USE OF EDIBLE LAMINATE LAYERS IN INTERMEDIATE MOISTURE FOOD RATIONS TO INHIBIT MOISTURE MIGRATION

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Natick, Massachusetts 01760-5000
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This report documents a storage study of a novel technology to inhibit moisture migration in multi-component foods, specifically shelf-stable military rations, conducted in FY 2013 and 2014 by the Natick Soldier Research, Development and Engineering Center (NSRDEC). Edible laminated layers (LL) were inserted as barriers in a model food system and later in a shelf-stable pizza to evaluate their ability to inhibit moisture migration and improve sensory quality. Moisture migration can produce unpleasing physical and chemical changes in multi-component foods, affecting safety, shelf life, and sensory quality. These phenomena occur over time due to differences in the water activity of individual components in the product. Five of the seven LL barriers evaluated inhibited moisture migration between sandwich layers that had differences in water activity. The effectiveness of the various LLs seemed to be largely dependent on film thickness and material. Two of the three films evaluated in the pizza proved effective in slowing moisture migration to the crust during 2 weeks of storage at 120 °F, but were inconsistent after 4 weeks at that temperature and 3 and 6 of storage at 100 °F. None of the three LLs significantly increased sensory quality characteristics in the pizza prototypes. This research will be useful in future product development for ration and commercial items that are prone to moisture migration.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................................................ iv

LIST OF TABLES ............................................................................................................................................... v

PREFACE ..................................................................................................................................................... vi

1.0 INTRODUCTION .................................................................................................................................... 1
  1.1 Industry Solutions ................................................................................................................................. 2
  1.2 Research and Documentation Approach ............................................................................................... 2

2.0 MODEL FOOD SYSTEM EVALUATION ............................................................................................ 3
  2.1 Development of Model System ............................................................................................................ 3
  2.2 Analysis Methodology ......................................................................................................................... 3
  2.3 Analysis Results .................................................................................................................................. 5
     2.3.1 Moisture Migration ......................................................................................................................... 5
     2.3.2 Texture Changes .............................................................................................................................. 6
     2.3.3 Color Changes ............................................................................................................................... 7

3.0 MULTI-COMPONENT FOOD SYSTEM EVALUATION ........................................................................ 8
  3.1 Preparation and Storage of Food System ............................................................................................. 8
  3.2 Analysis Methodology .......................................................................................................................... 9
     3.2.1 Moisture Migration ......................................................................................................................... 9
     3.2.2 Sensory Analysis ............................................................................................................................ 9
  3.3 Analysis Results .................................................................................................................................. 9
     3.3.1 Moisture Migration ......................................................................................................................... 9
     3.3.2 Sensory Analysis ............................................................................................................................ 10

4.0 CONCLUSIONS AND FUTURE RESEARCH .................................................................................... 11

BIBLIOGRAPHY .............................................................................................................................................. 13
LIST OF FIGURES

Figure 1: Final Model Food System. Bottom to top: MRE White Wheat Snack Bread, Origami Wrap® Film, American Cheese ............................................................................................................. 3

Figure 2: Effectiveness of Watson Inc. LLs in model system throughout 4 weeks of storage .......... 5

Figure 3: Effectiveness of NewGem Foods™ LLs in model system throughout 4 weeks of storage ... 6

Figure 4: Textural changes exhibited by bread in model system throughout 4 weeks of storage using NewGem Foods™ LLs ............................................................................................................. 7

Figure 5: Hunter LAB Colorimeter values of bread in model system throughout 4 weeks of storage using NewGem Foods™ LLs ............................................................................................................. 7

Figure 6: Shelf-stable pizza with LLs incorporated. Left to right: GemWrap®, single-sided HPMC, control (no LL), Origami Wrap® ........................................................................................................... 8

Figure 7: Moisture Migration from sauce into crust of shelf-stable pizzas over 2 weeks storage at 120 °F .................................................................................................................................. 9

