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Food stability determination by macro–micro region concept in the state diagram and by defining a critical temperature

Mohammad Shafiur Rahman *

Department of Food Science and Nutrition, Sultan Qaboos University, P.O. Box 34, Al Khod 123, Oman

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ABSTRACT

In the 1950s the concept of water activity was proposed for determining food stability. This concept is now being used although it has some limitations. Indeed, these limitations mean that the concept is not universally applicable and in fact is invalid under certain conditions. In order to address the limitations of the water activity concept, the glass transition concept was proposed in the 1960s, although significant application of the concept only started in the 1980s. Recently, it has become evident that the glass transition concept is also not universally valid for stability determination in all types of foods when stored under different conditions. Currently in the literature the need is emphasized to combine the water activity and glass transition concepts since both concepts could complement each other. The glass transition concept was used to develop the state diagram by drawing another stability map using freezing curve and glass transition line. In this paper an attempt is made to review the published methods used to combine both concepts. These approaches are graphical plot of glass transition conditions and water content as a function of water activity, and macro–micro region concept in the state diagram. In addition, a new approach is proposed in this paper by defining a critical temperature for stability and then relating it with water content, and other hurdles affecting food stability. The water mobility concept is also reviewed to provide another dimension of food stability in order to determine a more complete picture.

1. Introduction

Food preservation involves the action taken to maintain the desired properties or nature of foods, within a time frame, so that it remains safe and pleasant to consume. A stable food product can be developed by applying different processing techniques and by keeping it in appropriate conditions. Food stability determination from a scientific basis rather than empiricism is a challenge to food scientists and engineers. A relatively complete coverage of food preservation is available in the Handbook of Food Preservation and other references (Rahman, 2007a; Kalichevsky-Dong, 2000). Microbial death/growth and deteriorative physical, chemical and biochemical changes during processing and storage depend on many factors, such as water content, food composition, preservatives, pH, and environmental or processing factors (temperature, pressure, electricity, gases or vapors). A list of hurdles for increasing food stability is included in Table 1. A significant proportion of the food products on the supermarket shelf are preserved based on the main hurdle being pH, water activity, low temperature (freezing and refrigeration) or heat treatment (pasteurization and sterilization). In addition other hurdles are imposed in combinations, such as including spices and packaging.

In the 1950s the concept of water activity was proposed to determine the stability of foods and in the 1980s significant data on food stability as a function of water activity was published. To avoid the limitations of the water activity concept, the glass transition concept was extensively applied in the 1980s although the concept had initially appeared in the literature much earlier in the 1960s. The stability of foods is of the up most importance to both food scientists and engineers; and a better understanding of the factors controlling stability or reactions rates is clearly needed (Le Meste et al., 1997; Kalichevsky-Dong, 2000; Rahman, 2006). In this paper the concepts of water activity and glass transition are summarized and their applications and limitations identified. A macro–micro region concept combining water activity and glass transition concepts in the state diagram was first presented in the 18th International Congress of Chemical and Process Engineering (CHISA 2008), 24–28 August 2008, Prague, Czech Republic, and was subsequently published in the International Journal of Food Properties (Rahman, 2009). In this current paper an attempt is made to further explain the macro–micro region concept and to present its applications in food processing as well as in determining food stability during storage. In addition, a new approach is proposed by defining a critical temperature for stability, which

* Tel.: +968 2414 1273; fax: +968 2441 3418.
E-mail address: shafiur@squ.edu.om

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Nomenclature

G	modulus (Pa)
k	rate constant (day^{-1})
m	fragility parameter
NMR	Nuclear Magnetic Resonance
T	temperature (°C or K) or NMR signal
X	mass fraction (g/g sample)

Greek symbol

α	high-density region
β	low-density region

Subscript

b	BET-monolayer water
c	critical (where change in slope)
g	glass transition
gs	glass transition solids
gw	glass transition water
m	melting point of ice (i.e. freezing point)
ms	melting point of solids
s	solids
u	eutectic point
w	water
2	rate constant for decay of peroxide value in k

Superscript

$'$	maximal-freeze concentration condition in X, and T or storage in G
$'$	intersection point of freezing curve and glass line or loss in G
$'''$	initiation of glass transition at maximal-freeze concentration measured by DSC
iv	non-ideal plasticization above maximal-freeze concentration condition

could be further related with water content and other hurdles in food stability.

