Edible water vapor barriers: properties and promise

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Demand for edible barriers to retard water vapor transmission has resulted in a plethora of research in this emerging area. This review addresses the development of edible barriers and what is known about their physicochemical nature, and identifies key areas for new research and industrial applications. The development of edible water vapor barriers has focused upon barriers containing lipid (which are less permeable) or protein (which are more permeable). While the application of edible barriers to processed foods has been limited, the potential of edible barrier technology for both the extension of the shelf life of processed foods and the creation of innovative foods is promising.

Recent interest in edible barriers for food packaging has grown due to the following factors:

- environmental legislation;
- expanding distribution channels;
- consumer expectations for a variety of fresh foods;
- need for extended shelf life foods;
- opportunities for new foods with edible barriers.

The development of water vapor barriers has focused upon barriers containing primarily cellulose, lipid and protein. In general, barriers containing lipid are less permeable to water vapor than barriers containing proteins. However, protein-containing barriers do have applications as edible barriers for certain products, such as fresh fruits and vegetables, that have high rates of moisture loss.

Lipid-based edible barriers

The support matrix

A non-lipid support matrix is required to reduce the brittleness/fragility associated with barriers containing lipid and to allow application of the edible barrier onto the food. The most commonly used support matrices are modified celluloses of hydroxypropylmethyl cellulose, ethyl cellulose; and methyl cellulose (Ref. 6 and Kamper, S., MSc thesis, University of Wisconsin, Madison, WI, USA, 1983), which are dissolved in ethanol–water–plasticizer solutions. Other support matrices include chitosan [poly-(1→4)-glucosamine] and whey protein isolate (WPI) in solvent–plasticizer solutions. Selective structural engineering of cellulose has been used to create synthetic cellulose structures. However, extensive research into the water vapor permeation rates of different cellulose derivatives has not been reported in the literature. Theoretically, methyl cellulose would result in a more dense (less permeable) support matrix, because of its high solubility in ethanol. Ethanol aids the formation of a uniform solution of cellulose and reduces the time required for barrier preparation and drying.

Plasticizers of various types have been incorporated into edible barriers as a processing aid, to facilitate barrier application onto foods and to increase the machinability of the edible barrier. Food-grade polyethylene glycol is the plasticizer most commonly reported in the literature. Plasticizers reduce the brittleness of the film by interfering with the hydrogen bonding between the lipid and the cellulose entities. Thus, high polyethylene glycol concentrations result in barriers with high water vapor permeabilities (Kamper, S., MSc thesis). Details of the preparation of support matrices are found in Refs 3–10.

There are essentially two types of lipid barriers, laminates (in which the lipid is a distinct layer within the edible barrier) and emulsions (in which the lipid is uniformly dispersed throughout the edible barrier). A support matrix (which comprises 50–100% of the resultant edible barrier) either provides a means to support the lipid (in the case of a laminate barrier) or disperse the lipid (in the case of an emulsion barrier). Lipid-based emulsion and laminate barriers are discussed below.

Preparation of lipid-based barriers

Lipid is added to an emulsion barrier when the cellulose (or WPI or chitosan) within the support matrix is dissolved. Once a homogeneous mixture of the lipid and support matrix has been achieved, the barrier is cast upon an impermeable (glass or metal) level plate. The water and ethanol are evaporated from the mixture at an elevated temperature (60–90°C). Once the barrier has dried/cooling to a moisture content of 2–5%, it is peeled from the plate and stored in an environment with a controlled relative humidity and temperature before testing.

The formation of a laminate barrier involves a two-step process. The molten lipid is either painted, sprayed or poured to form a distinct layer on the dry support matrix (Refs 3–5, 11, and Kamper, S., MSc thesis). The laminate is then dried/cooling, the film peeled off the plate and stored in a humidity- and temperature-controlled environment before testing.

Structure/function of the lipid within edible lipid-based emulsion and laminate barriers

Water vapor permeability depends on the type, location, volume fraction and polymorphic phase of lipid in an edible barrier.
Published data indicate that, for the same concentration of lipid and plasticizer, emulsion barriers have lower water vapor permeability than laminate barriers (Ref. 6 and Kamper, S., MSc thesis). This is due in part to the high degree of inherent tortuosity (the increased path length for water vapor diffusion due to an interlocking network of lipid within the barrier) within emulsion barriers, and in part to the tendency of laminate barriers to crack on their surface (Koelsch, C., PhD thesis, University of Minnesota, MN, USA, 1992). Water vapor diffusion through emulsion barriers follows a more tortuous path than through laminate barriers because the lipid and support matrix entities are interlocked within emulsion barriers, whereas the lipid entity within laminate barriers interconnects with the support matrix at only one interface. Laminate barriers do, however, offer the advantage of being easier to apply due to the distinct natures of the support matrix and lipid. For example, during the lamination of lipid onto a support matrix, the temperatures of the two entities can easily be controlled separately; however, during the application of an emulsion barrier, the temperature of the emulsion mixture must be above the lipid melt temperature but below the temperature for ethanol/water volatilization.

