Modeling Shelf Life in Packaging Using Moisture Diffusion Properties

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Introduction

Shelf life and impact factors

Shelf life is the period after the manufacturing of a food product during which the product remains safe to consumers, retains desired sensory, chemical, physical and microbiological characters, and also complies with any label declaration of nutritional data (Kilcast et. al 2000). Many factors can influence shelf-life, and can be categorized into intrinsic and extrinsic factors. These factors can be combatted with different kinds of preservation methods that will help to extend the product's shelf life. The intrinsic factors used in shelf-life prediction models are characteristics of the food itself, e.g. pH, water activity (a_w), oxidative-reduction potential (E_h) and preservatives added to the food. The extrinsic factors that can effect shelf life and product quality are characteristics of the environment in which the food is stored, e.g. temperature, gaseous atmosphere and humidity.

Extrinsic factors in shelf life predicting

Storage conditions such as temperature, relative humidity and different lights (UV, IR and y etc.) have various impacts on food products. Food scientists have tried to prolong food products' shelf lives for years by employing many strategies, including altering the storage conditions. These elements all impact the shelf life of certain products like low moisture foods, and are used in shelf life prediction for these products.

Shelf life of low moisture foods

Low moisture food products normally have a long shelf life, but it can be cut short because of water absorption during storage. The control of initial water activity and moisture migration is critical to the quality and safety of low moisture foods. Ideally, food manufacturers will develop products with defined water activities to produce a safe product with optimum shelf-life (Labuza et. al 1998). The quality estimation of low moisture products must consider the microbial stability, physical properties, sensory properties and the rate of chemical changes, which all lead to loss of shelf-life. Excess water that has migrated through the package will be absorbed by low moisture food, changing its water activity, which can significantly influence its shelf life. The amount of moisture absorbed through the package prior to reflow has been known to have a strong influence on the susceptibility of low moisture products like popcorn cereal to moisture induced changes (Wong et al 1999). Generally, the moisture diffusion properties of packaging is critical to the prediction of the shelf-life of low moisture products.

Application of mathematical modeling for shelf life prediction requires sufficient knowledge of the product's spoilage mechanisms (Koutsoumanis et. al 2001). For low moisture products, since the water activity is very low and the foods are hygroscopic, they will easily absorb any moisture that diffuses through the packaging materials. In practice, low moisture foods, like cereal or formula, are not stored under controlled conditions, allowing for exposure to potentially high relative humidities (Koutsoumanis et. al 2001). Under these abusive conditions, any water that transfers through the packaging material will have a significant impact on its quality and thus shelf life.

While models have been proposed in the literature to predict shelf life using package properties, the models tend to be complicated in nature and difficult to put into application

(Azanha and Faria, 2005, Nobile et al. 2003). The objective of this project was to develop an easy to use shelf life model based on first principles and Fickian diffusion. The model determines shelf life based on maintaining the water activity in the package below (or above) a specified critical water activity. To facilitate application, a user-friendly, straightforward excel-based program was designed to provide a tool that would facilitate changing input parameters and then observing the impact on shelf life. This model will be able to be used for any products and packaging just by simply adjusting the variables accordingly.

Materials and Methods

Three different brands of corn flakes and two different brands of baby formula were obtained from a local grocery store. The baby formula was packaged in small single-serve packets that are foil-lined while the corn flakes were packaged in plastic bags placed inside cardboard secondary packaging. Table 1 outlines the properties of the sample products and their packaging.

Moisture Properties

The as-is water activity of each of the samples was determined using an AquaLab 4TE Water Activity Instrument (Decagon Devices, Inc Pullman, WA). Moisture sorption properties of each of the materials was determined at 25 °C using the Dynamic Dew Point Isotherm (DDI) method in the AquaLab Vapor Sorption Analyzer (Decagon Devices, Inc. Pullman, WA) with an starting water activity of 0.30 a_w, a final water activity of 0.85 a_w, and a flow rate of 80 ml/min. The DDI curves for each sample were used to determine the critical water activity using a Savistky-Golay 2nd derivative as described in Yuan et al. (2011). The average critical water activity was used across sample for each product type. Linear regression of the moisture sorption isotherm curves of each sample, using only data generated at water activities less than the critical water activity, was used to determine isotherm slope for each sample. The average slope was used across samples within a product type. Water vapor transmission rates (WVTR) of the foil line baby formula packaging was assumed to be 0.001 $g/m^2\ s$. The WVTR value for the cereal packaging was determined at 25 °C using the PERMATRAN-W Model 33 (Mocon, Minneapolis, MN).

