FOOD PRODUCT-PACKAGE COMPATIBILITY

PROCEEDINGS

edited by:

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Proceedings of a Seminar
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FOREWORD

Packaging is an integral part of the processing and preservation of foods. Foods are perishable commodities. Most will undergo some form of processing for preservation purposes. Associated with the basic food processing methods is proper food packaging. Selection of the food packaging system is very critical and is based on a knowledge of the composition and stability of the food product itself and on a consideration of the environmental factors to which the food product/package system is exposed during distribution and storage. The compatibility of the package with the method of preservation selected, as well as the effect of possible migration from the packaging material to the food contact phase on product quality and safety, must also be considered.

This book represents the proceedings of a seminar sponsored by the School of Packaging, Michigan State University, East Lansing, Michigan, July 14–16, 1986. The speakers were from industry, universities and government agencies and provided a very broad perspective on the general subject area, food product/package compatibility. Included in this book are chapters which are essentially reviews, while others represent original, in-depth research reports on important topics in food packaging. Major topics in food packaging addressed in "Food Product-Package Compatibility" include the performance and safety of packaging materials, test methods and results, migration and barrier studies, FDA acceptance criteria, design considerations, and tamper-evident packaging.

We believe that this book will be of value to those involved in food packaging development, testing, and selection of packaging materials. As our good friend Frank Paine has stated, "Without food packaging, current methods of production, marketing and distribution of foods would be impossible."

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An Overview of Food Component Interaction During Processing and Storage

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INTRODUCTION

When selecting an appropriate packaging system for a food product, a number of criteria must be considered. Foremost is the stability of the food product itself as food components such as proteins, lipids and certain vitamins can undergo detrimental changes as a result of exposure to light and oxygen and changes in water activity of the product. The stability of the product will thus be a function of its chemical, biochemical and physical nature and will be influenced markedly by the permeability or barrier properties of the package. Secondly, environmental factors, such as temperature, relative humidity, oxygen tension , and light intensity, to which the product/ package system is exposed during distribution and storage must also be considered when evaluating the barrier properties required of the package. In addition, the compatibility of the package with the method of preservation selected must also be addressed when selecting the packaging system.

Foods are affected by different environmental factors and hence have different packaging needs. Paine and Paine (1) reviewed the most important deterioration indices for several types of foodstuffs and concluded that "packaging....can influence the biochemical and microbiological deterioration of foods; physical and chemical changes, including the migration of chemicals into foods; flavor, color and texture; moisture and oxygen transfer; and the effects of temperature changes and light on foods. It is thus an integral part of the processing and preservation of foods, indeed, without it, current methods of production, marketing, and distribution would be impossible."

The major focus of this initial chapter is to provide a brief overview of the major chemical changes that occur in food during processing and storage. Factors influencing food quality will also be discussed. This introductory chapter will thus provide information on how the judicious choice of packaging materials can minimize such changes during distribution of the food products through the food chain. More detailed information pertaining to chemical changes in foods during processing and storage can be obtained in recent texts edited by Fennema (2) and Richardson and Finley (3).

PROCESSING OF FOODS

All foods are perishable commodities and can undergo deterioration through microbial growth, enzyme action and chemical changes. Karmas (4) identified six basic principles of food processing for preservation - moisture removal (drying, dehydration, concentration); heat treatment (sterilization, pasteurization, blanching); low-temperature treatment (freezing and refrigeration); acidity control (fermentation and acidic additives); chemical additives; and irradiation. Associated with the basic food processing methods is proper food packaging.

Chemical changes will occur during food processing and storage and these can be desirable, undesirable, of questionable consequence, or a combination thereof (5). The major chemical reactions that take place occur between the main food components - the proteins, carbohydrates, fats and vitamins. Hurrell (6) has summarized some of the important interactions of food components on processing (Figure 1). Proteins are the most reactive of the major food components and can react with fats and products of their oxidation, reducing sugars, polyphenols, and selected food additives. These reactions can occur during the heating or prolonged storage of proteinaceous foods.

