

**A model study on color and
related structural properties
of cured porcine batters**



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A model study on color and related structural properties of cured porcine batters

Proefschrift

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1. For kinetic analysis and mathematical modeling of processes in the manufacture of comminuted meats color is shown to be a more useful, reliable, and indicative parameter than hitherto acknowledged.

(This thesis)

2. The extent and behavior of entrapped air is the main event responsible for the changes in the lightness of porcine lean meats during chopping. This statement is, however, not valid for systems containing added porcine back fat.

(This thesis)

3. It should be realized that surface stiffness plays an important role in stabilizing gas bubbles not only in porcine batters but also in other food and biological systems such as beer and lung tissue.

4. "Composite material" theory can be used to explain the effect of entrapped air and batter formulation on the rheology and fracture of cooked porcine batters on a semiquantitative basis.

(This thesis)

5. An attempt to explore the exact mechanism responsible for an observation in a biological system, within a reasonable time period, requires either an enormous scientific experience or luck, probably plenty of both.

6. It is hoped that the multi disciplinary approach, including mathematics, chemistry, and physics, employed in this study contributes to advancing meat processing from a craftsmanship to a science.

7. In meat research qualitative and quantitative (e.g., using image analysis techniques) microscopy have proven to be useful tools in exploring the relation between structure and function.

8. Like all science and engineering, often the most visible result of solving one problem is the discovering of several more.

(W. M. Rand)

9. Progress in science is characterized by the trend of obtaining more and more knowledge over exceedingly narrow research scopes. If one takes this trend to its extreme, in future we will have enormous knowledge over nothing.

10. The recent events in the Eastern Block may accelerate achievement of a peaceful solution in the Middle East.

11. The reasonable man adapts himself to the world. The unreasonable one persists in trying to adapt the world to himself. Therefore all progress depends on the unreasonable man.

(George Bernard Shaw)

12. If one were properly to perform a difficult and subtle act, he should first inspect the end to be achieved and then, once he had accepted the end as desirable, he should forget it completely and concentrate solely on the means. By this method he would not be moved to false action by anxiety or hurry or fear. Very few people learn this.

(John Steinbeck)

13. Writing, like giving birth, is slow sometimes painful in the beginning but then it bursts out and everybody is happy.

14. Every generalization is dangerous, even this one.

(Alexandre Dumas)

15. The abbreviations PLMB, GLP, and RAP-AAP may also stand for the voweless family name of the author, Good Laboratory Practice, and a quick ape (in Dutch) respectively.

For Batia and Noam

ABSTRACT

Palombo, R. (1990), 'A model study on the color and related structural properties of cured porcine batters.' Ph.D. thesis, Agricultural University, Wageningen. (pp. 216, English and Dutch Summary and conclusions).

Key-words: porcine meat batters, batter processing, color, kinetic analysis, predictive mathematical modeling, entrapped air, surface rheology, bulk rheology, fracture.

Color, determined by tristimulus colorimeters, and related structural properties, i.e., microstructure, surface rheology, and bulk rheology, of cured porcine meat batters were studied.

Effects of various processing factors (such as, temperature, air pressure during chopping, and cutter type) on changes in color of porcine lean meat batters (PLMBs) during processing were characterized, analyzed, and predicted using graphical analysis, kinetic analysis, and mathematical modeling respectively. "Air pressure during chopping" had the greatest overall effect on color. The effect of "cutter type" was intermediate and that of "respiratory and proteolytic enzyme inhibitors" the least. Lightness (L^*) values for different time-temperature combinations during heating of PLMBs could be closely predicted using the constructed mathematical model.

A study on the mechanism responsible for changes in L^* of PLMBs during processing and subsequent storage at 15°C was performed. The extent and behavior of air entrapped within the PLMBs could explain the increase in their L^* during

chopping (phase 1), and during the first stage of a subsequent storage at 15°C until 24 h (phase 2). "Alterations in absorption traits" was found to be the main event responsible for the decrease in L^* during the second stage of phase 2.

Apparent surface dilational viscosity of the surface of PLMB dispersions was determined by single compression experiments. Evidence for its profound influence on the behavior of the entrapped air bubbles during phase 2 were provided using microstructural techniques, and an emulsifier (glycerol lacto palmitate) as a probe.

The influences of the factors "formulation of the batter" and "entrapped air" on the color, rheology, and fracture of some porcine batters were investigated. Both factors had marked effects on the behavior of raw porcine batters' color during processing. The color of the cooked batters, however, was far less affected by the two factors. A qualitative explanation for these findings, on the basis of the balance between the scattering (mainly influenced by, e.g., entrapped air and added porcine back fat), and absorption characteristics (mainly influenced by the amount and state of myoglobin) of the batter systems, was possible. The effects of the two factors on the rheology and fracture of the cooked batters were studied using uniaxial compression. Added water, porcine back fat, and entrapped air bubbles caused a decrease in the modulus of deformability. Addition of the last two to the the PLMBs caused decrease in some fracture parameters. The results were analyzed on the basis of the "composite material" theory.

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1. GENERAL INTRODUCTION

Meat processing may be defined as the transformation of meat raw materials to products. The meat systems investigated in this study are cured porcine batters produced in a chopper and ultimately cooked. These systems are considered as models for comminuted-cured-cooked-meat-products (CCCMP). Accordingly, the following introduction will be restricted to the description of CCCMP. Some meat products belonging to this group are frankfurters, bologna, wieners, and luncheon meats. In the literature, beside comminuted meats and meat batters various other terms are also used when such cured cooked meat products are discussed. Among these are, meat emulsions, meat homogenates, meat doughs and even chopped meats. In this thesis all these terms are used interchangeably.

CCCMP are foods produced from chopped animal tissue, having recognizable characteristics of color, flavor, texture and shape. Three of the major components of such products are lean meat, fatty tissue and water. Minor ingredients like salt, sodium phosphates, and sodium nitrite are used and are also highly effective in producing the typical texture, color, and flavor of the final CCCMP. Other ingredients used in commercial formulations are meat raw materials with high connective tissue content such as rind, non-meat extenders (fillers and binders), and seasonings (Kramlich, 1971).

It is generally accepted that the predominant functional component among the raw materials of CCCMP is muscle tissue (Schmidt, 1988). Its functionality is attributed to its salt soluble proteins and usually referred to as water and fat binding and gelation. It also contains the main pigment of meat: myoglobin (Mb) and thus is also responsible for the color properties of the final product. The stages of organization in a striated muscle are presented in Fig. 1.1. The hierarchial highly

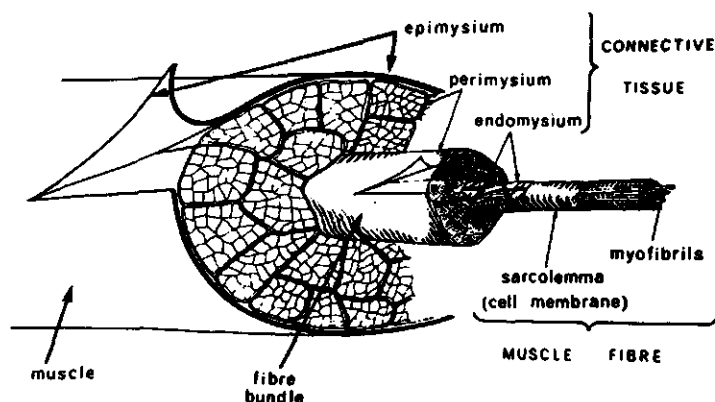


Fig. 1.1: Schematic representation of striated muscle structure (Winger, 1979).

ordered structure is responsible for the anisotropic character of this tissue. However, during decomposition in the presence of salt and phosphate, by e.g. grinding or chopping, a globally isotropic homogenate is produced. Such homogenate consists of a continuous aqueous proteinaceous sol in which fragments of muscle fibers and connective tissue are dispersed. The addition of fatty tissue and further comminution result in a batter referred to as multiphase system enclosing fat globules (cell clusters), emulsified fine fat particles, air pockets, and small air bubbles (Acton et al., 1983; Tantikarnjathap et al., 1983). After cooking, the meat batter can be described as a viscoelastic coagulated proteinaceous gel (usually referred to as matrix) in which water, fat and air are entrapped. An unstable matrix releases fat in to caps and water in the form of gel exudate (Schut, 1976; Smith, 1988).

Many processing procedures and formulations exist for the production of CCCMP and consequently a vast variety of them is witnessed at the locations of sale. Manufacture of such comminuted cured cooked meat products includes the following principal processing steps (Kramlich, 1971):

- (1) Comminution of the lean meat in the presence of water, salt, phosphates and curing agents (usually sodium nitrite and sodium ascorbate). The salt and phosphates are mainly responsible for solubilization of the salt soluble proteins that, as mentioned, are of supreme importance for the water and fat binding and gelation properties of the meat homogenate. The curing agents are added to produce the typical color and flavor of cured meat and to improve shelf-life.
- (2) Addition of fatty tissue (or fatty meats) and further comminution for a duration which is ordinarily set by a final batter temperature.

(3) Transport and stuffing.

(4) Cooking and cooling. Cooking is applied to coagulate the meat proteins and fulfills several functions: 1. Forms the characteristic firm texture of the final product. 2. Fixes the cured meat color by denaturation of the globin in the nitric oxide myoglobin (NOMb). 3. Extends the shelf-life of the product from a microbiological point of view.

(5) Storage and display.

Color, texture, and flavor are believed to be the most important sensory quality properties of meat products. Together with nutrients content and microbiological status they comprise the main components of the global term food quality.

Modern technologies in the production of CCCMP are featured by the desire to supply the customer with products of high uniformity and constant quality. This trend has been recently emphasized in the international congress of meat science and technology (ICoMST, Copenhagen, 1989). New technologies, implementing computer systems for automation, data acquisition and process-control (computer-integrated-manufacture (CIM)) has been presented. The advantages of these recent developments in labor-saving, especially under unpleasant working conditions, have also been stressed. However, it has been generally recognized that the lack of fundamental and systematical knowledge pertinent to quality and functional properties of meat raw materials and to the effect of processing factors on them, is limiting in achieving the high uniformity and constant quality goals. In addition, the incorporation of sophisticated "in-line" control systems for product composition and stability in the processing of comminuted meat products is restricted by this lack of basic and systematic knowledge. Consequently, a great deal of craftsmanship can still be observed in this field.

To this end two scientific approaches can be utilized for improving the present state of knowledge. The first is the application of kinetic analysis and mathematical modeling of food processes (Karel, 1983; Labuza, 1983; Lund, 1983; Paulus, 1984). The second is the use of basic research for elucidating the mechanisms that govern the quality changes observed during production.

The possible benefits from the first approach are:

(1) Analysis of the principal effect of processing variables on the food quality. It also offers a deeper insight into the interactive effects of several factors on the product quality.

(2) Simulation of the process by combining models for quality changes with models

for mass- and heat-transport (see also below).

- (3) Prediction of intermediate and end point values of specific quality parameters.
- (4) Optimization of the process conditions to arrive at the best achievable product quality.
- (5) The information gained by employing this approach can be incorporated in least cost formulations and expert systems programming.

The main advantage of the second approach is that knowing and understanding the mechanisms responsible for quality changes, should eventually lead to a better regulation and control of the processes. For meat processing this positive outcome becomes even more important owing to the recent notion for low-fat and low-salt cured meat products.

Obviously, the two approaches are interrelated. Combination of information, obtained for the same process, from both approaches offers the utmost improvement in the current state of knowledge.

The first part of this study employs the empirical approach of kinetic analysis and mathematical modeling for studying the changes in color of porcine lean meat batters (PLMBs) during processing. The purposes of the investigation have been:

- (1) To characterize the changes in psychometric color attributes of PLMBs during processing (Chapter 3).
- (2) To study the effect of some processing factors on the changes in color of PLMBs during processing, using kinetic analysis techniques (Chapter 4).
- (3) To construct a predictive model for the lightness attribute of a PLMB color during heating, using mathematical modeling techniques (Chapter 5).

The second part of the study makes use of the mechanistic approach. With strong reference to the unavoidable air entrapped in the meat batters, the purpose of the research has been to acquire more fundamental knowledge and, when possible, to elucidate the mechanisms responsible for:

- (1) Changes in the lightness attribute of color of PLMBs during processing and subsequent storage at 15°C (Chapter 7).
- (2) The influence of surface rheology of PLMBs on the behavior of entrapped air bubbles and on the corresponding behavior of L^* (Chapter 8).
- (3) The effect of air pressure during chopping and of formulation on color, rheology and fracture of some porcine batters (Chapter 9).

PART 1

CHANGES IN COLOR OF CURED PORCINE LEAN MEAT BATTERS

2. INTRODUCTION

Color is one of the most important quality properties of comminuted meat products. Formulation and processing conditions have dramatic effect on the behavior of color during manufacturing. A preliminary study has shown that variation in the lean-to-fat ratio in batter formulations results in a highly complex pattern of color changes during processing and in particular during heating. Consequently, a choice has been made to start with a study on color changes in a well defined porcine lean meat (PLM) system and to use the information obtained as a basis for a subsequent broader study including the composition factor.

This part of the study reports the characterization, analysis and prediction of changes in color of PLM batters (PLMBs) during processing using graphical analysis, empirical kinetic analysis and empirical mathematical modeling respectively.

In the following introduction a brief description of some relevant concepts pertaining to color theory, cured meat color, and kinetic analysis and mathematical modeling is presented.

2.1 Color theory

According to Billmeyer and Saltzman (1981), color is the physical modification of light by colorants as observed by the human eye and interpreted by the brain. Hence, color exists within the mind of the observer and is not an inherent physical entity of the object. Moreover according to this definition it is apparent that the term color includes a physical aspect (the interaction between the light and the colorant and the subsequent reflection of light) and a psychological aspect (the interpretation by the human brain). Further, three components are essential for the

production and measurement of color: a source of light, an illuminated object and an observer (Hunter, 1975).

In a psychological, subjective way (the psychological concept of color description), color is considered in relation to its perception (Hunt, 1978). It can be described in a visually uniform space such as the one constructed by Munsell (Francis and Clydesdale, 1975). The subjective or perceived attributes for describing color are: brightness, lightness, hue, saturation, chroma, and colorfulness (a full description and definition of these terms can be found in Hunt (1978)). In this study we use only the psychometric correlates lightness (L^*), hue angle (h^*) and chroma (C^*) for the perceived lightness, hue and chroma (see also below). Accordingly, we will here refer only to the latter three. For further simplification in conveying the meaning of these terms more general definitions will be given (Mclaren, 1980). Lightness specifies the extent of light reflection by an object. Hue is described by the color names and changes from red, via yellow and green, to purple etc. (excluding white, gray and black). Chroma is the strength of a specific hue judged in relation to its surroundings. More simply, it indicates the degree of difference of a color from gray.

In the psychophysical concept of color, color is considered in relation to the physical stimulus (Hunt, 1978). Its specification is based on the fact that color vision is trichromatic. That is to say, that any colored light can be matched by a mixture of the three primary monochromatic lights red, green, and blue. From experiments involving mixing of colored lights, and with the determination of the eye sensitivity to the spectrum from 350-750 nm (the highest sensitivity is at 555 nm), the "standard observer" curves have been established (MacDougall, 1984). On the basis of this knowledge the 1931 CIE (Commission internationale de l'Eclairage) X, Y, Z tristimulus system of color measurement has been established. For the specification of any color in this system three components are needed: The spectrum energy distribution of the illuminant, the reflectance spectrum of the object, and the tristimulus coefficients of the standard observer.