Figure 8: Cross section of control pizza (left) and pizza with least effective LL (right), Origami Wrap®, after storage for two weeks at 120°F .......................................................................................... 10
LIST OF TABLES

Table 1: LL prototypes chosen for moisture migration prevention analysis ............................................. 2
Table 2: Dough preparation .................................................................................................................... 8
Table 3: Sauce preparation ................................................................................................................... 8
PREFACE

This technical report documents a Science and Technology initiative for a novel technology to inhibit moisture migration in multi-component foods, specifically shelf-stable military rations. The US Army Natick Soldier, Research, Development, and Engineering Center (NSRDEC) completed this work between October 2012 and December 2014 under the Tech Base project titled “Laminated Layers”, TB 13-04, funded by the Combat Feeding Research and Engineering Program Board from FY13-FY14.

This novel technique was to insert edible laminated layers (LL) in ration components. Method development, moisture analysis, chemical assays, and sensory evaluations were performed to determine the effectiveness of the barrier systems at inhibiting moisture migration in a model food system. The best performing LLs were selected and further studied in a more complex food matrix: shelf-stable pizza.

The names and contact information of NSRDEC personnel which contributed to this study are:

<table>
<thead>
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<th>Role/Organization</th>
<th>Phone/Email</th>
</tr>
</thead>
<tbody>
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</tr>
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<td></td>
<td>US Army NSRDEC</td>
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</tr>
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</tr>
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<td></td>
<td>US Army NSRDEC</td>
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</tr>
<tr>
<td></td>
<td>US Army NSRDEC</td>
<td></td>
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USE OF EDIBLE LAMINATE LAYERS IN INTERMEDIATE MOISTURE FOOD RATIONS TO INHIBIT MOISTURE MIGRATION

1.0 INTRODUCTION

This report documents work performed, from October 2012 to December 2014, by the Natick Soldier Research, Development and Engineering Center (NSRDEC) to develop and incorporate edible laminate layer (LL) systems in shelf-stable military ration components to inhibit moisture migration and improve the quality of such ration components for the Warfighter.

Extended shelf life military ration components that are complex in nature, with multiple components (such as sandwiches with fillings, pizza with sauce, etc.), are highly desirable to the Warfighter. These multi-component, intermediate moisture foods tend to be more appealing to the Warfighter due to familiarity and fresh-like quality compared to ration items that are traditionally thermally processed (Barrett, A.). They also require minimal preparation and provide ease of consumption while on the go.

These intermediate moisture products with multiple components require careful engineering to ensure they maintain optimal sensory quality and safety throughout their shelf life. Moisture migration is largely to blame for the deterioration in the quality of these ration items throughout storage. It can yield displeasing physical and chemical changes within the food system, affecting its safety, shelf life, and sensory quality. Specifically, it can lead to lipid oxidation, non-enzymatic browning, crystallization, staling, and possibly microbial growth. These phenomena occur within a multi-component food system in which the components have significant differences in water activity. This is a particularly important issue for the military. Due to the stringent shelf-life requirements for First Strike Ration and Meal, Ready-to-Eat (MRE), moisture migration from one part of a component (e.g., sandwich filling) to another (e.g., bread) negatively affects ration components and restricts the development of highly requested multi-components items, such as shelf stable sandwiches and pizza. Many multi-component ration items have been successfully developed; however, not all meet the sensory requirements after storage, most often due to moisture migration.

For example, a shelf stable peanut butter and jelly sandwich has been requested by Warfighters, but developing an acceptable product has been unattainable due to the oil migration from the peanut butter to the bread, color migration from the jelly into the bread, and moisture migration from the bread to the peanut butter. The moisture migrates because the peanut butter has a lower water activity than the bread. Once the moisture migrates, a peanut butter with a higher water activity is more prone to lipid oxidation than its original state.

Careful formulation of the components within the ration to prevent moisture migration is not always effective (Barrett, A.).