Table 1: Packaging Description and water activities of sample products purchased on 11/14/2013.

Product	Package Size	Best by date	Shelf Life (days)	Water Activity	Critical Water Activity	Surface Area of Packaging (m2)
Kellog's Corn Flakes	18 oz. (510.3 g)	10/3/14	323	0.1898	0.6600	0.1600
Great Value Corn Flakes	18 oz (510.3 g)	10/19/14	339	0.1504	0.6600	0.1600
Post Grape nuts Flakes	18 oz (510.3g)	7/9/15	240	0.1998	0.6600	0.1600
Similac Advance singles infant formula	0.61 oz (17.3 g)	8/1/2014	627	0.1834	0.4300	0.0124
Enfamil Premium Infant Formula	0.62 oz (17.6 g)	9/1/14	292	0.1805	0.4300	0.0124

Shelf Life Prediction

Shelf life was predicted using a model derived from Fick's 1st law of diffusion which determines shelf life based on the change in water activity over time of a product in package as it approaches the critical water activity. The model uses the moisture diffusion properties of the product packaging and the storage conditions to calculate the change in water activity over a specific time period. From Fick's first law of diffusion, the evaporation rate (*E*), identified as the WVTR value of a package, can be determined using equation (1).

$$WVTR = E = \frac{ke_s\left(a_{wout} - a_{win}\right)}{x} \qquad (1)$$

Where WVTR is water vapor transmission rate (g/m_2 s), *k/x* is package permeance (g/m_2s *kPa*), a_{wout} is the storage relative humidity, a_{win} is the water activity of the product in the package, and es is saturated vapor pressure (*kPa*). The total evaporation or diffusion over time (*Q/dt*) is the product of evaporation and surface (*EA*) and is equal to the change in water mass over the change in time. By adding surface area (*A*) to equation (1), Fick's 1st law for evaporation, we get equation (2).

$$Q/dt = EA = \frac{\Delta Mass_{water}}{\Delta time} = \frac{ke_s A\left(a_{wout} - a_{win}\right)}{x} \qquad (2)$$

Where *k/x* is package permeance (g/m_2s *kPa*), awout is the storage relative humidity, a_{win} is the water activity of the product in the package, es is saturated vapor pressure (*kPa*) and *A* is the package surface area (m_2). The permeance value (*k/x*) in equations (1) and (2) actually

consists of several permeances in series. The inverse of permeance is resistance and since resistances are additive, the permeances in series can be combined using equation (3).

$$\frac{k}{x}_{total} = \frac{1}{\dfrac{x}{k_{food}} + \dfrac{x}{k_{package}} + \dfrac{x}{k_{boundary}}} = \frac{k}{x}_{package} \qquad (3)$$

The permeance of the packaging will be so much smaller, or the resistance to water vapor movement through the packaging will be so much greater than the other barriers shown in equation 3 that the permeance of the package can be assumed to be equivalent to the total permeance and will be used for all calculations in this model. Based on the calculation for the moisture content of a product, the change in mass of water of the product in the package can be related to the moisture content (*g/g* dry solids) and the dry mass of the sample (M_s) using equation (4).

$$\Delta Mass_{water} = moisture\ (\text{g/g dry solids})*M_s \qquad (4)$$

Combining equations (2) and (4) now provides an equation for the change in moisture content over time (5).

$$\frac{\Delta moisture}{\Delta time} = \frac{ke_s A\left(a_{wf} - a_{wi}\right)}{M_s x} \qquad (5)$$

Where *k/x* is package permeance (g/m_2s *kPa*), a_{wi} is the storage relative humidity, a_{wi} is the water activity of the product in the package, e_s is saturated vapor pressure (*kPa*), *A* is the package surface area (m_2), and M_s is the dry mass of the sample (*g*).