In contrast to the visually uniform space of Munsell, the 1931 CIE X, Y, Z system was found to be perceptually nonuniform (Francis and Clydesdale, 1975). This nonuniformity limited its application as a visually related system for color measurement and communication. Many attempts were made to improve its visual uniformity. One of the most successful mathematical transformations is the L^* , a^* , b^* color space suggested by the CIE in 1976 and known as CIELAB (Wyszecki and

Stiles, 1982). In this system color is described three dimensionally in terms of lightness (L^*), the vertical axis, and chromaticness co-ordinates: a^* , green ($-a^*$) to red ($+a^*$) and b^* , blue ($-b^*$) to yellow ($+b^*$). L^* , a^* and b^* form the axes of a three dimensional color space with cartesian co-ordinates. The psychometric color attributes L^* , h^* and C^* are calculated from the L^* , a^* , b^* color space by mathematical transformations of its coordinates. In the cylindrical space obtained, L^* is located on the vertical axis and is measured on a 0 (black) to 100 (white) scale, h^* is the angle $\arctan(b^*/a^*)$ measured from the $+a^*$ axis and C^* $[(a^*)^2 + (b^*)^2]^{1/2}$ is the distance from the L^* axis (Billmeyer and Saltzman, 1981). These attributes correspond closely to terms related to human vision (psychological color terms). When changes in color of a food system are aimed to be studied, using visually related color terms, the psychometric system is highly recommended (McLaren, 1980, 1985; MacDougall, 1986).

Color measurements performed throughout the whole study were done using tristimulus colorimeters. The essential elements of such an instrument for measuring color by diffuse reflection is given in Fig. 2.1. As stated previously, the X, Y, Z

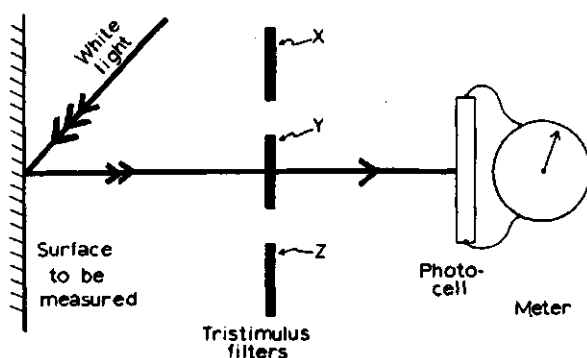


Fig. 2.1: Essential elements of a simple tristimulus colorimeter (Francis and Clydesdale, 1975). See text for further explanation.

tristimulus values are calculated by weighing the product of the reflectance spectrum with the illuminant energy distribution through the standard observer curves. The filters shown in Fig. 2.1 simulate the standard observer curves and thus enable the direct readout of the tristimulus values from the measuring unit (Francis and Clydesdale, 1975). The instruments we used gave directly the L^* , a^* and b^* values.

From these the psychometric L^* , h^* and C^* values were calculated for further analysis.

Finally, it should be realized that the light reflected from the surface of a translucent medium, such as meat, and thus its measured color, is dependent not only on its absorption characteristics but also on its scattering properties. This subject is treated in more details in the second part of the thesis.

2.2 Cured meat color

The main pigment in meat is myoglobin (Mb). Some minor amount of hemoglobin (Hb) may be also present but essentially its color properties are similar to those of Mb. The latter is a complex pigment comprising of a proteinaceous part, globin, and a prosthetic group named heme (Govindarajan, 1973). The heme group contains an iron atom that can exist in either a reduced form Fe^{+2} , or in an oxidized Fe^{+3} state. In its reduced form Mb has a purple color. On exposure to oxygen a covalent complex is formed (OxyMb) having a pink red color. This form has similar spectrum as that of nitric oxide myoglobin (NOMb) and carboxymyoglobin (COMb) which are also red covalent complexes. In all the latter four forms the iron is in the reduced form. The oxidized form of Mb (Fe^{+3}), metmyoglobin (MMb), has a gray-brown color.

NOMb is the pigment responsible for the typical color of cured meat. The complex chain of reactions between Mb, nitrite, oxygen and reducing systems ultimately leading to the formation of NOMb is not fully explored (Möller, 1973; MacDougall et al., 1975; Cassens et al., 1979). Basically, the initial step of the reactions between nitrite and Mb is the formation of MMb. The presence of reducing agents and lowering of the partial pressure of oxygen present in the system may induce concomitant formation of NOMb. The subsequent reduction of MMb to NOMb can follow a chemical pathway (Möller, 1973) or an enzymatic pathway (Walters et al., 1967). Twenty five to fifty ppm of nitrite in a meat product are reported to be sufficient for producing a stable typical color and flavor of the cured meat. The main factors affecting the formation and stability of NOMb are; temperature, oxygen pressure, light, and pH. In the process of cooking the globin in the Mb is denatured and the pink nitric oxide myochrome (DNOMb) is formed.

2.3 Kinetic analysis and mathematical modeling of food processes

Kinetic analysis and mathematical modeling is a rather young discipline in food engineering (Lund, 1983). The possible benefits of modeling in food processing have been discussed in Chapter 1. Basically, a mathematical model is an expression which describes the dynamic transitions in a certain quality parameter under defined processing conditions. The model is usually solved by a computer program.

Two types of phenomena take place during most food processing operations (Paulus, 1984):

- (1) Transport phenomena e.g. heat and mass transport.
- (2) Quality alteration phenomena e.g. chemical and physical changes in the processed food.

For the first, transport models can be constructed and for the second, models for quality alterations can be developed. For the sake of simulation and optimization of processes in food manufacture the information from both types of models is used.

The present study deals only with quality alteration phenomena. Reactions leading to quality changes in food systems are usually many, complex, and often interrelated. For such complicated cases the empirical approach of kinetic analysis and mathematical modeling is commonly used. This approach allows analysis of changes in quality parameters without reference to the detailed actual complex sequence of reactions leading to the change (Labuza, 1983). Evolving from thermodynamics and chemical kinetics theory, the basic equation for describing the rate of change in a quality parameter is (Saguy and Karel, 1980):

$$dQ/dt = CQ^{n'} \quad (2.1)$$

where:

- Q = quality parameter measured
- t = time
- C = rate constant
- n' = reaction order

Essentially, the order of the reaction is determined empirically. Most quality changes in food systems can be described by either zero or first order reactions. However, care must be exercised in interpreting the actual mechanism of the reactions

involved as being of the same order (Saguy and Karel, 1980).

Kinetic of quality alteration in food during processing may be affected by composition (e.g. formulation, pH etc.) and by environmental (temperature, oxygen pressure etc.) factors. One of the major environmental factors influencing the rate of change in a measured quality parameter is temperature. The soundest and most commonly used equation for describing the temperature dependency of this rate is the Arrhenius equation:

$$C = C_0 e^{(-E_a/R'T)} \quad (2.2)$$

where:

C = rate constant (min^{-1})

C_0 = constant (min^{-1})

E_a = activation energy (cal/mol)

R' = gas constant (1.986 cal/mol K)

T = temperature in kelvin (K).

Incorporation of the temperature effect into empirical models is highly desirable in particular for predictive models. The model thus constructed, allows the prediction of the effect of any time-temperature combination within the time-temperature ranges used for its formulation. It is important to note that changes in composition factors or in mechanisms leading to the quality alteration may induce considerable changes in E_a .

In this part of the study, we used the empirical approach for the purposes of kinetic analyses and construction of a predictive model for color changes during processing of PLMB systems.

3. CHARACTERIZATION OF CHANGES IN PSYCHOMETRIC COLOUR ATTRIBUTES OF COMMINUTED PORCINE LEAN MEAT DURING PROCESSING

R. Palombo and G. Wijngaards. 1989. Meat Science. In press.

3.1 ABSTRACT

Changes in colour during the processing of a comminuted porcine lean meat system were characterized using the psychometric colour attributes lightness (L^*), hue (h^*) and chroma (C^*). The effects of processing temperature, nitrite and air pressure during comminution were examined.

The pattern of changes as a function of processing time for L^* and C^* , but not for h^* , showed clear dependence on processing temperature (15°C, 30°C, 40°C, 50°C and 60°C). For C^* this dependence was much more complex than for L^* . Nitrite dramatically affected the pattern of change in h^* and C^* , but much less so changes in L^* . Varying the air pressure during comminution did not induce shifts in patterns of changes of the three colour attributes. However, it did have a marked effect on the absolute values and the extent of changes in L^* and to a much lesser extent in h^* and C^* . The findings of this study furnish the basis for a possible usage of the psychometric colour attributes as parameters for a quantitative kinetic analysis and modelling of the effect of processing factors during the production of comminuted meats.

3.2 INTRODUCTION

Comminuted and emulsion types of meat products are widely consumed, and as such they are of major relevance for the meat industry. Production of meat products with a desired constant quality requires extensive knowledge of the properties of

meat raw materials and meat batters as well as of the effect of processing treatments on them (Smits, 1984; Bertrand, 1984).

Colour is one of the most important quality characteristics determining the consumer's evaluation and acceptance (MacDougall, 1977). It can be described in subjective psychological terms using six attributes: brightness, lightness, hue, saturation, chroma and colourfulness. A full description and definition of these terms can be found in Hunt (1978). The Commission Internationale de l'Eclairage (C.I.E.) has established the psychophysical technique by which colours can be uniquely defined and expressed in tristimulus terms: X, Y and Z. Transformations have been made to improve the visual uniformity of this system. One of the most commonly used transformations for the measurement of food colour is the one suggested by the C.I.E. in 1976 and known as CIELAB. Using the L^* , a^* and b^* values of this colour space, the psychometric colour attributes lightness (L^*), hue (h^*) and chroma (C^*), which correspond closely to what the human eye perceives, can be calculated (McLaren, 1980; MacDougall, 1986).

Mainly using model systems, the mechanism and reactions responsible for the colour development of cured meat systems have been thoroughly studied (Fox, 1966; MacDougall et al., 1975). Research has also been carried out on the influence of processing steps and conditions on the colour of meat model systems and meat products. In particular, for the processing of frankfurters this research work was substantial (Tauber and Simon, 1963; Fox et al., 1967; Wirth, 1986; Paneras and Bloukas, 1987).

To comprehensively study the effects of processing factors on colour changes in meat model systems or meat products during processing, a continuous and time dependent analysis is required. However, only few reports dealing with such description and assessment of the changes in colour of comminuted meats during processing can be found (Tauber and Simon, 1963; Jenkins, 1984). Moreover, non of those studies made use of the visually related colour attributes L^* , h^* and C^* .

The present paper aims at the characterization of the continuous changes in colour during the processing of a comminuted porcine lean meat system. Processing temperature, nitrite and air pressure during comminution are used as process factors and the psychometric colour attributes as process parameters.

3.3 MATERIALS AND METHODS

Meat raw material

To overcome the difficulties inherent in controlling the homogeneity of meat raw materials, a standardized experimental procedure was applied. Lean meat from pig leg muscles was trimmed of excess fat and gross connective tissue to arrive at a desired constant composition of about 2.5% fat, 21% protein and 73% water. The meat was then cut into small pieces. Quantities of 6 kg were packed under vacuum in nylon-polyethylene laminate bags and frozen at -40°C.

Experimental procedure

In order to start the chopping stage at a constant and reproducible temperature of the meat, a strict thawing procedure was used. The day before use 18 kg of meat was thawed in two stages: 10 hours in a water bath at 15°C followed by overnight storage in a water bath at 4°C. The temperature at the start of each experiment was then always about 4°C.

Seventeen kg of meat was placed in a bowl-chopper (Kilia, West Germany, Laboratory model or Laska, Austria, model KT 60/3, for the nitrite and air pressure effects respectively) and coarsely chopped for 1 min at a knife speed and a bowl speed of 2500 and 20 rpm respectively for Kilia, and 2677 and 20 rpm respectively for Laska (These speeds were used through the whole chopping stage.). Then 2% salt (containing or not containing 0.6% sodium nitrite), 0.1% phosphate mixture ("Degens-Latuw", The Netherlands, commercial mixture) and 0.05% sodium ascorbate (Sigma, A-7631) were added dry. Chopping was then continued for another 6.5 min divided into 2 min chopping periods which were interrupted by breaks of 1-4 min for temperature measurement, sampling and when needed for obtaining the desired, reduced air pressure. Samples of the batter were transferred to 100-g cans. The cans were sealed and kept for 45 min in a water bath at 20°C (this stage was necessary to eliminate the adhesion of the batter to the lid of the can), heated at varying temperature-time combinations, and cooled for 1 h at 0°C (also during the heating and cooling steps the cans stayed in water bathes). For every temperature-time combination two replicate cans were opened and the colour of their surfaces was measured separately. The surface was measured since that part of the product was

most closely subjected to the applied thermal treatment. Colour measurements were performed with a Hunter D25M-9 Tristimulus colorimeter fitted with a D-25M optical sensor. The instrument gave the CIE 1976 L^* , a^* and b^* (CIELAB) values (for the 2° position of the "standard observer" and a "C"-type light source) from which the psychometric values lightness, hue and chroma were calculated (Wysecki and Stiles, 1982). For several selected samples a reflectance spectrum scan within the visible range (400-700 nm at 20 nm intervals) was performed on a Hunter LABSCAN model LS500 (using the same measuring conditions as for the Hunter D25M-9).

The experimental design included two levels for each of the factors "nitrite" and "air pressure". "Nitrite" was 0% or 0.012% sodium nitrite (included in the 2% added salt). The factor "air pressure" had the levels: atmospheric pressure or reduced pressure (0.15 bar). Within each experiment various temperatures and time points were investigated.

3.4 RESULTS AND DISCUSSION

In Figs. 3.1, 3.3, and 3.5 results of several typical experiments are presented. They demonstrate the principal pattern of changes in lightness (L^*), hue angle (h^*) and chroma (C^*) of porcine lean meat (PLM) batter during the various processing stages. The effects of temperature (for a system containing nitrite and chopped in air), nitrite (for a system chopped in air with the Kilia cutter), and air pressure during chopping (for a system containing nitrite and chopped with the Laska cutter) on these patterns is shown in Figs. 3.1, 3.3, and 3.5 respectively.

Temperature effect

Jenkins (1984) used the X, Y and Z tristimulus colour values for studying the effect of heat during curing on the colour of bacon. Paneras and Bloukas (1987) used the CIELAB colour system to study changes in colour during controlled production of high quality frankfurters. Both studies reported a remarkable interaction between temperature and duration of heating for the colour changes. Basically, it can be stated that, the combined effect of temperature and time on the colour of meat proceeds through several distinct stages. The initial stage of heating accelerates enzymatic and non-enzymatic reactions influencing the formation of cured

colour (Möhler, 1973). These reactions are gradually inactivated concomitantly with the massive denaturation of the proteins forming the meat batter's matrix. For bacon, this thermal denaturation of the meat proteins was shown to cause an increase in its opacity (Jenkins, 1984). MacDougall and Allen (1984) generalized this observation by modelling the effects of composition and temperature on the colour of meat products. They suggested that the changes in relative contribution of absorption (mainly affected by changes in the state of pigmentation) and scatter (mainly affected by changes in the state of the fibrillar proteins) characteristics due to cooking explain the corresponding dramatic transitions in the colour attributes. A change in one or both characteristics may induce a shift in the reflectance spectrum of the surface studied and consequently change the colour attributes L^* , h^* and C^* .

Some general trends can be considered from the results presented in Fig. 3.1. For each temperature applied, the colour values of the studied PLM batter change with time. Particularly in the processing stages "comminution" and "heating", dramatic and simultaneously occurring changes take place for all three attributes. This concomitance of changes, during the processing stages and storage at 15°C, is better visualized (for a PLM system treated similarly) by the three-dimensional presentation of changes in the three attributes in Fig. 3.2, where the corresponding processing stages (A through E in Fig. 3.1) are also presented. Additionally, from this presentation it is apparent that, after storage for 24 h at 15°C similar values of L^* , h^* and C^* to those of 1 min chopping are obtained (points a and b in Fig. 3.2). An explanation for this finding will be given later (see also "nitrite effect").

The changes during processing and subsequent storage at 15°C are characterized by the following successive stages: (1) An increase in L^* and h^* and a decrease in C^* during comminution; (2) A maximum or minimum at the end of comminution or shortly afterwards which, for h^* and C^* (but not for L^*), is followed by a period of moderate decrease and increase respectively. This slow rate of decrease or increase can be associated with the lag-phase in the formation of nitrosomyoglobin (NOMb) reported by Fox et al. (1967) for colour development during frankfurter processing; (3) A phase of more pronounced decrease in L^* and h^* and increase in C^* is followed by a plateau lasting until 24 h. The changes in this phase are mainly due to the reduction of the muscle pigment (Myoglobin (Mb)) to its NOMb form (MacDougall, 1977).