FACTORS INFLUENCING STABILITY OF FOODS

The major factors affecting food quality are summarized in Table 1. Many of the deteriorative changes in the nutritional quality of foods are initiated, or accelerated by light (7). Such changes may include the catalytic effect of light on the free radical reactions involved in fat oxidation (8), destruction of fat-soluble vitamins, loss of riboflavin and other water soluble vitamins, changes in proteins and amino acids, and changes in food pigments. Oxygen is also intimately involved in these light-induced reactions and thus it is desirable to maintain certain types of foods at a low oxygen tension, or at least to prevent a continuous supply of oxygen into the package.

The moisture content of a food has a very important influence on its stability because it controls the rate and type of deteriorative reaction (9). In fact, in dehydrated foods, many of the deteriorative changes in nutrient stability can be prevented by elimination of moisture infiltration into the package. Typical food deteriorative reactions influenced by water activity are lipid oxidation and non-enzymatic browning. The chemistry of these two reactions will be discussed in some detail, and how they are mediated by environmental factors. Physical changes will also occur in foods during storage and include textural changes and moisture loss. These, however, will not be addressed in this chapter.

LIPID OXIDATION

Lipids, especially those containing polyunsaturated fatty acids, are susceptible to oxidation, and the subsequent development of rancid flavors is a major cause of food deterioration. The susceptibility of fatty acids in foods to oxidation increases in a somewhat geometric fashion in relation to their degree of unsaturation. This is particularly true of the polar lipids in muscle foods which contain a higher percentage of polyunsaturated fatty acids than the neutral triacylglycerols. This is one reason why meat phospholipids are readily oxidized and contribute very significantly to warmed-over flavor development in precooked meat items (10).

The oxidation of unsaturated fatty acids is well documented, and unless mediated by other oxidants or enzyme systems proceeds through a free-radical chain mechanism involving initiation, propagation and termination steps (11):

Initiation

RH + O_2 ----> free radicals

ROOH ----> free radicals (e.g. R , RO ,
$(ROOH)_2$ ROO , HO etc)

Propagation

R. + O_2 ----> ROO.

RH + ROO. ---->ROOH + R.

Termination

R. + R. ----> RR

R. + ROO. ----> ROOR stable (non-
ROO + ROO ----> ROOR radical) end
+O_2 products

RH refers to any unsaturated fatty acid in which the hydrogen is labile by reason of its being on a carbon adjacent to a double bond. Initially, the rate of oxidation is slow as the hydroperoxides (ROOH) build up and decompose monomolecularly. When the hydroperoxide concentration is high enough (i.e. above 1% oxidation), bimolecular decomposition takes place (9), which adds more free radicals to the chain mechanism. Termination occurs through recombination of radicals to produce relatively unreactive products.

Factors influencing the rate and course of oxidation of fats are well established (Table 2) and include light, presence of catalysts (generally transition metals such as iron and copper and also heme pigments, particularly as they relate to muscle foods), enzymes (lipoxygenase), high temperature, and local oxygen concentration (9,12). Elimination of these factors can control the extent of lipid oxidation in foods (2).

Lipid oxidation in foods is also influenced to a large extent by water activity (9). Water activity (a_w), defined as the ratio of the partial pressure of water above the sample to the vapor pressure of pure water at the same temperature, is related to the moisture content of the food through the moisture sorption isotherm shown in Figure 2 (13). It is clearly established that fat oxidation in foods is rapid at low water activities (Figure 3). Starting at very low a_w values, it is apparent that the rate of oxidation decreases as water is added (14). Karel and co-workers (15,16) have advanced several hypotheses to explain the retarding effect water exerts on lipid oxidation. They proposed that water hydrogen bonds with amphipolar hydroperoxides, thereby slowing down the hydroperoxide decomposition process (15). The presence of water may also retard oxidation by hydrating or diluting heavy metal catalysts, apparently reducing their effectiveness as catalysts of the oxidative reaction (16). Karel (9) has also suggested that antioxidants produced as a consequence of non-enzymatic browning may also be operative in minimizing lipid oxidation in foods of intermediate moisture content.