A change in moisture content can be related to the water activity using the moisture sorption isotherm and equation (6).

$$\Delta moisture = \alpha \Delta a_w \qquad (6)$$

Where α is the slope of the moisture sorption isotherm (*g/g* dry solids) and a_w is the water activity. By combining equation 5 and equation 6, the model can now be tracked as a change in water activity as in equation (7).

$$\frac{\Delta a_w}{\Delta time} = \frac{k e_s A\left(a_{wf} - a_{wi}\right)}{\alpha M_s x} \qquad (7)$$

Where *k/x* is package permeance (*g/m*^{2}*s kPa*), a_{wf} is the storage relative humidity, a_{wi} is the water activity of the product in the package, Δa_w is the change in water activity, *Δtime* is the change in time, e_s is saturated vapor pressure (*kPa*), *A* is the package surface area (*m*^{2}), and M_s is the dry mass of the sample (g), and M_s is the slope of the moisture sorption isotherm (*g/g* dry solids). Rearrangement of equation (7) to bring the water activity terms together gives equation (8).

$$\int_{a_{wi}}^{a_w} \frac{\Delta a_w}{\left(a_{wf} - a_{wi}\right)} = \int_0^t \frac{k e_s A}{\alpha M_s x} \Delta t \qquad (8)$$

which after integration gives equation (9).

$$\ln \frac{\left(a_{wf} - a_w\right)}{\left(a_{wf} - a_{wi}\right)} = -\frac{k e_s A}{\alpha M_s x} t = -\frac{t}{\tau} \qquad (9)$$

$$\text{where } \tau = \frac{\alpha x M_s}{e_s A k}$$

Equation (9) can now be used to predict the change in water activity when stored under different ambient conditions over various time lengths with equation (10), and

$$a_w = a_{wf} - (a_{wf} - a_{wi})\exp(-t/\tau) \qquad (10)$$

the shelf life based on the water activity reaching a critical water activity with equation (11),

$$t_{shelf} = -\tau \ln\left(\frac{a_{wf} - a_{wc}}{a_{wf} - a_{wi}}\right) \qquad (11)$$

where a_{wc} is the critical water activity. Finally equation (9) can be used to determine the package permeance needed to achieve a desired shelf life by determining the time constant using equation (12)

$$\tau = \frac{t}{-\ln\left(\frac{a_{wf} - a_{wc}}{a_{wf} - a_{wi}}\right)} \qquad (12)$$

where time *t* will be the desired shelf life, and then solving for permeance by plugging the time constant into equation (13).

$$\frac{k}{x} = \frac{\alpha M}{e_s A \tau} \qquad (13)$$

The permeance can be converted to WVTR using equation (14), assuming that ASTM D3079 (2000) is used to determine the WVTR using desiccant.

$$WVTR = \frac{k(e_s a_{wf})}{x} = MassFluxDensity \qquad (14)$$

Where *k/x* is package permeance (*g/m*^{2}*s kPa*) from equation (13), a_{wf} is the control relative humidity used to determine the WVTR, and es is saturated vapor pressure (*kPa*) at the temperature used to determine WVTR.

Results

The shelf lives and water activities of the obtained cereal and baby formula products are outlined in Table 1. Attempts to obtain the WVTR of the cereal packagings were performed using the PERMATRAN-W Model 33 (Mocon, Minneapolis, MN), however successful data was not achieved. Five separate trials each using 2 replicates of each film were conducted, and every one failed to obtain an accurate WVTR for the films. It was postulated that this failure could be attributed to the rigid 3-D structure held by the packaging. Since the actual WVTR of the packagings could not be obtained, true comparisons to the products' listed shelf life and the shelf life prediction from the model could not be made.