An examination of the variable pattern of changes of L^* , h^* , and C^* at different heating temperatures is relevant. For L^* , (Fig. 3.1a) the increase in temperature

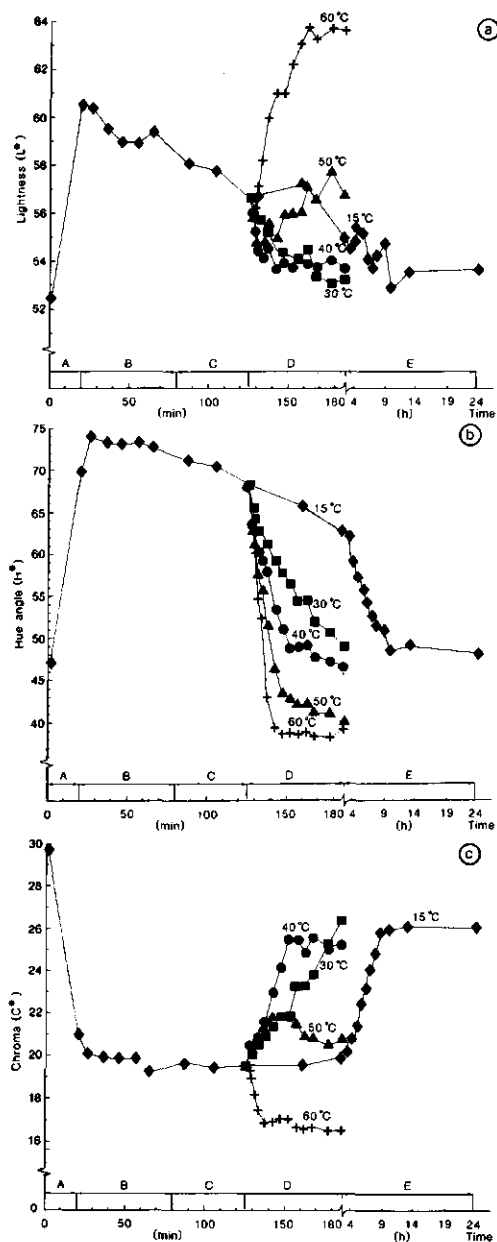


Fig. 3.1: Changes in lightness (a), hue angle (b) and chroma (c) of a porcine lean meat batter (containing nitrite and chopped under atmospheric air pressure) during processing and heating. A = comminution, B = transfer and filling, C = incubation at 25°C, D = Heating, and E = Storage at 15°C.

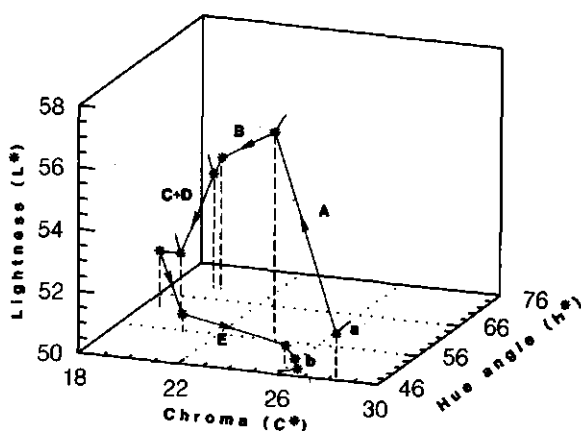


Fig. 3.2: Three-dimensional presentation of changes in color during processing stages and storage at 15°C of a porcine lean meat batter (containing nitrite and chopped under atmospheric air pressure). a = after 1 min of chopping; b = after 24 h storage at 15°C; \downarrow A-E \downarrow indicates the various processing stages. A through E explained in Fig. 3.1.

from 15°C to 30°C and 40°C results in an acceleration of changes over that obtained for 15°C. For temperatures of 50°C and 60°C the diminishing lightness pattern is followed by an increasing one. For h^* (Fig. 3.1b), a decreasing pattern at all temperatures is characterized by a positive association between rate of decrease and temperature applied. For C^* (Fig. 3.1c), a somewhat more complex dependence of the pattern of changes on temperature was observed. For 15°C, 30°C and 40°C the pattern was almost a mirror image of the pattern observed at the same temperatures for h^* . At 50°C a pattern with three different phases was found: an increase followed by a decrease and subsequently a levelling-off to a plateau. For 60°C an initial decreasing phase was followed by a plateau.

The balance between the absorption and scattering characteristic of the meat batter can be used to provide a qualitative explanation for these observations. The pronounced influence of salt and phosphate on solubilisation, extraction, and swelling of myofibrillar proteins is widely described in literature (Wismer-Pedersen, 1971; Offer and Trinick, 1983; Voyle et al., 1984; Wilding et al., 1986). Jenkins (1984) attributed the decrease in the tristimulus values of bacon during storage at temperatures between 0 and 30°C to an increase in its translucency due to the

action of the added salt and phosphate. This suggested mechanism may help to explain the finding that L^* values at 30°C and 40°C are lower than those obtained at 15°C. The dramatic increase in L^* with prolonged heating time at higher temperature (60°C) can be mainly attributed to massive protein denaturation causing higher scatter. As will be discussed later for the nitrite effect, the remarkable temperature-dependent decrease in h^* (Fig. 3.1b) can be largely explained by extreme shifts in the pigmentation state, thus affecting the absorption characteristics of the system. The rather complex pattern of changes in C^* , in particular the results for 50°C, can also be principally explained by this balance. At 50°C the obtained pattern can be interpreted to comprise the effects of transitions in absorption and scatter in a stepwise manner. An initial increase of the C^* value in which reactions affecting the absorption characteristics predominate is followed by a decreasing phase mainly steered by reactions affecting the scattering properties of the surface.

Additionally, it is noteworthy that, independent on a specific colour attribute, after a relatively short heating time at 60°C a constant end value is reached. Experiments (not reported here) in which higher temperatures were used, showed that the same holds for heating at 80°C for the same time intervals and up to 3 h. These findings imply that the typical pink opaque colour of cooked cured meat batter products is reached in a relatively short time at temperatures used during industrial processing.

To simplify further discussion for the nitrite and air pressure effects, only the results at 15°C and 60°C will be presented.

Nitrite effect

During processing and storage at 15°C, for the systems, with and without nitrite basically the same pattern of changes in lightness was obtained (Fig. 3.3a). A sharp increase during the chopping stage, which reaches a maximum value at the end of the comminution step, is followed by a gradual decrease over 6-8 hours having a somewhat variable shape and taking place at "filling", "45 min of incubation at 20°C" and partly at "15°C storage". Next, there is a levelling off to a constant final value (plateau). This plateau is obtained earlier and has a higher absolute position for the batter without nitrite. The reason for this finding can be the remarkable difference in the state of pigmentation of the two systems. An influence of nitrite on lightness

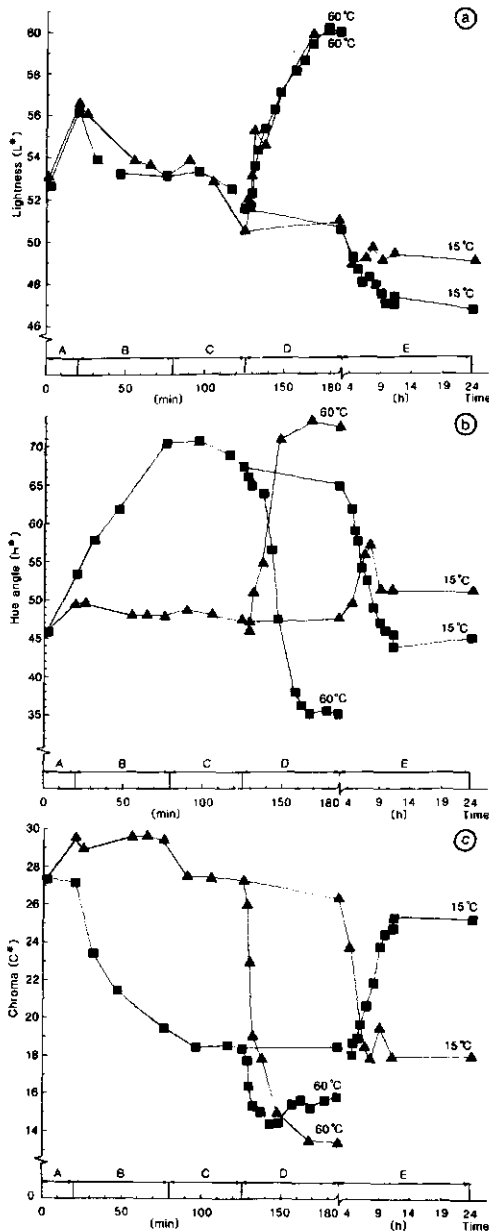


Fig. 3.3: Changes in lightness (a), hue angle (b) and chroma (c) of porcine lean meat batters during processing and storage at 15°C and, heating at 60°C for systems with (■) and without (▲) nitrite. A through E are explained in Fig. 3.1.

is hardly found for heating at 60°C. Both batters show similar dramatic increase in L^* with heating time.

Contrary to the system containing nitrite in the absence of nitrite, only a small increase in hue was found during chopping (Fig. 3.3b). During incubation at 20°C and 15°C, hue remained almost constant for 3 h. Subsequently, there was a temporary increase followed by a fast, but small, decrease. For heating at 60°C, a completely opposite behavior for hue in the systems with and without nitrite was observed. In the system containing nitrite, a sharp decrease was followed by a plateau. Whereas in the system without nitrite, a sharp increase was followed by a plateau. It is worthy of note that an increase or a decrease in h^* are essentially indicative for an increase in the proportion of metmyoglobin (MMb) or NOMb, respectively, in the PLM batter. This will be further discussed in the following section.

For the processing stages and storage at 15°C, in both systems, the observed behavior for chroma (C^*) was almost a mirror image of the pattern described for h^* (Fig. 3.3c). Decrease or increase in C^* was associated with increase or decrease in h^* respectively. In addition, as for h^* , the "end values" reached after 24 h storage at 15°C, were different. A definitely lower value was obtained for the system without nitrite. For the initial period of heating at 60°C, in both systems a steeply decreasing phase was observed, followed by an "end value" for the system without nitrite versus a moderate increase approximating a higher "end value" in the system with nitrite.

The different patterns obtained for h^* and C^* in the porcine lean meat batter with and without nitrite can be satisfactorily explained by referring to the rather complex and dynamic nature of the chemical reactions occurring among myoglobin (Mb), nitrite, oxygen and several reducing components (George and Stratmann, 1952; Fox, 1966; Fox et al., 1967; MacDougall et al., 1975; MacDougall, 1982; Wirth, 1986). During the "comminution" stage, and partly during the "filling" stage in the system containing nitrite (strong oxidative agent), a relatively high proportion of metmyoglobin (MMb) is formed. This causes a shift in the batter's h^* and C^* values from values characteristic of typical pink-red colour of the fresh meat (low h^* and high C^*) to values characteristic of the oxidized brown-gray meat surface (high h^* and low C^*). Subsequently at longer incubation times the endogenous reducing systems, together with the added sodium ascorbate, take over to produce the dark red (NOMb) (low h^* and high C^*) (Fox et al., 1967; MacDougall et al., 1975; MacDougall, 1982). This sequence of changes in the predominant form of Mb is also

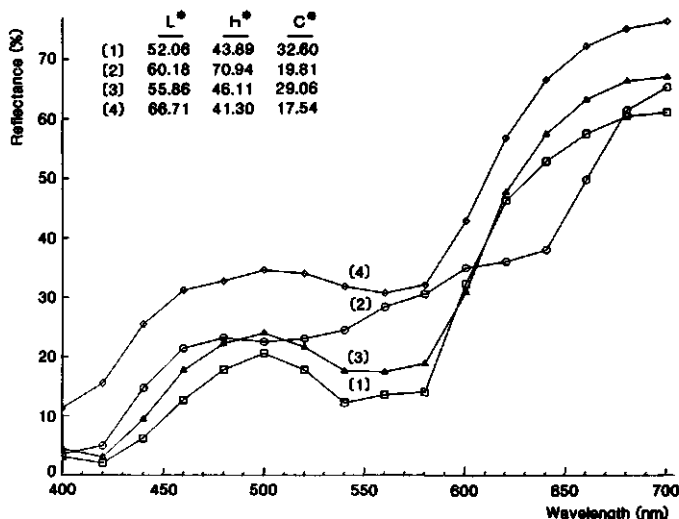


Fig. 3.4: Reflectance spectra of a porcine lean meat system (containing nitrite and chopped under atmospheric air pressure) at various processing steps. (1) = after 1 min of chopping; (2) = at end of chopping; (3) = after 24 h storage at 15°C; (4) = after 1 h heating at 60°C.

substantiated by results of reflectance spectrum measurements (Fig. 3.4). The patterns of the spectra after 1 min of chopping, at the end of chopping, and after 24 h of incubation at 15°C, together with the corresponding changes in the L^* , a^* and C^* values can be readily associated with the principal pattern of spectra for systems in which the predominant pigment forms are oxymyoglobin (OxMb), MMb, and NOMb respectively (Reith and Szakaly, 1967; Francis and Clydesdale, 1975).

In the system without nitrite only a very small amount of MMb, if any, is formed during the comminution step. Because of the oxygen beaten into the system, and the subsequent formation of OxMb, the batter acquires the typical pink colour of bloomed meat surface (Wirth, 1986). This might be one of the reasons for the relatively small increase in a^* and C^* values (Figs. 3.3b and 3.3c). At longer incubation times, and presumably highly associated with the partial oxygen pressure within the closed can, a distinct balance steering the changes in the state of Mb exists between oxidizing and reducing reactions. Previous (unpublished) experiments have shown that the sealed can, can be considered as a closed system with respect to its gas content and composition. Accordingly, due to any biochemical activity,

reduction in the oxygen partial pressure in the sealed can will result in accelerated MMb formation (George and Stratman, 1952). Consequently, a change in the proportion of MMb on or beneath the meat surface will occur, resulting in a change in the colour values. This may help to explain the marked decrease in C^* and the moderate change in h^* after 3 to 6 h incubation at 15°C. It is also partly supported by MacDougall (1986a) who reported that a MMb concentration of 20% on the surface of previously oxygenated raw meat causes a shift of 3 units in h^* yellowwards and a 3-unit decrease in the C^* value. Furthermore, with regard to these transitions in pigmentation, it should be stressed that for both conditions (with and without nitrite) equilibria systems among the different forms of the meat pigment (Mb) are the determinative factors affecting the absorption characteristics of the meat system (MacDougall, 1971,1977; MacDougall et al., 1975). Depending on process stage and condition, these equilibria shift to favour the formation of a specific form of myoglobin and, consequently, a change in the reflectance spectrum and a corresponding change in its L^* , h^* and C^* values.

As described under "Temperature effect", the initial stage of heating at 60°C accelerates enzymatic and non-enzymatic processes occurring at 15°C. A longer heating time results in inactivation of enzymatic activity, and the main pathways for reactions between Mb and nitrite are non-enzymatic reactions.

For the batter containing nitrite, the higher temperature induces a faster production of the red NOMb (decrease in h^*). Parallel to this, longer heating times induce thermal denaturation of matrix proteins and of the proteinaceous portion of the Mb molecule (Bernofsky et al., 1959). The effect of these transitions on the reflectance spectrum (Fig. 3.4) is a marked shift of the spectrum towards higher reflectance values (as indeed expected when the surface of the meat batter changes from a raw translucent medium into a cooked opaque surface). These transitions are suggested to be responsible for the remarkable increase in L^* , the large decrease in h^* and the moderate decrease followed by a slight increase in C^* (Figs. 3.3 and 3.4).

For the batter without nitrite, the production of MMb resulting from the reaction between Mb and the abundant oxygen within the system, together with the thermal inactivation of the enzymatic reducing system, produces the grayish brown colour of cooked meat (sharp increase in h^* and sharp decrease in C^*). The thermal denaturation of proteins mentioned previously occurs here as well and results in augmentation of the same trends.

