to the difference between uncoated nuts and any coated nuts. For this reason, the presence of DAM did not significantly improve the effectiveness of the coating.

Conclusions. WPI coatings can delay the development of rancidity of dry-roasted peanuts at both intermediate and low relative humidities. The fact that greater thickness and lower relative humidity provided a more effective coating indicated that the mechanism of protection of the coatings relies on its properties as an O_2 barrier. Continuity of the coatings was found to be a critical factor to effectively delay the development of rancidity.

Shrinkage of the coatings, resulting in the presence of peanut oil on the nut surface, is thought to affect lipid oxidation. This phenomenon needs further research.

Finally, the presence of a hydrophobic layer on the nut surface to limit the migration of WPI solution into the nutmeat did not change the effectiveness of the WPI coating to delay rancidity.

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