At higher water activities (a_w 0.5-0.6), water can accelerate lipid oxidation by increasing the mobility of the reactants and by solubilizing the catalysts. In addition, water swells the solid food matrix exposing new catalyst sites so that the rate of oxidation increases over that of food at lower water activity (17).

Products of lipid oxidation may not only be responsible for the development of off-flavors in foods, but they may also react with other food constituents such as proteins (18) (Figure 4). Protein-lipid interactions can take place in some foods and feeds such as frozen and dehydrated fish, fish meal and oilseeds, thus causing some degree of protein damage. Cheftel (19) has summarized the mechanisms involved in the covalent binding of peroxidizing lipids on proteins and the lipid-induced polymerization of protein as: (i), free-radical reactions, and (ii) carbonylamino reactions. In the free radical reactions, lipid free radicals such as R , RO and ROO can react directly with the protein causing extensive crosslinking of the protein chains through either protein-protein crosslinks or protein-lipid crosslinks. In the carbonylamino reactions, long or short chain aldehydes produced via hydroperoxide decomposition bind to amino groups of proteins by Schiff base-type reactions. Malonaldehyde, derived from the oxidation of polyunsaturated lipids with three or more double bonds (e.g., linolenate and arachidonate), may cause the formation of protein intra-or intermolecular crosslinks. Chio and Tappel (20) showed that reactions between malonaldehyde and amino acids lead to the formation of fluorescent complexes (N, N'-disubstituted 1-amino-3-imino propenes) which are similar to the so-called aging pigment, a lipoprotein isolated from tissues of aging animals. Carbonylamino reactions in foods are thought to play a role in the denaturation of protein (decrease in solubility and salt extractibility; texture hardening; loss of water-holding capacity) observed in frozen and freeze-dried fish products (19).

Sterols are another group of lipids which can undergo oxidation when subjected to environmental stress. Recently, it has been shown that cholesterol will readily oxidize in foods which have been exposed to light. Herian and Lee (21) exposed dry egg nog mix continuously to fluorescent light at room temperature for 90 days and reported the presence of two cholesterol oxidation products, 7 α- and 7 β-hydroxycholesterol. Mix stored in the dark did not contain detectable levels of the oxides. Luby et al. (22,23) studied the effects of packaging and light source on the oxidative stability of cholesterol in butter. Their results indicated that cholesterol oxidation occurred, although the oxidation products were detectable only after prolonged exposure to light. Of the various packaging materials investigated, only aluminum foil prevented cholesterol oxidation after 15 days of exposure to fluorescent light. Margarine wrap, opaque parchment, wet strength dry wax paper, and polyethylene film were not effective. In addition, daylight elicited oxidation in butter at 22°C at a greater rate than did fluorescent light.

Cholesterol oxides have also been reported in foods which have been subjected to heat. Cholesterol in tallow will undergo oxidation when heated at elevated temperatures similar to deep fat frying. Parks and Addis (24) reported the presence of 7 α-hydroxy-,7 β-hydroxy-, and 7-ketocholesterol, and α-epoxide in tallow heated continuously at 155°C for up to 400 hours. Similar results were reported by Bascoul et al. (25). Recent analyses by Missler et al. (26) of dried egg mixes also revealed the presence of several cholesterol oxides, with the α- epoxide, β-epoxide and 7-ketocholesterol predominating. These authors speculated that oxides of nitrogen produced during direct-fired spray drying of liquid egg may act as initiators of cholesterol oxidation.