Effect of air pressure during chopping

Fig. 3.5 presents the results of two typical experiments dealing with changes in L^* , h^* and C^* values of the PLM batters (containing nitrite) during the various processing stages. One result concerns PLM comminuted under atmospheric pressure, and the other one under reduced air pressure. For each of the colour attributes, in both systems, a similar pattern was observed (described in details under "Nitrite effect"). Closer examination of the results reveals several distinct effects of the air pressure during chopping. For the comminution and filling stages and for incubation at 15°C, lightness values were always higher for the system chopped under atmospheric air pressure. This result could be detected visually by members of the research team. For both systems heating at 60°C resulted in similar patterns, but the lightness value reached at the end of heating was higher for the system chopped under atmospheric air pressure.

During the "comminution" and "filling" stages, in both systems, an increase of h^* was obtained. Along the subsequent phase, an earlier occurrence of a somewhat steeper decrease was observed for the system chopped under reduced air pressure. This decrease levelled off to a plateau which was markedly lower than that of the batter comminuted under atmospheric pressure. For both systems, heating at 60°C resulted in a pattern similar to the pattern described under "Nitrite effect". The end value reached was lower for the system chopped under reduced air pressure.

For the batter containing nitrite, except for marked difference between the values at 1 min chopping, the changes in C^* during processing stages and storage at 15°C comprise almost a mirror image of the transitions described for h^* . For heating at 60°C, in both systems a similar pattern could be observed which is characterized by a decrease followed by an approximation to a plateau .

Comminution under reduced air pressure is expected to have a marked influence on changes in two main components of the meat batter: the muscle pigment Mb and the proteinaceous matrix in which this pigment resides.

With regard to the state of pigmentation, during incubation at 15°C, in the system chopped under reduced air pressure, the higher rate of decrease in h^* and increase in C^* (Fig. 3.5) can be mainly attributed to the markedly lower level of entrapped atmospheric oxygen. The effect of vacuum mixing on colour development during frankfurter processing, was studied by Tauber and Simon (1963) and Fox et al. (1967). Both studies applied vacuum mixing after the comminution stage and

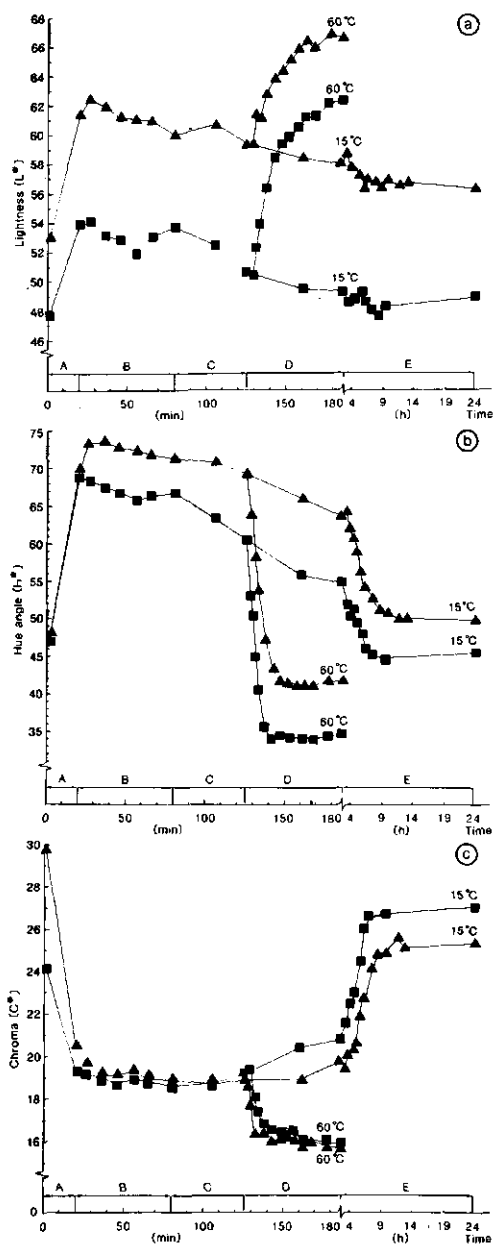


Fig. 3.5: Changes in lightness (a) hue angle (b) and chroma (c) of porcine lean meat batters during processing and storage at 15°C and, heating at 60°C for systems chopped under atmospheric air pressure (▲-▲) and under reduced air pressure (■-■) (both batters containing nitrite). A through E are explained in Fig. 3.1.

checked colour changes by chemical determination of NOMb. They reported that mainly due to the lower levels of entrapped oxygen, mixing under vacuum induced an earlier (i.e. elimination of "lag phase") and faster (higher rate) development of NOMb.

With regard to the matrix formed by the muscle proteins, comminution under reduced air pressure results in a more compact, less porous and consequently less light-scattering surface. This effect on the microstructure of the meat batter can be used to supply some explanation for the consistently lower values of L^* obtained for the system comminuted under reduced air pressure (Fig. 3.5). Wirth (1986), reported that chopping of frankfurter emulsions under atmospheric pressure, resulted in a lighter product not only because of the scattering of light by fat particles but also because of the light scattering by the air entrapped in the end product. Since no fatty tissue was added to the system in the present work, it is the quantity of air present in the system that is presumably responsible for the reported effect of low air pressure during comminution.

The same steering forces as mentioned for incubation at 15°C are also pertinent to the effects observed for heating at 60°C. The phase of steep increase for L^* , and the first decreasing phase for C^* , can be due to the increase in scattering attributable to the massive thermal denaturation of the muscle proteins.

A considerable amount of investigative work indicated that meat, being a translucent medium, has a unique and complex interaction with the light impinging on its surface (MacDougall, 1970, 1971, 1977, 1986a; MacDougall and Rhodes, 1972). As already argued under "Temperature effect", changes in either the scattering or the absorption characteristics of the meat batter, or both, will affect its measured reflectance spectrum. Consequently, and directly associated with the site and manner of the corresponding shifts in the reflectance spectrum, simultaneous transitions in the calculated L^* , h^* and C^* values may also occur (Hunter, 1975). In this light it is obvious that a certain extent of simplification was used in the above discussion related to the actual manner in which the different types of transitions affect the reflectance properties of the meat system. Moreover, these transitions often occur simultaneously and thus make their observed overall effect even more complex. Accordingly, great care must be exercised in using the obtained psychometric attributes for the construction of a detailed mechanistic interpretation of the phenomena observed.

3.5 CONCLUSIONS

The work presented here show that, changes in the visually related colour attributes during processing of PLM can essentially be characterized and to a large extent explained by known chemical and physical transitions. Based on the findings presented in this paper the following conclusions can be stated:

- (1) L^* and C^* , but not h^* , showed a clear dependence of their course of changes (as a function of time) on temperature. This dependence was demonstrated to be much more complex for C^* than for L^* .
- (2) Nitrite was shown to dramatically affect the course of changes in h^* and C^* , but much less so changes in L^* .
- (3) Air pressure during comminution, failed to detectably change the course of changes of the three colour attributes. However, contrary to the mentioned effect of nitrite, remarkable differences were found in the absolute values and extent of changes in L^* , and to a much lesser extent in h^* and C^* .

On the basis of the association between transitions occurring in the PLM system during processing and the findings reported here, the following general trends qualified as being of qualitative nature can be proposed:

- (1) Changes in lightness, and to a much lesser extent changes in chroma, can essentially be related to changes in physical characteristics of the meat system.
- (2) Changes in hue and chroma are primarily associated to chemical and biochemical reactions related to the state of the pigmentation.

Finally, the results presented in this paper furnish the basis for a possible application of the psychometric colour attributes as useful and indicative working parameters for the quantitative analysis and modelling of the effects of processing factors during the production of comminuted meats.

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See at the end of the thesis.

4. KINETIC ANALYSIS OF THE EFFECT OF SOME PROCESSING FACTORS ON CHANGES IN COLOR OF COMMINUTED MEATS DURING PROCESSING

Rachamim Palombo and Gerrit Wijngaards. 1989. J. Food Sci. In press.

4.1 ABSTRACT

Changes in the psychometric color attributes lightness (L^*), hue angle (h^*) and chroma (C^*) of porcine lean meat batters during processing were kinetically analyzed using the empirical approach of mathematical modeling. The changes during 24 hr storage at 15°C and during heating at 40°C, 50°C, and 60°C, were fitted into a model and analyzed for the effects of air pressure during chopping, cutter type and enzyme inhibitors. For changes in L^* and C^* at 40°C, 50°C and 60°C such kinetic analysis was not possible.

Among the factors studied, "air pressure" had the greatest overall effect on color. The effect of "cutter type" was intermediate and that of "enzyme inhibitors" least. The effects found could be ascribed to changes in absorption and scatter properties of the meat batters.

4.2 INTRODUCTION

A cornerstone in human endeavor at improving the quality and wholesomeness of nutrition has long been the application of thermal treatment for the processing and preservation of foods. However, in modern industrial production of food, in particular meat products, several additional stages such as comminution, filling, packaging and storage, which have marked consequences for nutritional as well as sensory properties (color, texture and flavor) of the end product have been introduced.

In recent years, growing consumer awareness has increased the interest in

changes in food quality during processing and storage (Labuza, 1982). To date, there is wide agreement as to the tremendous potential of modeling for the improvement of the quality of processed food. Saguy and Karel (1980) have enumerated the main benefits of modeling of quality deterioration during food processing and storage. These include analysis, simulation, optimization of processes and prediction of intermediate as well as final quality of products. MacDougall et al. (1988) assigned some of these benefits to the processing of meat. Lund (1982) reviewed the quantification of reactions that influence the quality of foods as a function of process factors. He emphasized that, at the present state of affairs, it is the lack of data and of models that hinders the exploitation of the huge potential of modeling. For the quality parameters of processed meat, in particular for the color parameter, this shortage is surprising (Holdsworth, 1985), since meat color is undeniably one of the most noticed appearance attribute, although such attributes as gloss and translucency are also of importance.

The color of an object can be described in different ways: a subjective, psychological one, based on human perception and an objective method which can be expressed in psychometric parameters. In subjective terms color can be described using three main perceived attributes: lightness, hue and chroma. Lightness gives the extent of light reflection by an object. Hue describes the changes from red via yellow and green to purple etc. (MacDougall, 1982). Chroma is the degree of difference of the color from gray. The psychometric color attributes: lightness (L^*), hue angle (h^*) and chroma (C^*) are calculated from the $L^* a^* b^*$ color space (suggested by the CIE (Commission Internationale de l'Eclairage) in 1976 and known as CIELAB) by mathematical conversion of its coordinates. In the cylindrical space obtained, L^* is located on the vertical axis and is measured on a 0 (black) to 100 (white) scale, h^* is the angle $\arctan(b^*/a^*)$ and C^* is the distance from the L^* axis $[((a^*)^2 + (b^*)^2)^{1/2}]$ (Billmeyer and Saltzman, 1981). These attributes correspond closely to terms related to human vision (psychological color terms). When changes in color of a food system are aimed to be studied using a visually related color terms the psychometric system is highly recommended (McLaren, 1980). Typical psychometric color values encountered in this study on meat batters, when a specific form of myoglobin predominated were: oxymyoglobin (OxyMb): $L^* = 53$, $h^* = 46$, $C^* = 27$; metmyoglobin (MMb): $L^* = 63$, $h^* = 73$, $C^* = 19$; nitric oxide myoglobin (NOMb): $L^* = 58$, $h^* = 49$, $C^* = 26$; denatured nitric oxide myoglobin (DNOMb): $L^* = 68$, $h^* = 36$, $C^* = 15$. The corresponding visual color changes ranged from

pink-red (OxyMb) via gray-brown (MMb) to red (NOMb) and light-red (DNOMb).

The color of a raw comminuted cured meat system is affected by reactions between myoglobin and nitrite, finally resulting in the formation of nitric oxide myoglobin (NOMb) and by changes in its scattering properties. The mechanism and reactions responsible for the color development of cured meat systems were extensively studied (MacDougall et al., 1975). Enzymatic and non-enzymatic pathways are responsible for the formation of NOMb. Watts et al. (1966) studied the enzymatic reducing pathways in meat by using several electron transfer blockers. They showed that amytal, completely prevented metmyoglobin reduction. The state of the meat proteins can have marked effect on its scattering and reflectance properties (MacDougall, 1982). Thus, proteolytic activity in comminuted meat system may induce changes in its reflectance characteristics. Inhibition of these enzymatic activities (reducing or proteolytic), is expected to affect changes in the reflectance and psychometric color attributes of meat batters.

As early as in the 1940s, a comprehensive study of the effect of heat treatments on color and color stability of bacon was reported by Winkler and Hopkins (1940). These authors measured the color by means of a photoelectric comparator and reported an interactive effect of time and temperature of heating on the color of the product. In a more recent work, remarkable progress has been made by MacDougall and Allen (1984) who used color as a quantitative parameter for modeling. In an extensive study they modeled the influence of composition on color, weight loss and mechanical properties of meat homogenates. They applied mixture design analysis to the construction of mathematical models for raw and cooked meat products. However, their work failed to provide detailed information on the continuous and profound changes in color during processing and heating of the meat homogenates. A contribution in this direction was presented by Jenkins (1984) who investigated the effect of time, temperature and polyphosphate on the color and opacity of sliced cured bacon. Jenkin's (1984) study comprises a comprehensive graphical analysis and application of the Kubelka-Munk theory, but it gives no kinetic mathematical description of the results pertaining to color changes during heating.

In a previous publication (Palombo and Wijngaards, 1989a), changes in psychometric attributes of color (lightness (L^*), hue angle (h^*) and chroma (C^*)) during processing of comminuted meats were characterized and related to physical and chemical transitions occurring within the meat batter. The overall effects of processing factors on these changes are highly complex. They are the sum of several

mechanisms which have not been exhaustively explored. In such complex systems the kinetic empirical approach of mathematical modeling is commonly used for the formulation of models for the purpose of analysis and prediction (Labuza, 1983; Paulus, 1984). However, great care must be exercised in using the obtained models for detailed mechanistical interpretation of the phenomena studied. A description of changes in a quality parameter with a first order model does not mean that a first order reaction mechanism is valid for the parameter under consideration, but that the changes can be described with sufficient precision by a model based on a first order mechanism.

To analyse and to predict the effect of processing factors on meat color changes during processing, a continuous and time dependent description is highly preferred. Parameters from the whole process interval can be defined and thus the reliability of analysis and prediction increases. Additionally, as stated by Paulus (1984), the information gained from kinetic modeling can be used for the construction of optimization models for cooking processes.

The present study makes use of the empirical approach of mathematical modeling (Labuza, 1983) in order to permit continuous kinetic analysis of the changes in color. The results related to the magnitude and significance of effects induced by the processing factors: air pressure, cutter type, enzymes inhibitors and solvents used to dissolve them on the color attributes L^* , h^* and C^* during the processing of comminuted porcine lean meat (PLM) will be reported.

4.3 MATERIALS AND METHODS

Meat raw materials

To overcome the difficulties inherent in controlling the homogeneity of meat raw materials, a strict and well standardized experimental procedure was applied. Lean meat from pig leg muscles was trimmed of excess fat and gross connective tissue to arrive at a desired constant composition of about 2.5% fat, 21% protein and 73% water. The meat was then cut into small pieces. Quantities of 6 kg were packed under vacuum in nylon-polyethylene laminate bags (van Hessen, Rotterdam, The Netherlands) and frozen at -40°C .

Experimental procedure

In order to start the chopping stage at a constant and reproducible temperature of the meat, a strict thawing procedure was used. The day before use 18 kg of meat was thawed in two stages: 10 hours in a water bath at 15°C followed by overnight storage in a water bath at 4°C. The temperature at the start of each experiment was then always about 4°C.