As shown in Fig. 1, the minimum water vapor permeability in a cellulose-based emulsion barrier is achieved when stearic acid is used as the lipid entity. The low permeability through barriers containing stearic acid can be explained by the fact that stearic acid forms an interlocking network: the effect of this network is significant enough that these barriers retard moisture transfer more effectively than those based on, say, myristic acid, which has shorter chain lengths, or behenic acid, which has such long chains that they hinder the formation of a tightly interlocking network. In essence, stearic acid provides the optimum chain length without hindering the formation of an interlocking network.

Kamper and Fennema and Koelsch (PhD thesis) have addressed the impact of lipid concentration on the water vapor permeability through an edible barrier. Water vapor permeability decreases with the addition of fatty acid from 28.98 g·mil·m⁻²·d⁻¹·mmHg⁻¹ for 9% stearic acid to 1.00 g·mil·m⁻²·d⁻¹·mmHg⁻¹ for 30% stearic acid [where film thickness is measured in mil: 1 mil = 0.001 in = 2.54×10⁻⁴ m; pressures are given as mm mercury: 1 mmHg = 133 Pa]. When the stearic acid concentration is in the range of 30–46%, the water vapor permeability remains relatively stable (in the range of 0.53–1.00 g·mil·m⁻²·d⁻¹·mmHg⁻¹). Epifluorescent microscopy coupled with digitized image analysis of films produced using seven different volume fractions (9–46%) of stearic acid within a cellulose support matrix yielded quantifiable results to describe the morphology of stearic acid within a cellulose support matrix (Koelsch, C., PhD thesis). Results suggested that the interlocking network of stearic acid chains within the support matrix reaches a maximum (i.e. maximum tortuosity) at ~30% stearic acid. Similar results were seen for palmitic acid (in volume fractions of 9–30%) within a WPI barrier. Permeability as a function of the volume fraction of palmitic acid or stearic acid within a matrix based on methyl cellulose, and of beeswax, stearyl alcohol or palmitic acid within a matrix based on WPI is shown in Fig. 2. This theory of an interlocking network of fatty acid chains within emulsion films is a plausible explanation for why the water vapor permeability of an emulsion barrier is approximately two times less than that of a laminate barrier of the same composition. Mathematical models to explain and predict the water vapor permeation as a function of the volume fraction and morphology of the fatty acid within a methyl cellulose support matrix have been published and are discussed below under the heading ‘Future research opportunities’.

Kester and Fennema related α, β and β’ polymorphic states of the fatty acid (lipid) component to the water vapor permeability. Results showed that barriers
Water vapor permeability as a function of the volume of palmitic acid and stearic acid within a methyl cellulose support matrix, and beeswax, palmitic acid and stearic acid within a whey protein isolate (WPI) support matrix, palmic acid : methyl cellulose matrix; stearic acid : methyl cellulose matrix; and (o), stearic acid : WPI matrix. (Fig. 2)

Zein
Prolamins such as zein are dissolved in 0.9% saline and alcohol solutions or ethyl alcohol since they are insoluble in water (Ref. 2 and Mendoza, M., MSc thesis, University of Massachusetts, Amherst, MA, USA, 1975; Trezza, T. and Vergano, P., unpublished). As with lipid barriers, when a plasticizer (e.g. glycerol) is used to decrease the brittleness of the barrier and allow its application to a food the water vapor permeability increases. As shown in Table 2, the addition of 3% glycerol increased the water vapor permeability of a specific zein barrier by 10% (Mendoza, M., MSc thesis); similarly, the addition of 20% glycerol to another type of zein barrier increased permeability by 30% (Trezza, T. and Vergano, P., unpublished). Thus, the degree to which a plasticizer impacts the water vapor permeability of these barriers was not published. Glicksman determined that the water vapor permeability of gelatin barriers with the addition of gums and CaCl₂ to induce crosslinking but the water vapor permeability of these barriers was not published. Glicksman determined that the water vapor permeability of gelatin barriers is largely a function of the relative humidity gradient due to the hygroscopic nature of gelatin. Water vapor permeabilities were in the range of 26.5–74.6 g·mil⁻²·d⁻¹·mmHg⁻¹ (~5–20 times greater than those of barriers containing fatty acids).