1.1 Industry Solutions

Extended shelf-life and moisture migration are issues not unfamiliar to industry. There is a constant push for more convenient shelf-stable foods as well as products that will have a longer shelf-life to maximize cost savings. Fortunately, industry has done some exploration of the uses of edible films and barriers to improve sensory qualities in commercial products. For example, edible films are currently used in frozen pizza, in microwave dinners, in ready-to-eat ice cream novelties, and as a replacement for seaweed in sushi.
These edible barriers are not directly applicable to military uses, so these films must be modified into LLs, which are edible barriers or films that can be inserted at the interface of a multi-component ration to prevent moisture migration. To modify these barriers to fit military needs, current commercial film technology had to be exploited, modified, and applied to the preservation of military ration components.

The type of barrier to be used in a food system is largely dependent on the food system itself. For example, a barrier used to prevent lipid migration would have different properties than a barrier used to prevent moisture migration. The properties in the film vary primarily in solubility.

1.2 Research and Documentation Approach

Moisture migration was the main focus of this effort. Based on a literature review and market survey, NSRDEC obtained seven LL barriers for testing; some of these were commercially available while others were developed specifically for this effort by the supplier. These prototypes, their main ingredients, and their solubility properties are listed in Table 1. To determine the effectiveness of each of the barriers, a model system was first developed. Once the most effective LLs were chosen based on performance in the model system, they were incorporated into a multi-component intermediate moisture food system of shelf-stable pizza. The methods used to develop the model systems, the tests conducted using them, and the results obtained from the tests are discussed in Chapter 2. The preparation of the multi-component food system (pizza), the tests conducted using it, and the results obtained from the tests are described in Chapter 3. The conclusions drawn from the studies and results and their implications on future research and development are discussed in Chapter 4.

Table 1: LL prototypes chosen for moisture migration prevention analysis.

<table>
<thead>
<tr>
<th>Supplier</th>
<th>Laminate Layer</th>
<th>Ingredients</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Watson, Inc.</td>
<td>Pullulan Beeswax Moisture Barrier (BWMB) film #1</td>
<td>Pullulan*, beeswax, glycerin, propylene glycol, starch, polysorbate 80</td>
<td>Water soluble</td>
</tr>
<tr>
<td>Watson, Inc.</td>
<td>Pullulan BWMB film #2</td>
<td>Pullulan*, white beeswax, glycerin, propylene glycol, polysorbate 80, modified starch</td>
<td>Water soluble</td>
</tr>
<tr>
<td>Watson, Inc.</td>
<td>Alginate BWMB film</td>
<td>Sodium alginate, gum Arabic, glycerin, beeswax, Aldo MO K FG</td>
<td>Water soluble</td>
</tr>
<tr>
<td>Watson, Inc.</td>
<td>Single-sided HPMC moisture barrier film</td>
<td>Hydroxypropyl methylcellulose, propylene glycol, citric acid, modified starch, white beeswax</td>
<td>Water resistant coating on one side</td>
</tr>
<tr>
<td>Watson, Inc.</td>
<td>Dual-sided HPMC moisture barrier film</td>
<td>Hydroxypropyl methylcellulose, propylene glycol, citric acid, modified starch, white beeswax</td>
<td>Water resistant coating on both sides</td>
</tr>
<tr>
<td>New Gem Foods™</td>
<td>GemWrap® (tomato flavor)</td>
<td>Tomato paste, apple puree concentrate, vegetable glycerin, soy protein isolate, powdered cellulose, fruit pectin, chipotle peppers, water, sorbitol.</td>
<td>Water soluble</td>
</tr>
<tr>
<td>NewGem Foods™</td>
<td>Origami Wrap® (tomato flavor)</td>
<td>Tomato paste, protein isolate, vegetable glycerin, fruit pectin, water</td>
<td>Water soluble</td>
</tr>
</tbody>
</table>