Seventeen kg of meat was placed in a bowl-chopper (either Kilia (Laboratory model, Kiel, West Germany) or Laska (model KT 60/3, Linz, Austria)) and coarsely chopped for 1 min at a knife speed and a bowl speed of 2500 and 20 rpm respectively for Kilia, and 2677 and 20 rpm respectively for Laska. (These speeds were used through the whole chopping stage. Additionally it should be noted that the knives of the two cutters differed in shape: the Laska cutter having knives with "4-cut" shape, and the Kilia cutter being crescent-shaped.) Then 2% salt with or without 120 ppm sodium nitrite, 0.1% commercial phosphate mixture ("Degens-Latuw", Vlaardingen, The Netherlands) and 0.05% sodium ascorbate (Sigma, St. Louis, USA) were added dry. Chopping was then continued for another 6.5 min divided into 2 min chopping periods which were interrupted by breaks of 1-4 min for temperature measurement, sampling and when needed for obtaining the desired air pressure. Samples of the batter were transferred to 100 g cans. The cans were sealed and kept for 45 min in a water bath at 20°C (this stage was necessary to eliminate the adhesion of the batter to the lid of the can during heating), heated at varying temperature-time combinations, and cooled for 1 h at 0°C (also during the heating and cooling steps the cans stayed in water baths). For every temperature-time combination two replicate cans were opened and the color of their surfaces was measured separately with a Hunter D25M-9 Tristimulus colorimeter fitted with a D-25M optical sensor. The instrument gave the CIE 1976 L^* , a^* and b^* (CIELAB) values (for a 2° position of the "standard observer" and a "C"-type light source) from which the psychometric values L^* , h^* and C^* were calculated (McLaren, 1980).

Experimental design

Four processing variables (air pressure, cutter type, enzyme inhibitors and solvents used to dissolve them) were investigated by means of five treatments in

12 experiments, each of which was performed on a different day. These were: four replicate experiments for chopping under atmospheric pressure in a Laska cutter, three replicate experiments for chopping under reduced air pressure (0.15 bar) in a Laska cutter, two replicate experiments for chopping under atmospheric pressure in a Kilia cutter, two replicate experiments for chopping under atmospheric pressure in a Kilia cutter, with addition of the solvents (see below) used to dissolve the enzyme inhibitors (E.I.S.) and one experiment for chopping under atmospheric pressure in a Kilia cutter, with addition of the following solutions of enzyme inhibitors (E.I.): (1) 100 ml of the proteinase inhibitor Trasylol (Bayer, Leverkusen, West-Germany; 1 ml of Trasylol solution (0.15 M NaCl) contains 10 000 KIU (Kallikrein Inactivator Unit)) in which 34 g of the electron transfer blocker malonic acid (Janssen, Beerse, Belgium) have been dissolved (the pH was equalized to the meat batters by means of NaOH pellets with stirring and under cooling). (2) 340 ml propylene glycol containing 34 g of the electron transfer blocker Amytal (Sigma, St. Louis, USA). The levels of the two blockers were in accordance with Watts et al. (1966). Either, the solutions of the E.I. (1 and 2) or the solvents used to dissolve them were added after 1 min of chopping together with the other dry additives.

Within each experiment tristimulus color measurements were performed on the meat batters as described in the experimental procedure. Four temperatures were employed: 15°C, 40°C, 50°C and 60°C. The reason for using these temperatures was that, at higher temperatures very rapid changes in color occurred. With the experimental procedure employed, sufficient number of sampling points for kinetic analysis of the effect of process factors was practically impossible. The processing stages ("chopping"; "filling" and "45 min incubation at 20°C") followed by storage at the first temperature (15°C) were monitored from 1 min of chopping until 24 hr, with at least 20 measured time points; the other temperatures (40°C, 50°C and 60°C) were checked from the end of the "45 min incubation at 20°C" stage until 3 hr later, with at least 15 measured time points. The results of heating at 40°C, 50°C and 60°C were analyzed as a split-plot arrangement, with treatments as main plots and temperatures as subplots. For all temperatures means of treatments were compared by t-tests using standard errors obtained from the analysis of variance. Iterative fitting of kinetic data and other statistical analyses were performed using the Genstat statistical package (Anonymus, 1977).

4.4 RESULTS AND DISCUSSION

For the sake of clarity the analysis of the results and further discussion are separated into: results related to changes during processing and subsequent storage for 24 hr at 15°C, and results obtained during thermal treatment at 40°C, 50°C and 60°C.

Changes in L^* , h^* and C^* during processing and storage at 15°C

Results from representative experiments for lightness (L^*), hue angle (h^*) and chroma (C^*) of porcine lean meat (PLM) batters after the 5 different treatments and storage at 15°C are presented in Fig. 4.1. The pattern of changes in L^* and h^* included a sharp increase during the chopping and filling stages followed by a gradual decrease and an approximation to a constant final value after about 6-8 hr storage at 15°C. The pattern obtained for C^* was almost a mirror image of the pattern obtained for h^* . For the different treatments L^* , h^* and C^* exhibited a similar pattern of changes. The corresponding visual color changes included, a shift in the batter's L^* , h^* and C^* values from values characteristic of typical pink-red color of fresh bloomed meat (predominant pigment form oxymyoglobin) to values characteristic of the oxidized brown-gray meat surface (predominant pigment form metmyoglobin). Subsequently, at longer storage time it turned red (predominant pigment form nitric oxide myoglobin). Detailed description of these transitions was given by Palombo and Wijngaards (1989).

To allow quantitative analysis, some characteristics (e.g., processing steps or model parameters) were defined for two distinguishable stages (Fig. 4.1): (1) The initial increasing or decreasing stage from 1 minute after the onset of chopping until a maximum or a minimum value (Table 4.1), and (2) The subsequent decreasing or increasing stage lasting until a plateau level after 24 hr (Table 4.2). For the second stage the empirical approach of kinetic mathematical modeling was applied (Labuza, 1983). A modification of a first-order model obtained by adding an initial and end values was used. For L^* and h^* the following form of the non-linear model was used:

$$h^* = a - b(1 - e^{-ct}) \quad (4.1)$$

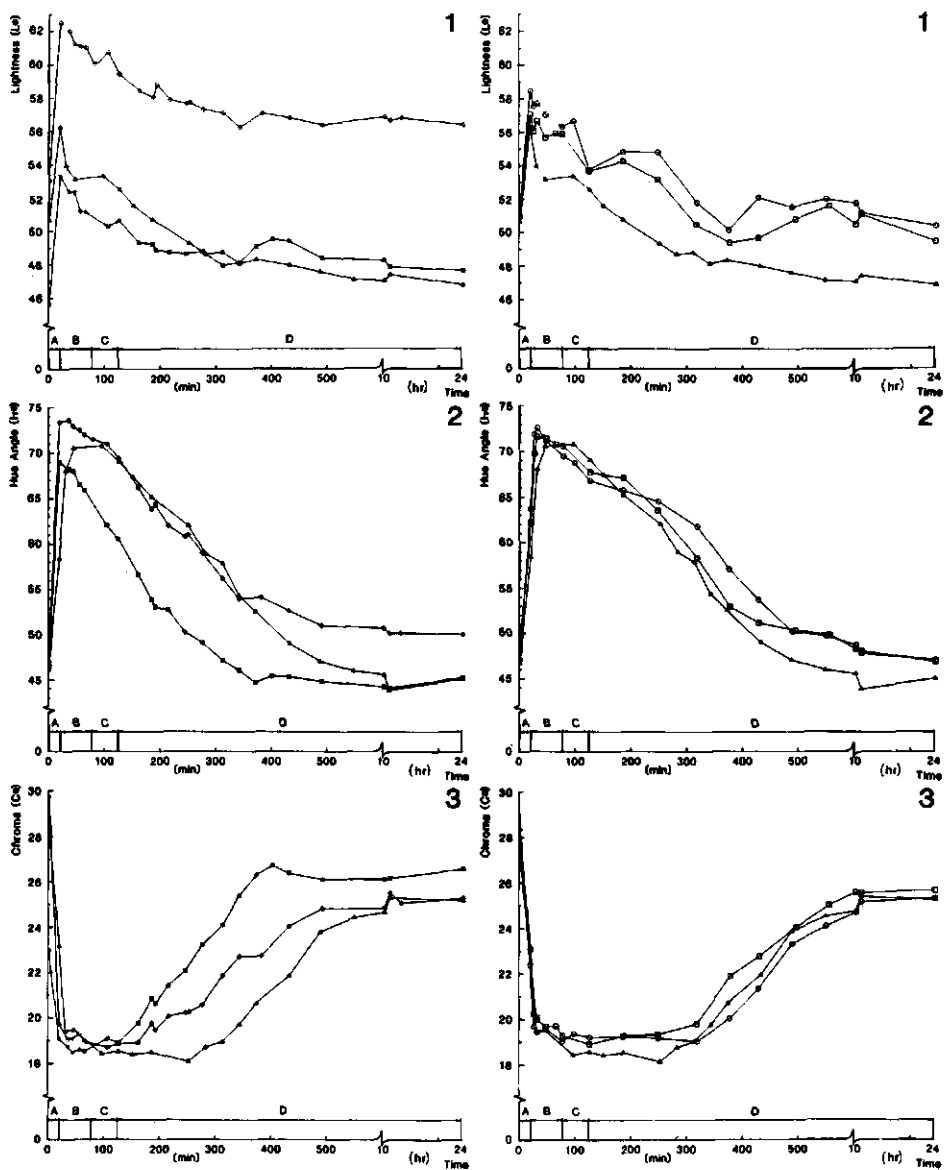


Fig. 4.1: Typical pattern of changes in lightness (in lightness units) (1), hue angle (in degrees) (2), and chroma (in chroma units) (3), of porcine lean meat (PLM) during processing and storage at 15°C. (Δ-Δ) PLM chopped under atmospheric pressure in a Kilia cutter; (◇-◇) PLM chopped under atmospheric pressure in a Laska cutter; (x-x) PLM chopped under reduced air pressure in a Laska cutter; (□-□) PLM chopped under atmospheric pressure in a Kilia cutter with addition of solvents used to dissolve the enzyme inhibitors; (o-o) PLM chopped in a Kilia cutter under

where:

a = initial value; b = extent of decrease; a-b = final value; C = rate constant (min^{-1}); t = time (min).

For the C^* , because of a different pattern of changes, the following modification of the previous model was used:

$$C^* = a - b(e^{-ct}) \quad (4.2)$$

where:

a = final value; b = extent of increase; C = rate constant (min^{-1}); a-b = initial value; t = time (min).

The models were fitted over a range starting at points where sufficient changes occurred. For L^* , values from end of chopping (e.o.c.) until 24 hr storage at 15°C were used. For h^* and C^* values from the time periods 3 to 24 hr and 5 to 24 hr were respectively used. Representative results of the curve-fitting procedure used for each of the color attributes together with the corresponding models are shown in Fig. 4.2. These examples demonstrate that the models predict the data fairly precisely. Statistical analyses revealed that for all three of the color attributes the variation of the differences between predicted and measured values was comparable with the standard deviation obtained from the replicate measurements.

Air pressure effect. The values of L^* and h^* after 1 min of chopping, maximum values and the differences between these were higher ($p < 0.05$) for the samples chopped under atmospheric pressure (Table 4.1). Comparable results were found for C^* , but the calculated difference values were not higher ($p > 0.05$) for samples chopped under atmospheric pressure.

It is evident from Table 4.2 that chopping under reduced air pressure resulted in a lower ($p < 0.01$) initial and final values of L^* and h^* than was obtained for the samples chopped under atmospheric air pressure. The former samples had a higher ($p < 0.001$) initial value (t = 5 hr) for C^* ; its final value, however, was almost the

atmospheric pressure with addition of enzyme inhibitors. A = comminution, B = transfer and filling, C = incubation at 20°C , D = storage at 15°C .

Table 4.1 Summary of t-tests for replicate means of changes in Lightness(L*, in Lightness units), Hue angle (h°, in degrees) and Chroma (C*, in Chroma units) of the porcine lean meat batters for various processing steps

Color attribute	Processing step	Processing variable								S.E. ⁽⁴⁾	
		Air pressure		Cutter	E.I. solvents		E.I.	AKS (n=2)	AKSE (n=1)		
		VL ⁽¹⁾ (n=3)	AL (n=4/2)		AK (n=2)	AKS (n=2)					
Lightness (L*)	after 1 min of chopping(X)	48.85	p<0.01	52.94	p<0.05	49.66	n.s. ⁽³⁾	51.31	n.s.	51.88	1.27
	maximum value(Y)	52.43	p<0.001	59.17	n.s.	57.45	n.s.	56.73	n.s.	57.80	0.92
	Y-X	3.58	p<0.01	6.23	n.s.	7.59	n.s.	5.42	n.s.	5.92	1.05
Hue angle (h°)	after 1 min of chopping(X)	46.51	p<0.05	47.25	p<0.01	46.82	p<0.05	47.73	n.s.	47.1	0.36
	maximum value(Y)	69.15	p<0.01	72.79	n.s.	70.98	n.s.	71.31	n.s.	72.57	0.85
	Y-X	22.64	p<0.01	25.54	n.s.	24.70	n.s.	23.58	n.s.	25.47	1.02
Chroma (C*)	after 1 min of chopping(X)	25.03	n.s.	26.11	n.s.	27.14	n.s.	27.85	n.s.	27.35	0.96
	minimum value(Z)	17.58	p<0.05	18.88	n.s.	19.02	n.s.	18.81	n.s.	18.51	0.63
	X-Z	7.45	n.s.	7.23	n.s.	8.12	n.s.	9.06	n.s.	8.83	1.11

(1) First letter indicates the pressure of air; V for reduced air pressure; A for atmospheric pressure. Second letter indicates the cutter type: L for Laska; K for Killa. Third letter, S, indicates addition of the solvents used to dissolve the enzymes inhibitors. Fourth letter, E, indicates addition of enzyme inhibitors.

(2) Number of replicates.

(3) Not significant; p>0.05.

(4) Standard error.

Table 4.2 Summary of t-tests for replicate means of model parameters for Lightness(L*, in Lightness units and for the process interval of: and of chopping until 24 hr), Hue angle(h*, in degrees and for the process interval of: 3 hr until 24 hr) and Chroma(C*, in Chroma units and the process interval of: 5 hr until 24 hr) of the porcine lean meat batlets

Color attribute	Model parameter	Processing variable								S.E. ⁽⁴⁾	
		Air pressure		Cutter	E.I. solvents			E.I.			
		VL ⁽¹⁾ (n=3)	AL (n=4) ⁽²⁾		AK (n=2)	AKS (n=2)	AKSE (n=1)				
Lightness (L*)	Initial value (a)	53.40	p<0.001	59.50	p<0.05	57.30	n.s. ⁽³⁾	56.43	n.s.	57.53	0.98
	Final value (a-b)	47.68	p<0.001	52.12	p<0.05	50.26	n.s.	49.01	n.s.	49.94	0.92
	Rate constant (c)	0.0073	p<0.001	0.0045	p<0.001	0.0075	p<0.02	0.0056	p<0.02	0.0035	0.0006
Hue angle (h°)	Initial value (a)	54.92	p<0.001	67.03	p<0.05	63.36	p<0.02	68.35	n.s.	68.98	1.50
	Final value (a-b)	44.14	p<0.01	46.39	n.s.	46.46	n.s.	45.76	n.s.	44.51	0.76
	Rate constant (c)	0.00939	p<0.001	0.0051	n.s.	0.0058	n.s.	0.0054	p<0.05	0.0038	0.0006
Chroma (C°)	Initial value (a+b)	22.96	p<0.001	19.91	n.s.	20.9	n.s.	19.32	n.s.	17.75	0.67
	Final value (a)	25.87	n.s.	25.54	n.s.	26.74	n.s.	25.70	n.s.	25.34	0.83
	Rate constant (c)	0.0234	p<0.02	0.0065	n.s.	0.0111	n.s.	0.0063	n.s.	0.0046	0.0078

(1) First letter indicates the pressure of air; V for reduced air pressure; A for atmospheric pressure. Second letter indicates the cutter type: L for Laska; K for Killa. Third letter, S, indicates addition of the solvents used to dissolve the enzymes inhibitors. Fourth letter, E, indicates addition of enzyme inhibitors.

(2) Number of replicates.

(3) Not significant; p>0.05.

(4) Standard error.