Protein-based edible barriers
Protein barriers, while more permeable to water vapor than barriers containing lipid, do have promise in certain food applications. The following discussion considers edible barriers containing either animal-derived (gelatin) or vegetable-derived (zein, gluten, WPI) protein. Unlike the lipid barriers, which contain a support matrix, the protein itself acts as both the support matrix and the water vapor barrier component of the film. Although animal proteins have been used historically to form edible barriers (e.g. sausage casings), the majority of recent research has focused on vegetable proteins. This shift in favor of vegetable proteins may be due to economic factors as well as the broad range of edible barriers that can be derived from the various vegetable proteins. Most of the research on the ingredient structure/function and water vapor permeability of barriers made from vegetable proteins has occurred within the last five years.

Collagen
Collagen, a natural polyamide, is the most prevalent edible barrier and is commonly used for sausage casings. Its derivative, gelatin, has been used as a key ingredient in edible barriers. Mazza and Qi formed gelatin barriers with the addition of gums and CaCl₂ to induce crosslinking but the water vapor permeability of these barriers was not published. Glicksman determined that the water vapor permeability of gelatin barriers is largely a function of the relative humidity gradient due to the hygroscopic nature of gelatin. Water vapor permeabilities were in the range of 26.5–74.6 g·mil⁻²·d⁻¹·mmHg⁻¹ (~5–20 times greater than those of barriers containing fatty acids).
permeability two orders of magnitude larger than those developed in laboratory environments.

Gluten

Gontard et al. assessed the structure/function of ingredients within gluten edible barriers manufactured from 5-12.5% gluten, 20-45% ethanol and 30% glycerol. The lowest water vapor permeability (25.84 g·mil·m⁻²·d⁻¹·mmHg⁻¹) was achieved when the barrier was made with 10% gluten and 45% ethanol and at a pH of 4.5. The barrier with the highest water vapor permeability was made as above except at a pH of 2.0. Gennadios and Weller developed a barrier composed of gluten and soy protein (2:1). The pH and level of plasticizer were not reported. The resultant permeability was ten times that reported by Gontard et al. Use of high-glutenin gluten as a support matrix within an edible barrier has particular promise due to its inherent fibrous structure, its high degree of extensibility and the presence of α-helices (which restrict interactions with other molecules such as water). Research on the water vapor permeability of high-glutenin gluten has not been reported.

WPI

McHugh et al. explored the impact of WPI concentration (7.9 and 12% in solution before drying), solution pH (5.0-10) and plasticizer type (glycerol, sorbitol, polyethylene glycol) on the water vapor permeability through barriers composed of WPI, lipid and plasticizer. The results showed that the optimum concentration for development of WPI-based barriers is 10% (concentration in solution before drying), largely due to the fact that strong gelling occurs at concentrations exceeding 10%. Strong gels inhibited barrier formation at pH values greater than 9.0 when heterogeneous barriers were formed. WPI barriers using 50% sorbitol as the plasticizer had significantly lower water vapor permeabilities than those containing either 50% glycerol or 50% polyethylene glycol. Water vapor permeability as a function of the percentage glycerol increased linearly with increasing level of barrier hydration (higher RH values) and gluten-based barriers may be a result of the increased level of barrier hydration (higher RH values) in the zein barriers. More research is needed to establish firmly how water vapor permeation is affected by the relative humidity.

Selecting and developing an edible water vapor barrier

As with synthetic barriers, some edible barriers are applicable in certain situations and inapplicable in others. For example, it would be more appropriate to use an edible barrier with a low water permeability for a food with a high water activity (aₕ) and long shelf life than a barrier with a high water permeability. Predicting the required water vapor permeability that an effective edible barrier must exhibit saves both time and energy in the development or selection of an appropriate edible barrier.