*Pullulan is a polysaccharide polymer produced from the fungus Aureobasidium pulluns.
2.0 MODEL FOOD SYSTEM EVALUATION

2.1 Development of Model System

For initial purposes, the model system needed to favor moisture migration in a quick and consistent manner. Early model systems included a high water activity gradient and included the following:

- White bread (Aw~0.960) with creamy peanut butter (Aw~0.363)
- Unsalted Saltine crackers (Aw~0.204) with Velveeta cheese (Aw~0.942)
- Melba Toast (Aw~0.118) with Velveeta cheese (Aw~0.942)

These model systems were configured so that the LL was placed between the high water activity component and the low water activity component, and equal gram weights of each were included in the system. For the control, no barrier was used. All samples were wrapped in plastic wrap and stored at 40 °F for 4 days. However, the water activity gradients between the components were too large, and the Velveeta cheese and peanut butter proved difficult to work with for analytical purposes. For example, it was difficult to separate peanut butter from the LL or bread to take moisture measurements.

The final model system was an “open-faced” sandwich configuration. MRE white wheat snack bread (aw= 0.780) and Stop and Shop American Cheese Singles (aw=0.955) were used. The height of the cheese portion was equal to the height of the bread in order to supply an “unlimited reservoir” of moisture to the bread to encourage maximum migration. The water activity gradient between the two components was great enough to allow evident moisture migration in a short period of time. It was also important that the water activity gradient be somewhat close to what it is in a typical multi-component military ration.

Figure 1: Final model food system. Bottom to top: MRE White Wheat Snack bread, Origami Wrap® Film, American cheese.

2.2 Analysis Methodology

Once the model system was determined, bench top studies of the seven LL prototypes were performed. Each LL was placed at the interface of the model system: between the bread and cheese. A control sample, which did not contain an LL, was also tested. The top three performing LLs were evaluated further and were used in model system storage studies.
Moisture diffusion was measured gravimetrically. For these gravimetric tests, composites were constructed using a slice of MRE White Wheat Snack bread cut into four equal squares (~8 cm x 8 cm), with a height measuring approximately 1.3 cm. American cheese slices were cut into dimensions equal to the bread, and each LL was cut into squares (~8 cm x 8 cm). The weight (g) of each component was recorded.

An LL prototype was inserted between the bread and cheese components in the model system “sandwich”, either in a single layer, double layer, or both. It was ensured that the film fully covered the bread so that no cheese came into direct contact with the bread. For the control, no barrier was inserted between the bread and cheese. The samples were made in triplicate for each storage time, wrapped in plastic wrap, and then sealed in military grade tri-laminate foil pouches. The samples were stored at 40 °F for 3, 7, 14, and 28 days. These samples were stored at refrigerated temperatures because they were not shelf-stable.

The weight of each component of the sandwich, recorded prior to assembly, was determined at each pull in order to measure the amount of moisture sorption, expressed as grams absorbed per gram (dry basis) of bread. Moisture measurements were taken using a vacuum oven to determine the mass of each component. After 3 days, the first batch of sandwiches was pulled from storage. The components of the sandwich were carefully separated, and the analytical measurements were repeated. This process was performed for each storage pull.

It was predicted that moisture would migrate from the cheese, which had a higher water activity, into the bread, which had a lower water activity if no barriers were in place. Furthermore, it was predicted that similar moisture migration would be inhibited in the sandwiches containing the LLs.

The initial weights of the receptor phases were determined prior to assembly, and at each pull the bread and cheese were weighed in order to determine the extent of sorption. Grams of moisture migrated per gram of dry weight bread were calculated. For each pull, moisture absorbed through each of the films was compared to moisture absorbed in the control samples, with significance determined through a paired two-way statistical comparison, using all data in combined pull/replicate arrays.

Statistical analysis consisted of paired sample t-test comparisons of data arrays and also determination of reductions in the slopes of [% moisture gained vs. time] relationships, calculated using linear regression.