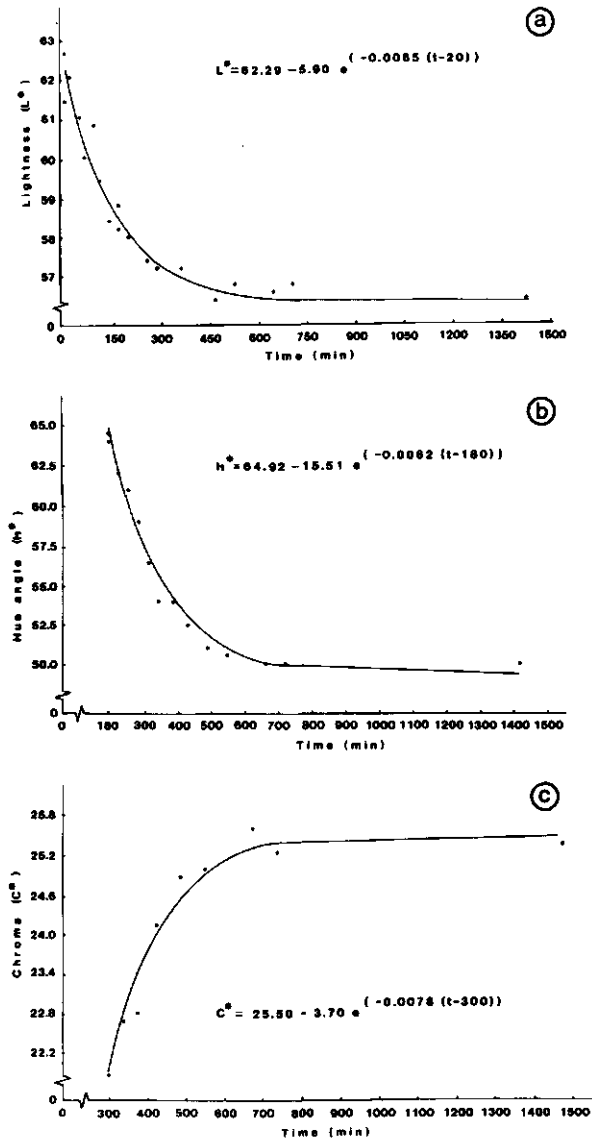


Fig. 4.2: Representative results of curve fitting for changes in L^* (a), h^* (b) and C^* (c) of a porcine lean meat batter during storage at 15°C for 24 hr.

same for atmospheric and reduced air pressure. For all three color attributes, the rate constant was significantly higher for chopping under reduced air pressure.

Basically, two different processes can be suggested to explain the changes seen

in L^* , h^* and C^* during the chopping stage and shortly afterwards. One process concerned the changes in scattering properties of the matrix formed by the muscle proteins, and the other one the transitions in the state of the pigments residing in this matrix. Accordingly, these striking effects for all three color attributes can be satisfactorily explained by the salient difference in extent of entrapped air and oxygen level within the meat batter (Watts et al., 1966; Klettner and Ambrosiadis, 1980; Wirth, 1986).

As more light is reflected from a surface, it appears lighter and less colored (Francis and Clydesdale, 1975). Because of a difference in refractive index, the air bubbles entrapped in the meat batter act as scattering elements. This may explain the consistently higher lightness and hue angle (and to a lesser extent lower chroma) for the system chopped under atmospheric pressure.

As to the effects induced by transitions in pigmentation, a marked inhibitory effect of oxygen on the reducing systems of beef and pork slurries has been reported by Watts et al. (1966). Fox et al. (1967) showed that during frankfurter processing, mixing under vacuum induced an earlier and faster development of NOMb, i.e., a faster change in color from gray brown (MMb) to dark red (NOMb). These findings can be used to explain the lower rate constants obtained for all three color attributes of the system chopped under atmospheric pressure.

Cutter effect. As can be seen in Table 4.1, there was no significant difference for the three color attributes of the meat batter between the two cutters, except for L^* and h^* at "1 min chopping".

For the changes in L^* during the decreasing phase, the analysis of the model parameters showed a higher ($p < 0.001$) rate constant and lower ($p < 0.05$) initial and final values for the Kilia cutter (Table 4.2).

The velocities of the bowl and knives were similar for the two cutters. However, the knives differed in shape. Theoretically these differences are expected to slightly affect the intensity of comminution and the amount and distribution of entrapped air, which may in turn affect the refraction properties and pigment state of the meat batters. However, the reflection of these differences in the measured color attributes was small and mostly non-significant.

Effects of enzyme inhibitors (E.I.) and their solvents (E.I.S.). The reason for monitoring the effect of the E.I.S. on color parameters is that propylene glycol has

been reported by Watts et al. (1966) to increase the reductive capacity of meat. However, except for a significant solvents effect on h^* after "1 min chopping", no significant effect of E.I. and E.I.S. on L^* , h^* or C^* was detected for the initial processing phase (Table 4.1). During the subsequent process phase, a significantly lower rate constant for L^* and h^* in the system containing E.I. was obtained (Table 4.2). The final values of L^* , h^* and C^* were not significantly influenced by the presence of E.I.

Proteolytic enzymes are expected to accelerate the swelling of the matrix proteins and thus the increase in translucency of the meat batter promoting a decrease in L^* . Therefore, the lower rate of decrease of L^* for the system containing E.I. may be explained by at least partial blockage of proteolytic activity.

The influence of the enzymatic reductive system on color development of cured meat has been extensively studied by Watts et al. (1966) and reviewed by Giddings (1974) and MacDougall et al. (1975). The lower rate constant for h^* (Table 4.2) in our porcine lean meat batter containing E.I. can be explained by some blockage of the enzymatic reductive pathway. As demonstrated by Watts et al. (1966), these effects were expected to be much more profound in a deaerated system since the reductive system reacts preferentially with oxygen as long as it exists in the batter. Ledward et al. (1977), suggested that the minor effect of respiratory E.I. can also be attributed to the partial inhibition of the enzymatic reductive system by mincing. Thus, reductive activity by non-enzymatic systems such as coenzymes, ascorbic acid and other reducing compounds becomes relatively more important in the formation of color in comminuted cured meat systems (MacDougall et al., 1975).

Both respiratory and proteolytic enzyme inhibitors were used together in this experiment. Therefore, both transitions in absorption, mainly due to blockage of respiratory enzymes, and transitions in scatter, mainly due to blockage of proteolytic enzymes, can be responsible for the observed overall changes in L^* , h^* and C^* .

Changes in L^* , h^* and C^* during heating at 40°C, 50°C and 60°C

Typical patterns of changes in color parameters (for the five treatments) during heating at different temperatures for L^* , h^* and C^* respectively, are presented in Figs. 4.3, 4.4 and 4.5. Clearly, L^* , h^* and C^* showed markedly different patterns. The patterns obtained for L^* and C^* were occasionally multiphasic and more temperature-dependent than those for h^* . This became particularly complex for

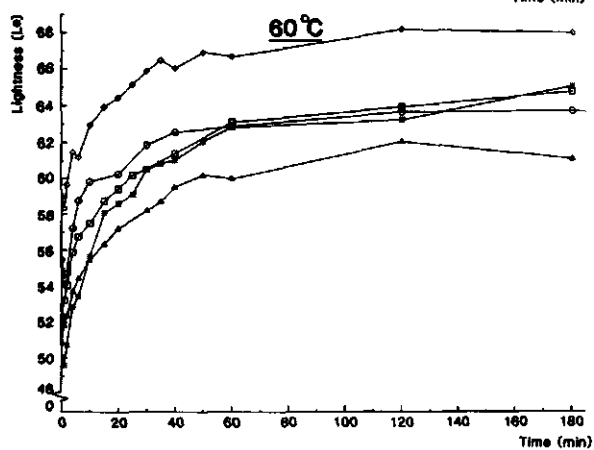
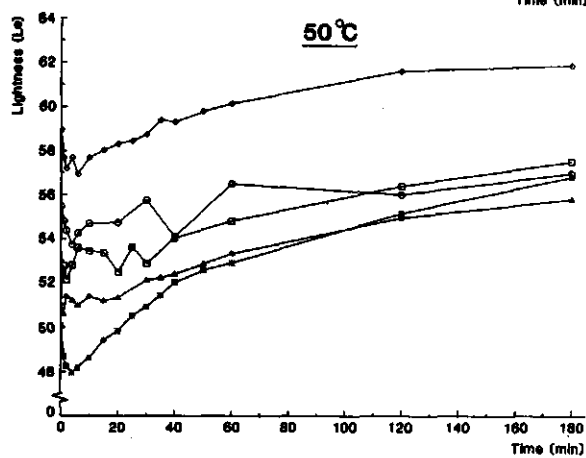
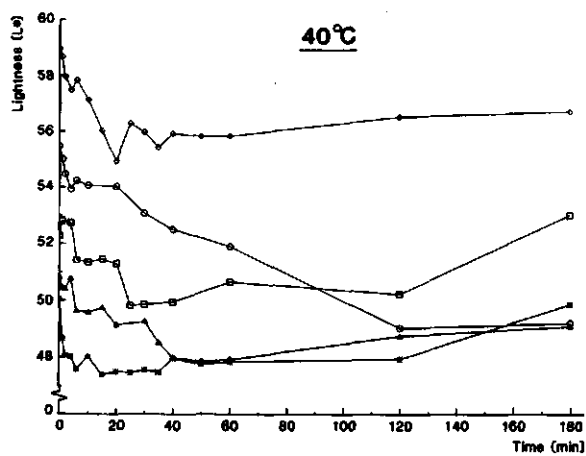
changes in C^* of the batters prepared under different conditions and treated at different temperatures (Fig. 4.5). In fact, for L^* and C^* it was impossible to describe with sufficient precision the relation between the measured values and processing time in a simple and readily interpretable mathematical model (as was done for the results obtained at 15°C). This mathematical kinetic analysis could be done for h^* and to a lesser extent to L^* .

Changes in L^* and h^*

The temperature dependence of changes in L^* and h^* of porcine lean meat batters containing nitrite has been qualitatively characterized (Palombo and Wijngaards, 1989a). Here, changes in L^* during heating were quantified by monitoring the values for the end of heating (180 min). The results of the analysis for the different processing factors are presented in Table 4.3. Changes in h^* during the decreasing phase were quantified in the same non-linear model as used for processing and storage at 15°C. Also here, the model was fitted over a range of points where sufficient differences occurred (i.e. different starting time points for the various treatment-temperature combinations). The results of statistical analysis of the final values and calculated rate constants are presented in Table 4.4. For both L^* and h^* the analysis of variance revealed a significant interaction between treatments and temperatures. Accordingly, the calculated parameters for each temperature are presented below.

Air pressure effect. Similar to the findings for storage at 15°C the values of L^* at the end of heating were lower for the system chopped under reduced air pressure (Table 4.3). Further, a clear treatment-temperature interaction (i.e., the higher the temperature the smaller the difference between the treatments.) was observed. Significantly lower final values and a higher rate of decrease for h^* values were obtained for the system comminuted under reduced air pressure (Table 4.4). Also here, a treatment-temperature interaction existed, but such that the higher the temperature the larger the difference between treatments. Thus, monitored by L^* and h^* the meat batter comminuted under reduced air pressure was always darker and redder than the batter chopped under atmospheric pressure. This observation was also visually apparent.

During heating two simultaneously occurring processes caused the apparent



changes in L^* and h^* : (1) Changes in absorption characteristics due to the transitions in pigmentation and (2) Changes in scattering properties due to the thermal denaturation of the meat proteins (Palombo and Wijngaards, 1989a). The difference in L^* at end of heating and the final h^* value of the heated batter can be attributed to the combined effect of the initial difference in the amount of entrapped air bubbles (which act as scattering elements) and the difference in the pigmentation state (Klettner and Ambrosiadis, 1980).

The significantly and consistently lower rate constant values for the decrease of h^* (Table 4.4) during the heat treatment of the system comminuted under atmospheric pressure can be mainly attributed to the well documented inhibitory effect of entrapped oxygen on the reducing pathways present in meat batter systems (Watts et al., 1966; Fox et al., 1967; Giddings, 1974; Wirth, 1986). This finding stimulated a more detailed analysis of the temperature dependence of this effect. For this purpose, the Arrhenius model was employed:

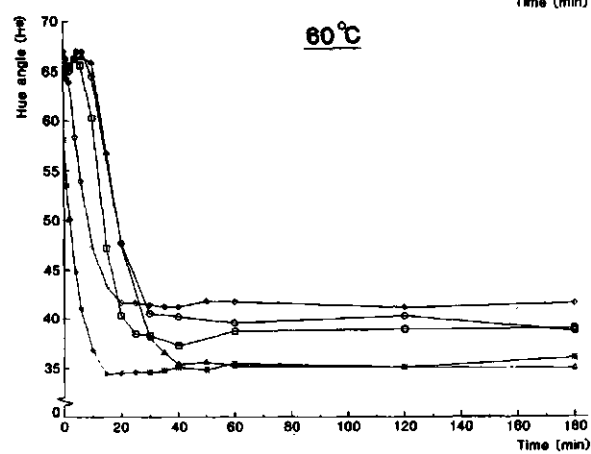
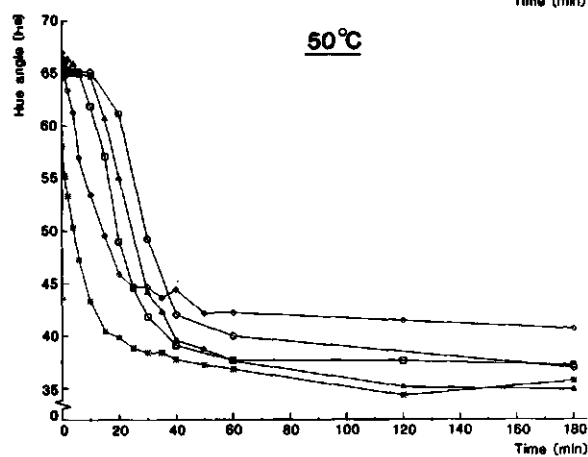
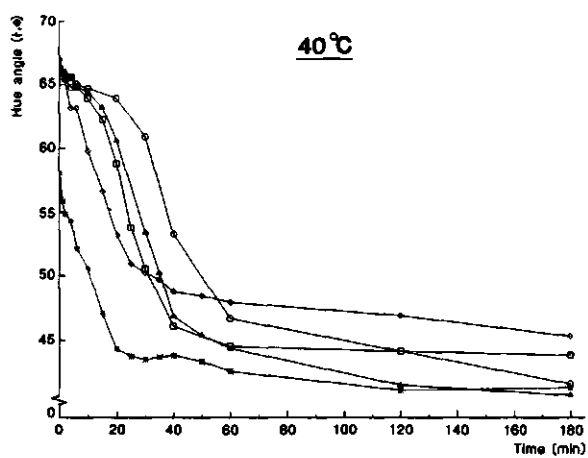
$$C = C_0 e^{(-E_a/R'T)} \quad (4.3)$$

where:

C = rate constant (min^{-1}); C_0 = constant (min^{-1}); E_a = activation energy (cal/mol); R' = gas constant (1.986 cal/mol K); T = temperature in kelvin (K).

Rate constants of individual replicate experiments were used to derive the corresponding E_a . The correlation coefficients were high (0.90-0.99) and supported the adequacy of this model for analysis. The mean values of E_a for the two treatments are presented in Table 4.4. General ranges for E_a have been published by Saguy and Karel (1980) who mentioned a range of 10-30 kcal/mol for reactions related to color changes in foods. The values found were in a similar range. The

Fig. 4.3: Typical pattern of changes in lightness (in lightness units) of porcine lean meat (PLM) during heating at 40°C, 50°C and 60°C. (Δ - Δ) PLM chopped under atmospheric pressure in a Kilia cutter; (∇ - ∇) PLM chopped under atmospheric pressure in a Laska cutter; (\times - \times) PLM chopped under reduced air pressure in a Laska cutter; (\square - \square) PLM chopped under atmospheric pressure in a Kilia cutter with addition of solvents used to dissolve the enzyme inhibitors; (\circ - \circ) PLM chopped in a Kilia cutter under atmospheric pressure with addition of enzyme inhibitors.



significantly higher value of E_a for batter chopped under reduced air pressure indicated a markedly higher sensitivity to temperature changes. A change in E_a due to a specific treatment might indicate a change in the physicochemical properties of the system. It is likely that thermal denaturation of the meat proteins and transitions in pigmentation have different E_a values. Assuming that the E_a for the latter is the higher one, and that during chopping under reduced air pressure the process with the higher E_a predominates, then a steeper slope for the Arrhenius plot will be obtained as indeed resulted from our analysis.