A procedure has been developed to determine what water vapor permeability an edible barrier must have to be the predominant factor in retarding moisture loss from a food coated with an edible barrier. This procedure, which has been detailed by Hong et al., involves the empirical determination of the rate of water vapor loss (i.e. moisture migration) from the food, the application of classical diffusion equations and the concepts of Tanoukis et al. The final result is a

Table 1. Summary of the water vapor permeabilities of selected edible barriers containing lipid in or on a cellulose support matrix

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Permeability (g·mil·m⁻²·d⁻¹·mmHg⁻¹)</th>
<th>RH (%)</th>
<th>Thickness (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion lipid barriers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid/soy matrix</td>
<td>0.53</td>
<td>12-56</td>
<td>1.9</td>
</tr>
<tr>
<td>Steric acid/soy matrix</td>
<td>0.17</td>
<td>0-85</td>
<td>1.3</td>
</tr>
<tr>
<td>Stearic acid/palmitic acid</td>
<td>0.24</td>
<td>0-85</td>
<td>1.5</td>
</tr>
<tr>
<td>Olive acid/soy matrix</td>
<td>19.31</td>
<td>0-85</td>
<td>1.3</td>
</tr>
<tr>
<td>Laminate lipid barriers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid/palmitic acid</td>
<td>0.30</td>
<td>0-97</td>
<td>2.2</td>
</tr>
<tr>
<td>and bpe wax</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid/palmitic acid</td>
<td>0.46</td>
<td>0-85</td>
<td>4.4</td>
</tr>
</tbody>
</table>

- Data taken from Ref. 4
- Data taken from Ref. 1
- Data taken from Ref. 11
- RH, Relative humidity

\[ \text{Oxygen permeability was } \frac{11 \text{ g·mil·m}^{-2} \cdot \text{d}^{-1} \cdot \text{mmHg}^{-1}}{29} \text{ for these parameters.} \]

Subsequent work addressed substituting WPI/16% sorbitol for the methyl cellulose support matrix commonly used in lipid emulsion barriers. While the films are predominantly protein based, lipid entities have been added to complement the barrier properties. Transmission electron microscopy showed that the lipid (in this case stearyl alcohol) was a discrete entity within the WPI. This differs from the configuration of lipid within the methyl cellulose support matrix, in which the lipid forms an interlocking network within the support matrix (Koelsch, C., PhD thesis). This difference in the morphology of the lipid within the two support matrices could explain the difference in the water vapor permeability of the two types of barriers shown in Fig. 2.

The water vapor permeability through a palmitic acid/methyl cellulose matrix was 2.93 g·mil·m⁻²·d⁻¹·mmHg⁻¹, while the permeability through a palmitic acid/WPI matrix was 4.65 g·mil·m⁻²·d⁻¹·mmHg⁻¹ at a volume fraction of 29% palmitic acid.

A select listing of the reported water vapor permeability properties of edible barriers containing protein is shown in Table 2. The greater water vapor permeability values for the zein-based barriers as compared with the WPI- and gluten-based barriers may be a result of the increased level of barrier hydration (higher RH values) in the zein barriers. More research is needed to establish firmly how water vapor permeation is affected by the relative humidity.
Table 2. Summary of the water vapor permeabilities of edible protein barriers

<table>
<thead>
<tr>
<th>Barrier</th>
<th>Permeability (g·mil·m⁻²·d⁻¹·mmHg⁻¹)</th>
<th>RH (%)</th>
<th>Thickness (mil)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zein barriers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zein</td>
<td>226.12</td>
<td>50-100</td>
<td>8.0</td>
</tr>
<tr>
<td>Zein/20% glycerol</td>
<td>318.89</td>
<td>50-100</td>
<td>8.0</td>
</tr>
<tr>
<td>Zein/3% glycerol</td>
<td>1462.00</td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>WPI barriers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WPI/28% palmitic acid/16% sorbitol</td>
<td>4.65</td>
<td>0-100</td>
<td>5.4</td>
</tr>
<tr>
<td>WPI/28% beeswax/16% sorbitol</td>
<td>4.94</td>
<td>0-100</td>
<td>6.73</td>
</tr>
<tr>
<td>WPI/28% stearyl alcohol/16% sorbitol</td>
<td>11.21</td>
<td>0-100</td>
<td>5.9</td>
</tr>
<tr>
<td>WPI/16% sorbitol</td>
<td>12.78</td>
<td>0-100</td>
<td></td>
</tr>
<tr>
<td>Gluten barriers</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gluten/20% glycerol, pH of 4°</td>
<td>23.84</td>
<td>0-100</td>
<td>1.9</td>
</tr>
<tr>
<td>Gluten/20% glycerol, pH of 2°</td>
<td>42.56</td>
<td>0-100</td>
<td>1.9</td>
</tr>
<tr>
<td>Gluten/soy protein isolate</td>
<td>248.83</td>
<td></td>
<td>0.3</td>
</tr>
</tbody>
</table>

- Data taken from Trozza, T. and Vergano, P., unpublished
- Data taken from Mendoza, M., MSc thesis
- Data taken from Ref. 11
- Data taken from Ref. 19
- Data taken from Ref. 2
- RH, Relative humidity
- WPI, Whey protein isolate

Future research opportunities

Basic research

The majority of the research into edible barriers has explored the barrier component within the edible barrier. Research into the modification, or use, of alternatives to cellulose and proteins currently used as the support matrices, and also into the selection or development of plasticizer is needed. Specifically, research into the influence of the support matrix on the morphological character of lipid within the edible barrier is a critical next step in understanding edible barrier ingredient functionality. Little is known about the oxygen permeability, organoleptic properties, tensile strength, scalability, glass transition temperature and grease resistance of developed edible barriers.