Two negative effects of moisture migration are deterioration in texture quality and deterioration in appearance quality. Texture and color analysis were performed to assess these effects for each storage pull on the three NewGem Foods™ samples (2 LLs): GemWrap® and single- and double-layer Origami Wrap®.

In the model system, deterioration in texture quality was expected to be exhibited as soggy bread. To quantify this, texture analysis that measures maximum force, in newtons, was performed on the bread in the sandwiches to assess staling, which could offset some of the negative effects of moisture migration over time. Plain pieces of bread were also stored in the same manner as the sandwiches to serve as baselines for textural measurements of the bread in the sandwiches. This baseline was used to determine if the bread staled over time. It was expected that the refrigerated storage temperature required for the shelf-stable samples would promote staling.

Deterioration in appearance quality can be manifested as color changes. For instance, bread that becomes soggy due to moisture migration may exhibit darkening due to Maillard browning and other chemical reactions. Objective color analysis was performed to quantify changes in appearance throughout storage.
Measurements were taken using a Hunter LAB colorimeter using the L*a*b* scale, which differentiates darker and lighter shades.

2.3 Analysis Results

2.3.1 Moisture Migration

Figure 2 demonstrates the effectiveness of three of the five LLs supplied by Watson, Inc. The single-sided HPMC was prepared with a double layer, and the dual-sided HPMC was prepared with a single layer. The double layer, single-sided HPMC performed best with a 26% reduction of slope (% moisture gained vs. time) in comparison with the control, closely followed by the single-layer, double-sided HPMC demonstrating a 23% reduction, and Pullulan #1 (with a single layer) with a 21% reduction. The reductions in moisture sorption were all significant at p<0.002. No results were obtained for the other two Watson LLs (Pullulan BWMB film #2 and the Alginate BWMB film) because they were exceedingly water soluble. They essentially melted into the bread within 24 h, leaving a sticky, gluey film that made it difficult to separate the components for analysis and would have been organoleptically unacceptable. Furthermore, these films did not demonstrate an ability to prevent moisture migration.

Figure 2: Effectiveness of Watson Inc. LLs in model system throughout 4 weeks of storage.

Figure 3 shows the differences in moisture migration inhibition for the two LLs (three samples) provided by NewGem Foods™. Both a single-layer and a double-layer sample of the Origami Wrap® were prepared and evaluated. The double-layer Origami Wrap® demonstrated a significant level of moisture migration inhibition (p<0.001) and reduced slope (% moisture gained vs. time) by 14% in comparison
with the control. Also significant were the data showing that single-layer GemWrap® and the single-layer Origami Wrap® reduced (% moisture gained vs. time) slope by 7% and 6%, respectively.

Figure 3: Effectiveness of NewGem Foods™ LLs in model system throughout 4 weeks of storage.

In summary, five of the seven LLs listed in Table 1 presented significant moisture barrier effectiveness in the model system, including two separate samples (single layer and double layer) of the Origami Wrap®. Increasing film thickness by incorporating a double layer of the barrier generally progressively inhibited moisture sorption into the bread as well. However, adding a second layer of the barrier also caused issues with the cohesiveness of the entire system, which would prove to be problematic for future studies and applications.

2.3.2 Texture Changes

The results of the texture analyses are shown in the Figure 4. A higher reading in maximum force (N) indicates a firmer texture, whereas a lower measurement indicates a softer and possibly soggier texture.
2.3.3 Color Changes

As shown in Figure 5, where a lower L-value indicates a darker appearance, the results from the colorimeter readings proved to be inconsistent because the bread itself had varying color measurements to begin with. Furthermore, the red color of the Origami Wrap® and the GemWrap® films transferred to the bread over time, although the color transfer did not necessarily indicate moisture migration.
3.0 MULTI-COMPONENT FOOD SYSTEM EVALUATION

The double-layer Origami Wrap®, single-layer GemWrap®, and double-layer, single-sided HPMC film were chosen for evaluation in the multi-component food system.