Cutter effect. At all temperatures, values of L^* at the end of heating and the final values of h^* were lower ($p < 0.05$) for the Kilia cutter (Tables 4.3, 4.4). For h^* , similar to findings for the "air pressure" effect, a treatment-temperature interaction was observed such that the higher the temperature the larger the difference between treatments. For L^* , no interaction was detected. Except for 60°C, the two cutters did not differ in rate of h^* change of the meat batter (Table 4.4).

These findings might be explained by differences in number and size distribution of the entrapped air bubbles in the batter. Due to its mechanical characteristics (mainly the shape of knives), the Laska cutter might cause the number of air bubbles to be higher and the bubbles to be smaller on the average. Such a difference might be of major importance when thermally induced effects of air bubbles on the absorption and scattering properties are considered.

Effects of enzyme inhibitors (E.I.) and their solvents (E.I.S.). Except for 40°C and 60°C for L^* and h^* respectively, there was no E.I.S. effect on h^* or L^* (Tables 4.3 and 4.4). For L^* no E.I. effect could be detected at all the temperatures checked (Fig. 4.4). For h^* , no effects ($p > 0.05$) were found for the final values and the rate

Fig. 4.4: Typical pattern of changes in hue angle (in degrees) of porcine lean meat (PLM) during heating at 40°C, 50°C and 60°C. (▲-▲) PLM chopped under atmospheric pressure in a Kilia cutter; (◊-◊) PLM chopped under atmospheric pressure in a Laska cutter; (x-x) PLM chopped under reduced air pressure in a Laska cutter; (□-□) PLM chopped under atmospheric pressure in a Kilia cutter with addition of solvents used to dissolve the enzyme inhibitors; (○-○) PLM chopped in a Kilia cutter under atmospheric pressure with addition of enzyme inhibitors.

Table 4.3 Summary of t-tests for replicate means of changes in lightness(L*, in Lightness units) of the porcine lean meat batters after 3 hr heating at various processing temperatures

Processing temperature (°C)	Processing variable							S.E. ⁽⁴⁾
	Air pressure		Cutter		E.I. solvents			
	VL ⁽¹⁾ (n=3)		AL (n=4) ⁽²⁾		AK (n=2)	AKS (n=2)	AKSE (n=1)	
40	49.11	P<0.001	54.47	P<0.01	49.20	52.58	n.s. ⁽³⁾	53.5
50	56.01	P<0.01	59.71	P<0.05	57.08	n.s.	n.s.	57.54
60	64.31	n.s.	65.86	P<0.01	62.06	n.s.	n.s.	63.76

(1) First letter indicates the pressure of air: V for reduced air pressure; A for atmospheric pressure. Second letter indicates the cutter type: L for Laska; K for Kilia. Third letter, S, indicates addition of the solvents used to dissolve the enzymes inhibitors. Fourth letter, E, indicates addition of enzyme inhibitors.

(2) Number of replicates.

(3) Not significant; p>0.05.

(4) Standard error.

Table 4.4 Summary of t-tests for replicate means of model parameters and activation energy (Ea, only for the air pressure effect) for Hue angle (h*, in degrees) of the porcine lean meat batters during heating

Model parameter	Temperature (°C)	Processing variable							S.E. ⁽⁴⁾	
		Air pressure		Cutter		E.I. solvents				
		VP ⁽¹⁾ (n=3)	AL (n=4) ⁽²⁾	AK (n=2)	AKS (n=2)	AKSE (n=1)	E.I.			
Final value (a-b)										
	40	41.16	p<0.001	43.69	p<0.05	42.83	n.s. ⁽³⁾	42.93	n.s.	42.89
	50	35.89	p<0.001	38.78	p<0.01	37.24	n.s.	36.81	n.s.	36.48
	60	34.29	p<0.001	38.36	p<0.01	35.56	p<0.05	37.72	n.s.	38.02
Rate constant (C)										
	40	0.0721	p<0.01	0.0449	n.s.	0.0484	n.s.	0.0547	n.s.	0.0543
	50	0.1059	p<0.01	0.0641	n.s.	0.0577	n.s.	0.0621	n.s.	0.0402
	60	0.2267	p<0.001	0.1117	p<0.05	0.0843	p<0.02	0.1075	n.s.	0.0820
Activation energy(Ea) ⁽⁵⁾ {Kcal/mol}										
		12.8	p<0.05	9.1						

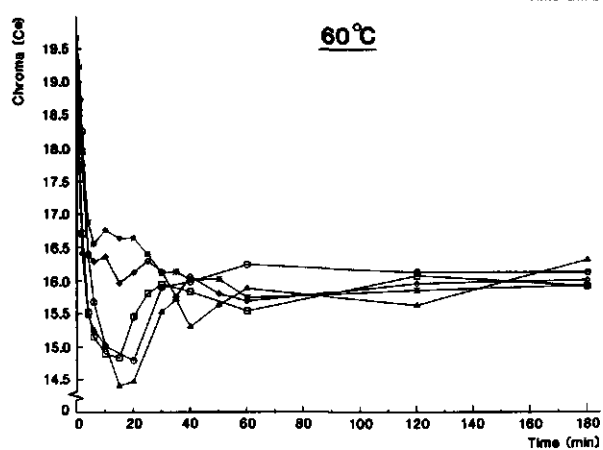
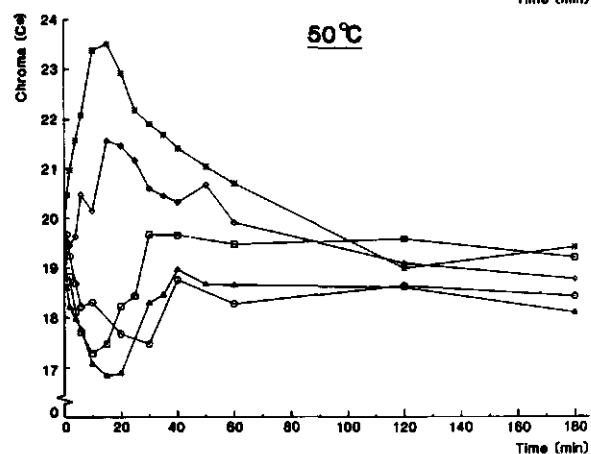
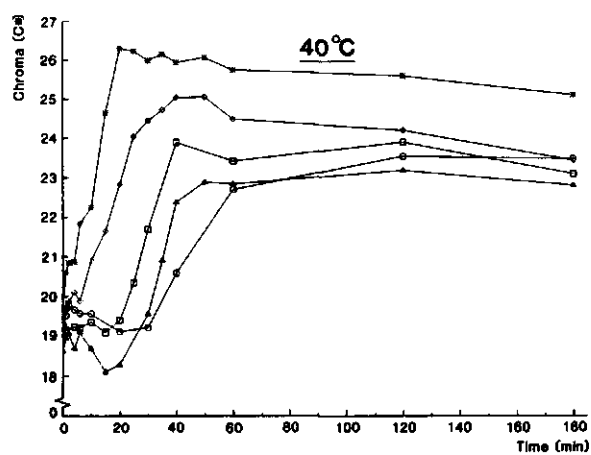
(1) First letter indicates the pressure of air: V for reduced air pressure; A for atmospheric pressure. Second letter indicates the cutter type: L for Laska; K for Killa. Third letter, S, indicates addition of the solvents used to dissolve the enzymes inhibitors. Fourth letter, E, indicates addition of enzyme inhibitors.

(2) Number of replicates.

(3) Not significant; p>0.05.

(4) Standard error.

(5) Calculated for each individual experiment. The S.E. for this comparison was 1.8.



constants (Table 4.4). However, at 40°C the significantly lower rate constant obtained for the system with E.I. at 15°C (see Table 4.2) was related to a longer initial phase of moderate changes in h^* (Fig. 4.4). Thermal inactivation of the muscle tissue enzymes can satisfactorily explain the results for heating at 50°C and 60°C for both L^* and h^* (Whitaker, 1972; Reed, 1975).

Changes in C^*

The extremely variable pattern of changes in C^* at 40°C, 50°C and 60°C for the different treatments hampered quantitative kinetic analysis. The results visualized in Fig. 4.5 show marked effect of air pressure on C^* . Additionally, a distinct effect of cutter type on the pattern of changes existed.

The first step in trying to explain these results should take into account the aforementioned balance between the batter's absorption and scattering characteristics. Heating caused simultaneous acceleration of the reduction reactions affecting the formation of the red nitric oxide myoglobin (NOMb) pigments and the denaturation of the muscle proteins. The first type of reaction will essentially induce an increase in chroma, and the heat denaturation of proteins will basically cause a decrease in chroma. These statements are supported by results of an experiment (not reported) in which the PLM batter was heated at 50°C after 24 hr storage at 15°C. The reduction reactions were then largely completed and the majority of the pigments were in the NOMb form. The complex pattern of three phases observed in Fig. 4.5b changes to a simpler one comprising only a decrease and an approximation to a plateau.

Since at 50°C both types of the aforementioned reactions occurred simultaneously, their overall effect on the observed pattern of changes in chroma depended on the balance between them. Therefore, an increase in C^* meant that the

Fig. 4.5: Typical pattern of changes in chroma (in chroma units) of porcine lean meat (PLM) during heating at 40°C, 50°C and 60°C. (Δ - Δ) PLM chopped under atmospheric pressure in a Kilia cutter; (\diamond - \diamond) PLM chopped under atmospheric pressure in a Laska cutter; (\times - \times) PLM chopped under reduced air pressure in a Laska cutter; (\square - \square) PLM chopped under atmospheric pressure in a Kilia cutter with addition of solvents used to dissolve the enzyme inhibitors; (\circ - \circ) PLM chopped in a Kilia cutter under atmospheric pressure with addition of enzyme inhibitors.

effect of chemical transitions predominated. Whereas a decrease in C^* meant that the effect of protein denaturation predominated.

This equilibrium can also be used to explain the different patterns obtained for the different cutters. As discussed previously, the meat batters produced by the two cutters may differ in the extent and distribution of the entrapped air and thus of oxygen, and the extent of its inhibitive effect on the reducing reaction.

For batter chopped in the Kilia cutter, due to the higher oxygen-induced inhibition of reduction reactions, the initial rate of these reactions was relatively slow. Thus, the equilibrium system shifted to favor the effect of protein denaturation, and the initial overall effect was a decrease in C^* . This phase was followed by an increase in C^* as the chemical reduction reaction predominated.

For the batter chopped in the Laska cutter, due to a smaller oxygen-induced inhibition, the chemical reactions predominated and induced an initial sharp increase in C^* . This increase was followed by a decrease in which the denaturation of proteins is the predominate reaction.

Both systems approached a similar final value, since for both batters the concentration of myoglobin (Mb) was similar and nitrite was added in excess.

4.5 CONCLUSIONS

Changes in L^* , h^* and C^* during storage of porcine lean meat batter for 24 hr at 15°C, and changes in h^* during heating of the batter at 40°C, 50°C and 60°C, could be fitted into a model. Using the model's parameters, an analysis of the effect of the various processing factors was possible. Changes in L^* and C^* at 40°C, 50°C and 60°C showed a complex dependence on temperature and treatment.

Among the factors investigated for L^* , h^* and C^* , the overall effect of "air pressure" was most important, followed by "cutter type" and, finally, "enzyme inhibitors". Further, for the values of L^* and h^* at the end of heating, a clear and significant treatment temperature interaction was found for "air pressure" effect and partly for "cutter type" effect. A similar interaction could be observed for C^* . Higher cooking temperature lowered L^* and C^* and caused an increase for h^* . These findings are important when one considers the effect of the process factors studied on the color of a cooked emulsion-type meat product.

An attractive application of these results could be to use the predictive

techniques of mathematical modeling to predict intermediate and end-point color values during the processing of comminuted meat batter.

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REFERENCES

See at the end of the thesis.

5. PREDICTIVE MODEL FOR THE LIGHTNESS OF COMMINUTED PORCINE LEAN MEAT DURING HEATING

Rachamim Palombo and Gerrit Wijngaards. 1989. J. Food Sci. In press.

5.1 ABSTRACT

A mathematical model for the prediction of lightness values (L^*) of a comminuted porcine lean meat (PLM) system (about 2.5% fat) during heating was constructed using kinetic data collected from process temperatures of 50°C, 60°C, 80°C and 100°C and heating times of up to 3 h. The procedure of model formulation included regression analysis of L^* versus time to obtain the model parameters and description of the temperature dependence of these parameters using linear and Arrhenius models. By solving the final predictive model numerically, the value of L^* was closely predicted for different temperature-time combinations during heating of the PLM system. The work presented here can be used as basis for further development of predictive models during meat processing operations.

5.2 INTRODUCTION

Kinetic analysis and mathematical modeling are used in food processing to fulfill several objectives: to gain comprehensive knowledge about the process through analysis of the effect of processing factors (MacDougall and Allen, 1984), to optimize the process, and to predict intermediate and end-point characteristics of the product (Labuza, 1982; Lund, 1983). Recent developments in food production offer the incorporation of the knowledge thus obtained in least cost formulation and expert system programming.

Lund (1982) emphasized the fact that nutrients as food quality attributes have

received wide attention in quantification through modeling studies, and that other attributes like texture, flavor and particularly color have been less widely used as quantitative attributes. Recently, some progress has been made in applying modeling techniques to the study of fermentation of meat (Demeyer et al., 1986) and of the effect of composition and processing factors on the color of meat products (Jenkins, 1984; MacDougall and Allen, 1984; MacDougall et al., 1988).

Modeling of changes in quality attributes of foodstuffs during thermal processes using the kinetic empirical approach includes theoretical considerations and empirical data fitting (Rand, 1983; Paulus, 1984). Heating procedures can affect the quality factors and especially the color of meat products through many physical and chemical mechanisms (MacDougall and Allen, 1984). Therefore, the kinetic empirical approach of modeling is commonly used for the formulation of models for the purpose of analysis, simulation, optimization and prediction (Karel, 1983; MacDougall et al., 1988).

In a previous publication (Palombo and Wijngaards, 1989b) we described the successful application of mathematical modeling techniques for the analysis of the effects of processing variables on color changes during processing of comminuted porcine lean meat (PLM) batters. The purpose of the present study is to demonstrate how, through mathematical modeling, intermediate and end point values of the lightness (L^*) of a PLM batter can be reasonably well predicted for different combinations of cooking times and temperatures.

5.3 MATERIALS AND METHODS

Meat raw material

Lean meat from pig leg muscles was trimmed of excess fat and gross connective tissue to obtain a desired constant composition of about 2.5% fat, 21% protein and 73% water. The meat was then cut into small pieces. Quantities of 6 kg were packed under vacuum in nylon-polyethylene laminate bags (van Hessen, Rotterdam, The Netherlands) and frozen at -40°C.

Experimental procedure

In order to start the chopping stage at a constant and reproducible temperature of the meat, a strict thawing procedure was used. The day before use 18 kg of meat

was thawed in two stages: 10 hours in a water bath at 15°C followed by overnight storage in a water bath at 4°C. The temperature at the start of each experiment was then always about 4°C.