Predictive methods

Attempts to predict water vapor permeability through a barrier based on the water vapor permeabilities through the distinct phases [i.e. the support matrix (the continuous phase) and the barrier components (the dispersed phase)] have been moderately successful in specific applications. Extensive research into the physicochemical nature of components within an edible barrier is needed to allow predictions of water vapor permeability and to understand further how the properties of an edible barrier can be optimized in a manner similar to that commonly used to develop synthetic polymers.

Applications of edible barrier technology

With the plethora of edible barriers, some of which are shown in Tables 1 and 2, the creative application of these barriers within new processed foods is imminent. While oxygen permeabilities have not been reported extensively in the literature, edible oxygen barriers do have particular promise for the packaging of oxygen-sensitive foods. The major hurdle to the application of edible barrier technology in the processed food industry is the lack of industrial-scale processes to produce edible barriers. This is a necessary step towards the increased use of edible barriers and realization of the important role they will play in future food product and package development. Potential industrial applications of edible barriers include:

- retaining the flavor and maintaining water activity differences between foods within heterogeneous food systems (such as enrobing differently spiced crackers within a cracker package, components within a frozen pizza and the crust of frozen pies);
- allowing controlled flavor release by enrobing sensitive flavors with a temperature-sensitive barrier that will release the flavor upon heating;
- extending the shelf life of controlled/modified-atmosphere packaging (CAP/MAP) foods by enrobing fruits and vegetables with different respiration rates with different edible barriers;
- reducing the rate of degradation reactions in complex food systems by selectively enrobing lipids, proteins, and water to decrease the rates of lipid oxidation, nonenzymatic browning and microbial growth.

References

5. Green, J. and Fennema, O. (1989) J. Food Sci. 54(4), 1403-1408
The increasing economic pressures currently being placed upon animal producers demand more-efficient utilization of low-grade feedstuffs. In addition, consumer awareness and new legislation require that any increase in animal production cannot be achieved via growth-promoting drugs or other chemical substances. One increasingly popular approach to this problem is to supplement animal diets with hydrolytic enzymes in an attempt to aid the digestion and absorption of poorly available nutrients, or to remove antinutritional factors from the diet. Concerns raised by this practice include the ability of such enzymes to survive processing temperatures and even the animals' digestive tract.

Enzymes are routinely employed in a myriad of industrial applications. Traditional applications include their use in food processing as well as in the brewing, baking and leather-bating industries. Selected proteolytic activities are also incorporated into detergent preparations. Such applications are described extensively in the literature and have gained widespread scientific and industrial acceptance. An increased understanding of enzymes and their properties now suggests several novel applications for these biological catalysts. One such application which, to date, has gained only limited attention from the general scientific community, is the use of selective enzyme activities in the animal-feed industry.

Virtualy all enzymes employed in the animal-feed industry are hydrolyases, which are used directly as feed additives to achieve any, or all of the following objectives:

- supplementation of the endogenous digestive activities of the host animal, including proteases and amylases;
- removal of antinutritional factors such as β-glucans and phytic acid from problematic feedstuffs;
- to render certain nutrients more-readily available for absorption and to enhance the energy value of cheaper feed ingredients.

Antinutritional factors in feed

The bulk of animal-feed constituents are vegetable in nature. As a consequence, many feedstuffs contain components that may be considered antinutritional. Such antinutritional factors (ANFs) interfere with the digestibility, absorption or utilization of nutrients and, hence, adversely affect animal performance. Most ANFs are produced by plants as natural protection against attack by microbes, insects and birds. Several studies have shown that the protective effects of ANFs are related directly to their ability to perturb metabolic processes in microorganisms and insects. Because of similarities in digestive processes, ANFs can also be expected to disturb the digestive processes of farm animals. In general, ANFs are antinutritional because organisms ingesting them lack the appropriate enzymes in their gastrointestinal tracts to render them ineffective. ANFs work in a variety of ways, from the complexing of important...