3.1 Preparation and Storage of Food System

Four types of shelf-stable pizza were prepared, each containing a different sample (three with an LL and the other with the control (Figure 6). The dough, sauce, and cheese were prepared separately. The pizza dough formulation is shown in Table 2. The dough was divided (~850 g/ half-sheet pan) and sheeted before being placed on paper lined sheet-pans. Sheets of each LL were laid down and lightly pressed onto the raw dough. The pizza sauce formulation is shown in Table 3. Approximately 215 g of sauce were spread evenly onto the surface of the LLs, leaving ~1 cm perimeter without sauce. Approximately 200 g of a 50/50 blend of part-skim low-moisture mozzarella cheese and a shelf-stable cheese (Thiel Pasteurized Process Mozzarella Cheese Product) was distributed evenly on top of the sauce. The control was prepared in the same way, but no LL was included in the preparation. The pizza was baked in a Hobart oven for 13 min at 375 °F. Once cooled to 80 °F, each pizza was cut into 15 equal pieces, placed in a tri-laminate foil pouch with an oxygen scavenger, and sealed.

Figure 6: Shelf-stable pizza with LLs incorporated. Left to right: GemWrap®, Single-sided HPMC, Control (no LL), Origami Wrap®.

Table 2: Dough preparation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (%)</th>
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<tbody>
<tr>
<td>Flour</td>
<td>55.07</td>
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<tr>
<td>Water</td>
<td>26.50</td>
</tr>
<tr>
<td>Shortening (Trans fat free)</td>
<td>5.58</td>
</tr>
<tr>
<td>Glycerol</td>
<td>6.50</td>
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<tr>
<td>Yeast</td>
<td>2.50</td>
</tr>
<tr>
<td>Salt</td>
<td>1.28</td>
</tr>
<tr>
<td>Sodium stearyl lactylate</td>
<td>0.75</td>
</tr>
<tr>
<td>Sugar</td>
<td>0.35</td>
</tr>
<tr>
<td>Starplex 90</td>
<td>0.35</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>0.33</td>
</tr>
<tr>
<td>Xantham gum</td>
<td>0.22</td>
</tr>
<tr>
<td>Calcium sulfate</td>
<td>0.22</td>
</tr>
<tr>
<td>ABM50</td>
<td>0.20</td>
</tr>
<tr>
<td>Alpha Amylase</td>
<td>0.05</td>
</tr>
<tr>
<td>Sorbic acid (encapsulated)</td>
<td>0.10</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 3: Sauce preparation

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tomato Paste</td>
<td>18.45</td>
</tr>
<tr>
<td>Crushed Tomatoes</td>
<td>49.80</td>
</tr>
<tr>
<td>Glycerol</td>
<td>8.00</td>
</tr>
<tr>
<td>Rice Syrup</td>
<td>5.00</td>
</tr>
<tr>
<td>Parmesan/Romano cheese</td>
<td>5.75</td>
</tr>
<tr>
<td>Olive oil</td>
<td>4.00</td>
</tr>
<tr>
<td>Sugar</td>
<td>2.00</td>
</tr>
<tr>
<td>Garlic powder</td>
<td>2.10</td>
</tr>
<tr>
<td>Onion (dehyd/chopped)</td>
<td>1.80</td>
</tr>
<tr>
<td>Salt</td>
<td>1.60</td>
</tr>
<tr>
<td>Italian Seasoning (McCormick)</td>
<td>1.30</td>
</tr>
<tr>
<td>White Pepper</td>
<td>0.15</td>
</tr>
<tr>
<td>Pepper, Red Ground</td>
<td>0.05</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
</tr>
</tbody>
</table>
3.2 Analysis Methodology

One of each of the four pizza types (each divided into 15 pieces) was placed into storage for 2 weeks at 120 °F, 4 weeks at 120 °F, 3 months at 100 °F, and 6 months at 100 °F. Moisture migration and sensory analyses were performed at each of the four intervals.