Cholesterol oxidation products in foods are of interest because some products may be mutagenic (27), carcinogenic (28), or produce toxic effects in cell cultures (29,30). Thus, the presence of cholesterol oxidation products in foods of animal origin may represent a significant health hazard which has gone largely unnoticed in the past (26).

NON-ENZYMATIC BROWNING

Non-enzymatic browning is another of the major chemical reactions occurring in foods. In general, there are three principal pathways by which this reaction can occur (13): high temperature caramelization, ascorbic acid oxidation, and the Maillard reaction. This latter reaction has been studied extensively and it has been the focus of several major reviews (31, 32, 33) and two recent international symposia (34, 35). The Maillard reaction is extremely pertinent during storage of dry and concentrated food products, and it is a major concern in processing when heating, drying and concentrating steps are involved (9).

Maillard reactions are complex and as yet, are not completely delineated. Mauron (36), however, has divided the Maillard reaction into three stages: (i) early Maillard reactions which are chemically well-defined steps without browning; (ii) advanced Maillard reactions which lead to the formation of volatile or soluble substances; and (iii) final Maillard reactions leading to insoluble brown polymers. The initial reaction involves a simple condensation between the carbonyl group of the reducing sugar and the free amino group of an amino acid or protein, resulting in a product known as a Schiff's base (Figure 5). Subsequent cyclization and isomerization under acidic conditions (Amadori rearrangement) produces a 1-amino-1-deoxy-2-ketose derivative (Amadori compound). Lysine, because of its free -amino group, is involved in such reactions and can lead to loss of nutritional value of the food (36).

Following the formation of the Amadori compound, the reactions leading to formation of the brown pigments are not as well defined as the carbonyl-amino reaction. According to Hodge (31), the deoxyketosyl compound can undergo loss of the amine from C_1 to produce a methyl dicarbonyl intermediate, which in turn will undergo fission to give products such as aldehydes, dicarbonyls and reductones. A 3-deoxyhexosone intermediate, also produced from the Amadori compound (Figure 5), will undergo dehydration to produce hydroxymethylfurfural. The reactions following the formation of these primary intermediates are very complex and their chemistry is not well elucidated. They do result, however, in the formation of brown melanoidin pigments and the production of N-heterocyclic flavor compounds such as pyrazines and pyrroles (31).

The Strecker degradation, defined as the oxidative degradation of amino acids by α-dicarbonyls produced by fission of the methyl dicarbonyl intermediates (Figure 5) is another major pathway in the Maillard reaction. Amino acids are degraded to the corresponding aldehydes containing one less carbon than the parent amino acid. While Strecker aldehydes appear to be important auxiliary flavor compounds, the enolamines can also condense to give substituted pyrazines which frequently occur as flavor volatiles. Commercially, the Strecker degradation is used to produce the distinctive flavors of chocolate, honey, bread and maple syrup (37).

Both storage temperature and product water content affect the rate of non-enzymatic browning reactions in foods. Dehydrated food products such as nonfat dry milk and whey powders are especially vulnerable to the effects of these environmental factors because of their relatively high concentrations of lactose which can participate in the Maillard reaction (38). Non-enzymatic browning shows a maximum at water contents in the intermediate moisture range (Figure 3). This is due to water's dual role as a solvent and as a reaction product (9). In general, at low water activities (a_w <0.4), the rate of browning is low because of lack of adequate solvent water, i.e., the slow diffusion of reactants limits the rate of reaction. As water activity increases above 0.4, freer diffusion enables faster reaction to take place up to a water activity of approximately 0.65. At higher water contents, mass action effects are introduced and the resultant dilution of reactants slow down the browning process. In addition, water can retard the rate of the initial glycosylamine reaction in which water is a product (14).

The susceptibility of dehydrated foods to adverse chemical changes during storage has resulted in what Karel and Heidelbaugh (7) describe as the application of protective food packaging. The influence of water content on oxidative and browning reactions has necessitated the use of packaging materials of low permeability to moisture and gases, and packaging of the food product under vacuum, under inert gases, or in modified gas atmospheres. Use of in-package desiccation and in-package oxygen scavengers was also alluded to.