2. Water activity concept

In the 1950s scientists began to discover the existence of a relationship between the water contained in a food and its relative tendency to spoil (Scott, 1953). It was observed that the active water could be much more important to the stability of a food than the total amount of water present. Thus, it is possible to develop generalized rules or limits for the stability of foods using water activity. For example, there is a critical water activity level below which no microorganisms can grow. Pathogenic bacteria cannot grow below a water activity of 0.85, whereas yeasts and molds are more tolerant to reduced water activity, but usually no growth occurs below a water activity of about 0.6. It has been widely recognized that the concept of water activity has been accepted as a valuable tool for determining microbial stability (Chirife and Buera, 1996). A complete discussion on the microbial response to low water activity was presented by Rahman (2009).

A food product is the most stable at its "monolayer moisture" content, which varies with the chemical composition, structure and environmental conditions, such as temperature. The BET-monolayer value can be determined from the well known BET-equation. The BET-monolayer estimation is an effective method for estimating the amount of water molecules bound to specific polar sites in a food matrix and it does not simply apply to the product surface. A more detailed explanation of the BET-monolayer, including their estimation and validity was recently provided by Rahman and Al-Belushi (2006). In general the rule of water activity concept is: *Food products are most stable at their "BET-monolayer moisture" content or "BET-monolayer water activity" and unstable above or below BET-monolayer*. However, experimental evidence showed that optimal moisture for stability was in the multilayer adsorption region (Caurie, 1971a, b). In many other instances it has been shown that optimal water content for stability is not exactly the BET-monolayer. The reason for this variation is due to the fact that the BET theory of adsorption was developed based on many simplified assumptions, which are not realistic when food is considered.

Table 1
List of various hurdles in food stability.

Inhibition	Inactivation	Avoid recontamination
Acidification	Blanching	Aseptic packaging
Adding antioxidants	Cooking	Hygienic processing
Adding preservatives	Electrifying	Hygienic storage
Change in phase transitions	Extrusion	Packaging
Change in state transitions	Frying	
Chemical modifications	Irradiation	
Control of pH	Light	
Decrease of oxygen	Magnetic field	
Fermentation	Pasteurization	
Gas removal	Pressure treatment	
Increase of carbon dioxide	Sanitation	
Low temperature storage	Sound	
Reduction of water activity	Sterilization	
Structural modifications		
Surface coating		

Adapted from Rahman (2007a).

One of the earlier food stability maps based on the water activity concepts contained growth of micro-organisms and different types of bio-chemical reactions (Labuza et al., 1972). The updated food stability map based on the water activity is presented in Fig. 1 (Rahman, 2009). In this present map, the trends of microbial growth, bio-chemical reactions and mechanical characteristics are presented in the three zones of water activity. This stability map indicates that different types of dynamics in reaction rates can happen as a function of water activity. An example is shown in Fig. 2 using the process of non-enzymatic browning. This figure illustrates the non-enzymatic browning rate at 70 °C in a gelatinized starch medium as a function of water activity and moisture content (Acevedo et al., 2008). The figure shows that the reaction rate increased with increasing water activity up to the BET-monolayer (i.e. reached a peak) followed by a decrease in the reaction rate with further increases in water activity. In this example, the matrix is most stable below the BET-monolayer as expected; and above BET-monolayer, reaction rate decreased instead of showing an increasing trend (i.e. stability increased at least for non-enzymatic browning). However, this could be explained due to the dilution effect of solvent water at higher moisture. However, the purpose of this example is not to overemphasize the BET-monolayer or to draw conclusions concerning non-enzymatic browning, but rather to present an example of a food stability map including the BET-monolayer.

The limitations of the water activity concept are identified as (Rahman and Labuza, 2007; Rahman, 2005, 2006; Chirife, 1994;