3.2.1 Moisture Migration

Moisture migration in the shelf-stable pizza was measured similarly to the method used for the model system. For each pull, including time zero, the crust portion of the pizza was carefully separated from the sauce and cheese. A sample of the bread was taken from the middle area of the crust by scraping off the top layer in contact with the sauce and extracting approximately 2.5 g. It was ensured that this sample of bread was not part of the bottom, in contact with the pan it was baked on. The exact weight of the bread sample was taken before and after being dried in the vacuum oven to determine the amount of water absorption into the bread. For each pull, moisture absorbed through each of the LLs was compared to moisture absorbed when no film was employed.

3.2.2 Sensory Analysis

Samples for sensory analysis were presented to a blind panel of 12 trained sensory technicians who rated appearance, odor, flavor, texture, and overall quality using a 9-point quality scale. Each pizza was cut into fourths, and each panelist received one-fourth of the slice to rate. Significant difference due to film incorporation was evaluated using a two-way comparison. Samples were also ranked according to average sensory scores. https://col125.mail.live.com/ol/

3.3 Analysis Results

3.3.1 Moisture Migration

After 2 weeks at 120 °F, as shown in Figure 7, the GemWrap® and single-sided HPMC barriers were more effective at slowing moisture migration into the pizza crust than the Origami Wrap® and control. Cross sections of the control pizza and the Origami Wrap® pizza are shown in Figure 8.

Figure 7: Moisture migration from sauce into crust of shelf-stable pizzas over 2 weeks storage at 120 °F.
Figure 8: Cross section of control pizza (left) and pizza with least effective LL (right), Origami Wrap®, after storage for 2 weeks at 120 °F.

Data from storage at 4 weeks at 120 °F, 3 months at 100 °F, and 6 months at 100 °F demonstrated inconsistent moisture measurements. This may have been because there was a circumference of crust around the edge into which moisture from the sauce migrated into, without going through the barrier.

While total moisture sorbed was reduced by each barrier, results were not significant at the p<0.05 level. However, it is worth noting that the single-sided HPMC film was almost significant at 2 weeks at 120 °F, with a p-value of 0.08.

3.3.2 Sensory Analysis

After 2 weeks at 120 °F, HPMC scored significantly lower in all attributes with the exception of odor. After 4 weeks at 120 °F, there were significant differences seen among all attributes except odor and flavor, but the control scored the highest in appearance, texture, and overall quality. After 3 months at 100 °F, the control scored significantly lower in odor as the only significant difference. After 6 months at 100 °F, there were no significant differences among treatments.

In conclusion, the sensory results seemed to be inconsistent. This may be because the panelists were unclear as to what was asked of them due to the novelty of the product, as well as inconsistency within the pizza itself; the pieces towards the center of the pan tended to have a much moister, doughier texture, whereas the pieces towards the edges tended to be less doughy and more desirable. In turn, the pieces towards the edges fared better throughout storage.
4.0 CONCLUSIONS AND FUTURE RESEARCH

Edible LL barriers included in this research inhibited moisture migration between sandwich layers that had differences in water activity. Some barriers inhibited moisture migration more than others, but the effectiveness of the LLs seemed to be largely dependent on the film thickness and the material. Although the films did not significantly increase sensory quality characteristics in the pizza prototypes, it was evident that they were effective in the model system. This research will be useful in future product development for ration and commercial items that are prone to moisture migration.

The data from this research was immediately transitioned to the Joint Statement of Need (JSN) “Next Generation Bakery Items”. The information in this study will continue to be used for future product development. Though it is likely that the effectiveness of a barrier is largely dependent on the system that is used, the research conducted during this study can still provide useful information in determining which barrier to use.
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BARRETT, A. Zein-Base Edible Barriers of Moisture Migration Control in Multilayer Foods. 2008.