DEGRADATION OF VITAMINS

Much information is available on the chemical changes induced in vitamins through the processing and storage of foods. The intent of this overview is to introduce some concepts which will be discussed in more detail later in the text. The subject of vitamin stability has been discussed in many reviews (39-43). The reader is also referred to the classic text Nutritional Evaluation of Food Processing (44) and to Chapter 3, Vitamins in Nutritional and Safety Aspects of Food Processing (45) for more detailed information on vitamin loss during food processing.

One vitamin which has been extensively studied is ascorbic acid. This vitamin is highly sensitive to changes in the environment such as pH, temperature, concentration of trace metal ions, oxygen, and enzymes. The chemistry of ascorbic acid degradation has been reviewed by Archer and Tannenbaum (45). They concluded that it is not feasible to construct clearly defined precursor-product relationships for any but the earliest products in the reaction pathway because so many factors can influence the degradation reactions. When oxygen and metal ions are present in food systems, ascorbic acid is degraded to dehydroascorbic acid which then will undergo hydrolysis to yield the biologically inactive 2,3-diketogulonic acid. Although further reactions in ascorbic acid degradation have little nutritional impact, they do contribute to non-enzymatic browning in some food products.

Kirk (39) reviewed the effects of water activity on the stability of ascorbic acid in various low and intermediate moisture foods and model systems. Studies by Kirk et al. (46) on the degradation of reduced and total ascorbic acid indicated that the rate of destruction increased as the total moisture and water activity increased. This has been attributed to the role of water as a solvent in hydrating and mobilizing the reactants (oxygen and ascorbic acid) and metal catalysts. Thus, it is apparent that the nature of the packaging material can influence the stability of ascorbic acid, particularly in foods of very low moisture content.

Vitamin A occurs in animal foods as retinol and in plant foods as a variety of carotenoids, principally β-carotene. These compounds possess a series of conjugated double bonds, thus making them highly susceptible to oxidation. Archer and Tannenbaum (45) have summarized the pathways involved in the destruction of β-carotene in processed and stored foods (Figure 6). When oxygen is present, destruction depends on temperature and is promoted by light, enzymes, traces of iron and can undergo cooxidation with lipid hydroperoxides. Light-catalyzed oxidation yields the 5,8-epoxide (mutachrome) which can undergo further fragmentation to produce volatile components possessing haylike flavor. Chemical oxidation of -carotene appears to yield primarily the 5,6-epoxide (45). In the absence of air, β-carotene, when heated as in canning, is transformed into neo-isomers with lower vitamin A activity.

Kirk (39) has indicated that little information is available concerning the loss of fat-soluble vitamins over the wide range of moisture content, water activities, temperature, oxygen content, and concentration of metal catalysts that exist in dehydrated food systems. Because of their propensity to undergo oxidation, vitamins A and E exhibit stability curves in dehydrated systems characteristic of unsaturated lipids (30). Thus, the rate of vitamin loss is a function of enzymes, water activity, and temperature. Again, the choice of packaging material has a major influence on the stability of vitamin A and its precursors during storage of dried food products.

SUMMARY

This initial chapter has provided a brief discussion of the two major chemical changes which occur during processing and storage of foods, viz., lipid oxidation and non-enzymatic browning and how they are influenced by environmental factors. Knowledge of such factors is important in making decisions about the type of packaging materials to be used for a particular food. Subsequent chapters in this text will address further other deteriorative reactions (e.g., color stability in meats) that occur in foods during processing and storage and how these changes are controlled by packaging. This overview, as well as other references in the text, reflect how the judicious choice of packaging systems are important in maintaining food quality during storage. Other chemical reactions such as the oxidation of meat pigments and vitamins will be discussed in subsequent chapters as will the various packaging techniques designed to minimize deteriorative reactions in foods.

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