Additionally, an accurate comparison of shelf life would require use of the same critical water activity (a_{wc}) at which shelf life ends. The a_{wc} values listed in table 1 are those associated with the glass transition of the product, after which point the quality and stability of the food deteriorates very quickly (Carter et. al 2012). In actuality, the a_{wc} set for these products are probably much more conservative, most likely indicating a noticeable change in texture or loss to do some other quality loss factor. In this model, any a_{wc} desired by the user can be used to determine shelf life. The a_{wc} can be adjusted to indicate whatever quality

parameter is most important to the low moisture food of interest. The user can choose to end shelf life at either slight or extreme changes in texture, consistency, clumping of powders, staling, potential for microbial growth, or other factors that are associated with a certain a_w in the product. If the a_w accompanying the (un) desirable change in the product is not already known, some experimentation will be needed to determine this value.

In some products, other reactions such as oxidation of lipids and nutrients might be equally or more important in the deterioration that ends shelf life. These reactions are usually not accompanied by a huge change in aw; however, studies have shown that the oxidative stability of low moisture cereals is affected by relative humidity (Risbo 2006), therefore an a_{wc} could be designated for the point at which the rate of oxidative reactions begin to increase significantly. If other chemical reactions are vitally important to shelf life, more complex modeling in the software will be needed to take those parameters into account. Generally speaking, the more complexity a food product has, the more experimentation and mathematical modeling will be needed to obtain an accurate shelf life model. Nonetheless, when moisture migration is a key factor in product quality and shelf life, this model can be used to successfully determine the shelf life of a product under a given set of conditions, demonstrate how changes in environment or packaging will affect the shelf life, and show what WVTR is needed by a packaging to obtain a shelf life of a desired length (see attached excel sheet for examples of implementation of the model).

Discussion

Determining the useful shelf life of a product is an important part of product development and quality assurance. There are several different types of chemical reactions and environmental conditions that can degrade food quality. The types of reactions and stimuli that will have the biggest negative impact on a food product is dictated by the composition of that food. For most low moisture foods, moisture migration from the environment, through the packaging, and into the food during storage presents one of the biggest threats to the quality of the food. For most low moisture foods, moisture migration from the environment, through the packaging, and into the food during storage presents one of the biggest threats to the quality of the food. Many of the factors influencing shelf life, including moisture migration, can be controlled by packaging, therefore package selection is a crucial part of maintaining the stability and quality of a food. In this study, a user friendly shelf life prediction model was created using first principles and Fickian diffusion. This model can be used to successfully determine the shelf life of a product under a given set of conditions, demonstrate how changes in environment or packaging will affect the shelf life, and show what WVTR is needed by a packaging to obtain a shelf life of a desired length.

Shelf life is a subjective concept. An expiration or best by date on a product may indicate that the product is no longer safe for consumption, has experience degradation in the level of nutrients listed on the package, or has suffered a decrease in quality in one form or another. When shelf life is based on a parameter of quality, the manufacturer may choose to end "usable" shelf life at whatever quality marker they see fit. They can be very conservative in their designation of shelf life, giving the product a shorter shelf life to ensure the highest quality, or more liberal, allowing more of a possible quality decline to provide a longer shelf life. This flexibility and subjectiveness of shelf life can be observed in the baby formulas listed in Table 1. Although the two brands were purchased on the same day, have similar compositions, water activities, and presumably identical packaging, their shelf lives differ by 11 months. While slight variances in formulation might give one brand a higher level of intrinsic preservation, it is also possible that the two brands use different quality parameters for shelf life determination, or one brand uses a more conservative measure than the other.

Conclusion

While there is much subjectivity regarding shelf life decisions, the manufacturer of a product should make educated choices in determining the proper shelf life after much experimentation and predictive modeling. The model created in this study is a useful tool to aid developers in determining the shelf life and optimal packaging for their low moisture products. Once a critical water activity has been decided, the model will give accurate predictions on the number of days it will take until the product reaches that value in a given environment. The model can also show users how certain environmental conditions will alter the shelf life, and what WVTR values are needed by their packaging to attain a desired shelf life. While this particular model does not account for all factors influencing shelf life, when moisture migration is a key concern to the quality of a product, this model will serve as a valuable, easy to use prediction aid to manufacturers of low moisture foods.

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