Seventeen kg of meat was placed in a Kilia bowl-chopper (Laboratory model, Kiel, West-Germany) and coarsely chopped for 1 min at a knife and a bowl speed of 2500 and 20 rpm respectively (these speeds were used through the whole chopping stage which was done under atmospheric pressure.). Then 2% salt with 120 ppm sodium nitrite, 0.1% commercial phosphate mixture ("Degens-Latuw", Vlaardingen, The Netherlands) and 0.05% sodium ascorbate (Sigma, St. Louis, USA) were added dry. Chopping was then continued for another 6.5 min divided into 2 min chopping periods which were interrupted by breaks of 2 min for temperature measurement and sampling. Samples of the batter were transferred to 100g cans. The cans were sealed and kept for 45 min in a water bath at 20°C (this stage was necessary to eliminate the adhesion of the batter to the lid of the can). Subsequently, the cans were heated at varying temperature-time combinations (see experimental design), and cooled for 1 h at 0°C (the heating and cooling steps were performed in water bathes). For each temperature-time combination two replicate cans were opened and their surface color was measured separately with a Hunter D25M-9 Tristimulus colorimeter fitted with a D-25M optical sensor. The instrument gave the CIE 1976 L^* , a^* and b^* (CIELAB) values (for a 2° position of the "standard observer" and a "C"-type light source) from which the psychometric values lightness (L^*), hue angle (h^*) and chroma (C^*) were calculated (McLaren, 1980).

Experimental design

Two experiments, each of which was done on different days, were performed according to the experimental procedure. In the first experiment the batter was heated at 50°C, 60°C, 80°C and 100°C. In the second experiment (denoted 'replicate experiment') the heating temperatures were 50°C, 60°C and 70°C. The corresponding thermal treatments prevailed from the end of the "45 min, 20°C incubation" stage (defined as 0 time of heating) until 3 h later for 50°C, 60°C and 70°C, 1 h later for the 80°C and 0.5 h later for 100°C, with at least 9 measured time points at each temperature.

Data processing

Iterative fitting of kinetic data and other statistical analyses were performed by using the Genstat statistical package (Anonymus, 1977).

5.4 RESULTS

Changes in lightness (L^*) of PLM batter during heating at various temperatures are presented in Fig. 5.1. At all temperatures, L^* values initially increased rapidly with cooking, especially so at 80 and 100°C. The theoretical basis for this pattern, together with qualitative characteristics, have been presented in a previous publication (Palombo and Wijngaards, 1989a). Basically, cooking causes denaturation of proteins forming the meat batter's matrix and the batter's surface gradually becomes more opaque and light scattering. Relatively more light is reflected from it and its L^* value increases.

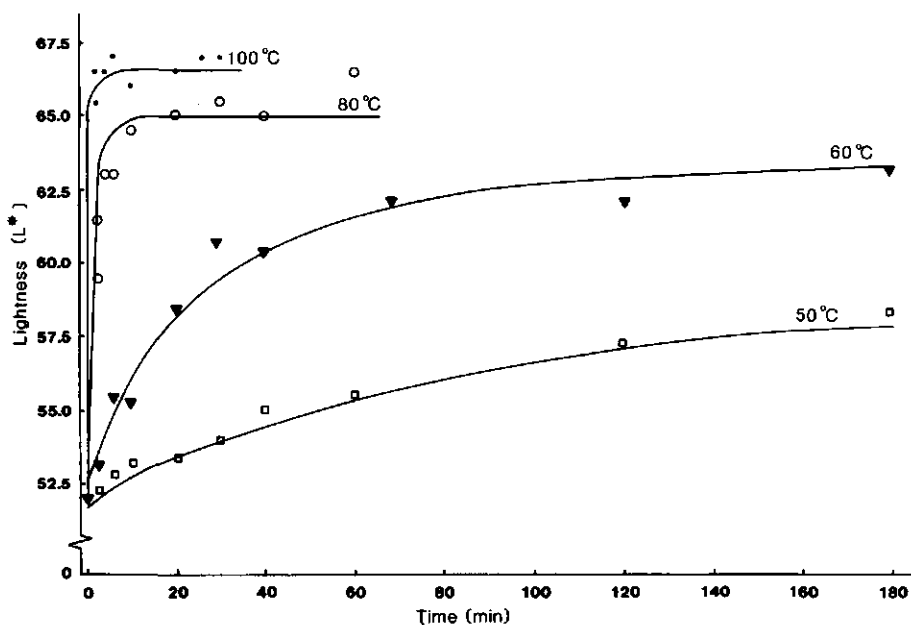


Fig. 5.1: Effect of heating temperature and time on lightness values of the PLM batter. Symbols ($\square, \nabla, \circ, \bullet$) represent actual data points. Lines represent values predicted using the model $L^* = a - be^{-ct}$.

Model for changes in L^* as a function of time at a constant heating temperature

The empirical approach of kinetic mathematical modeling (Labuza, 1982) was applied to the construction of a predictive model for L^* values of the PLM batter during these thermal treatments.

The following non-linear model was used:

$$L^* = a - be^{-ct} \quad (5.1)$$

where:

a = final value (L^* units); b = extent of increase (L^* units); $a - b = L^*$ at 0 time of heating; C = rate constant (min^{-1}); t = time (min)

The curve-fitting procedure, demonstrated that the model predicted the data reasonably well (Fig. 5.1).

The predictive model for L^* at different time-temperature combinations

The calculated values of the parameters (Eq. 5.1) for the different temperatures are given in Table 5.1. The predicted values for the initial value ($a-b$) for the four temperatures were similar (Table 5.1). In fact, the variation between them was comparable with the standard deviation obtained from the replicate measurements. Therefore for the purpose of model formulation, their mean value (52.43) was used.

To describe the dependence of the b parameter of Eq. 5.1 on temperature, the following linear model was used:

$$b = d + uT \quad (5.2)$$

where:

b = the extent of increase (L^* units); d = constant (L^* units); u = rate constant (L^* units/K); T = temperature in kelvin (K).

Linear regression of the derived b values (Table 5.1) versus temperature (T) resulted in the following model:

Table 5.1: Values of model parameters for the various cooking temperatures, as calculated from the model $L^* = a - be^{-ct}$

Model parameters	50°C	60°C	80°C	100°C
$a^{(1)}$	59.67	62.89	64.93	66.69
$a-b^{(2)}$	52.19	53.26	52.37	51.89
$C^{(3)}$	0.0095	0.0356	0.6443	2.3450
(S.E.) ⁽⁴⁾	(0.0034)	(0.0070)	(0.1790)	(0.2684)

(1) a = final value (L^* units).

(2) $a-b = L^*$ at 0 time of heating.

(3) C = rate constant (min^{-1}).

(4) Standard error for C .

$$b = 38.66 - 0.144T \quad r = -0.992 \quad (5.3)$$

This equation predicts the data reasonably well (Fig. 5.2).

The Arrhenius model was used to describe the temperature dependence of the c parameter of Eq. 5.1 :

$$C = C_0 e^{(-E_a/R'T)} \quad (5.4)$$

where:

C = rate constant (min^{-1}); C_0 = constant (min^{-1}); E_a = activation energy (cal/mol);

R' = gas constant (1.986 cal/mol K); T = temperature in kelvin (K).

Linear regression of the natural logarithm of parameter C versus $1/T$ resulted in the following equation:

$$C = e^{37.87 - 13697/T} \quad r = -0.991 \quad (5.5)$$

The good fit between the model and the data is shown in Fig. 5.2, and the high correlation coefficient supports the adequacy of this model.

Using the calculated mean value for (a-b) and substituting the terms for b (Eq. 5.3) and c (Eq. 5.5) in Eq. 5.1 results in the following final predictive model:

$$L^* = 13.76 + 0.144T + (33.86-0.144T) * e^{-N} \tag{5.6}$$

where: $N = e^{(37.87-13697/T)*t}$

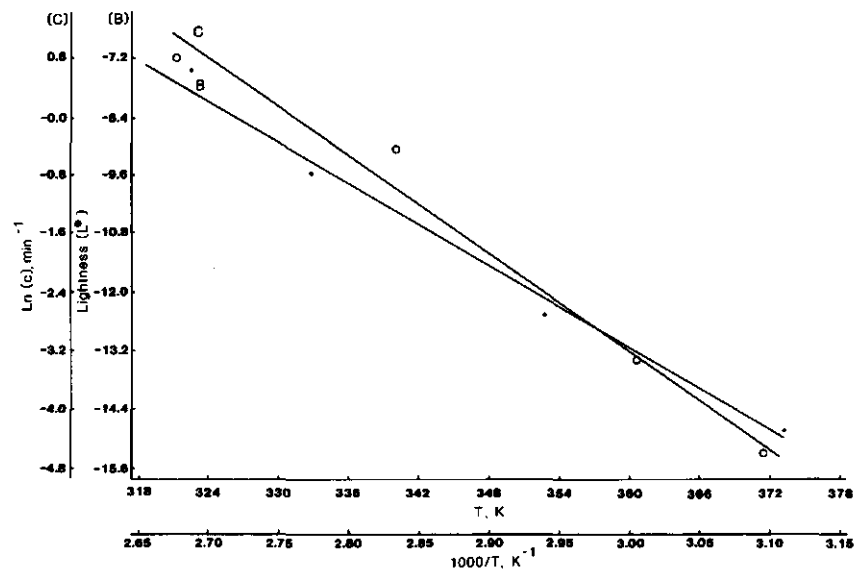
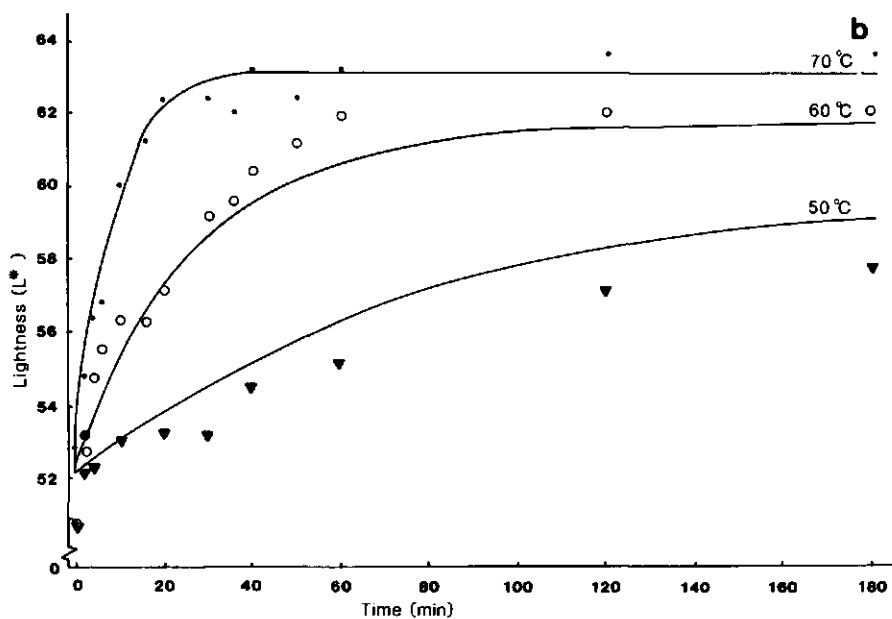
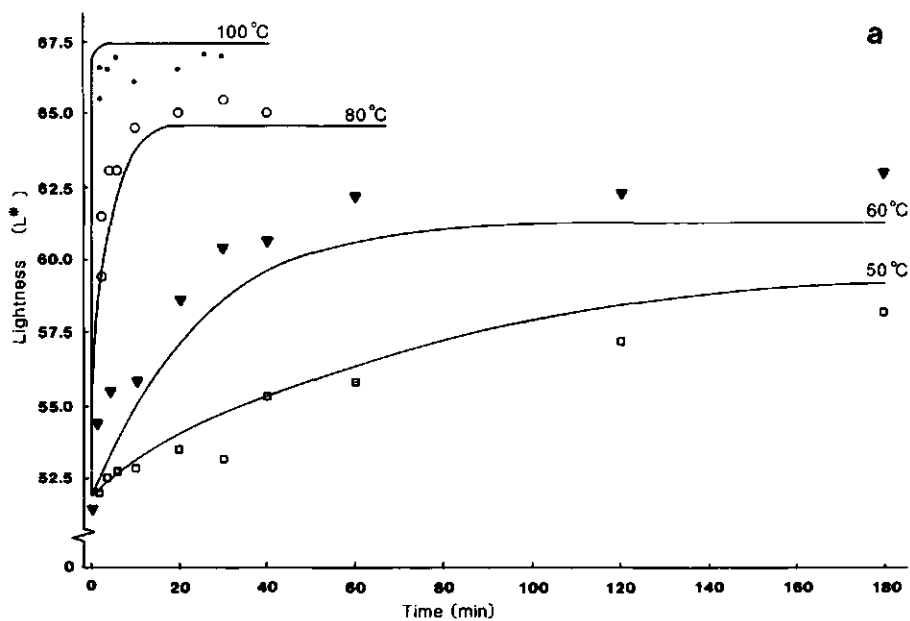


Fig. 5.2: Effect of temperature on the parameters of the model $L^* = a - be^{-ct}$. Solid circles represent derived values for b, using the model $b = d + uT$. Line B is the associated regression line of best fit. Open circles represent derived values for C, using the Arrhenius model $C = C_0e^{(-E_a/RT)}$. Line C is the associated regression line of best fit.

Verification of the model

For the same data set (Fig. 5.3a), good accordance between measured and predicted values was obtained. This finding is supported by results from analysis of variance (Table 5.2). The standard deviations of residuals (SD res.) in the measured data for L^* is of a magnitude similar to that of the corresponding predicted values.



The mean of residuals (Mn res.) gives some indication for systematical error in prediction and principally agrees with the patterns seen in Fig. 5.3a. Moreover, even in case of any consistent over or under estimations, their magnitude was comparable to that of the SD res. of the measured data.

A more substantial check of the usefulness of the model for predicting L^* values was performed by applying the verification procedure to a data set from the 'replicate experiment' [which included also heating at 70°C (Fig. 5.3b)]. The results

Table 5.2: Analysis of variance values of the standard deviations of residuals (SD res.) and means of residuals (Mn res.) obtained from verification procedure for the final predictive model for L^* (Eq. 5.6)

Temp. (°C)	Predicted L^* values		Measured L^* values
	SD res.	Mn res.	SD res.
<u>Data-set used for model formulation</u>			
50	0.50	0.48	
60	0.82	-0.88	0.88 ^(a)
80	1.19	-0.93	
100	0.41	0.86	
<u>Data-set from the 'replicate experiment'</u>			
50	0.53	0.80	
60	0.71	-0.39	0.42 ^(b)
70	0.64	0.35	

(a) value obtained from the whole data-set (4 temperatures).
 (b) value obtained from the whole data-set (3 temperatures).

Fig. 5.3: Prediction of lightness values of PLM batters during heating.
 a. using original data from Fig. 1.
 b. using data from the 'replicate experiment'.
 Symbols (□,▽,○,●) represent actual data points. Lines represent values predicted using final model (Eq. 5.6).

for SD res. and Mn res. (Table 5.2) show that the model appears to predict the data fairly precisely even for a temperature not used for its formulation.

5.5 DISCUSSION

Lund (1983) demonstrated that for the estimation of Arrhenius parameters and thus the values of the predicted attribute, the one-step, nonlinear regression model is more effective than the "classic" two-step method used here (i.e. regressing L^* versus time to obtain the model parameters and describing the temperature dependence of these parameters by a linear and Arrhenius models). However, using this one-step method for our data set did not result in an improvement of the predictive powerfulness of the model. Verification of the model resulted in comparable values to those presented in Table 5.2.

Palombo and Wijngaards (1989b) showed that the pattern of changes in L^* of PLM batters during heating was highly dependent on temperature and other processing variables used. However, the results presented in this study, deal with a temperature range in which consistently similar patterns of L^* were obtained. Accordingly, successful construction of a useful predictive model for L^* during the heating stage was possible. In the same publication, they showed that also h^* [hue angle - a psychometric color attribute calculated from the a^* and b^* values of the CIELAB color space by the following mathematical conversion $h^* = \arctan(b^*/a^*)$. It quantifies the change in color from red to yellow to green to purple etc. (McLaren, 1980)], has a consistently similar pattern of changes in the temperature range studied here. Thus, the same procedure for formulation of a predictive model can be used. For C^* [chroma - a psychometric color attribute calculated from the a^* and b^* values of the CIELAB color space by the following mathematical conversion $C^* = [(a^*)^2 + (b^*)^2]^{1/2}$. It quantifies the degree of difference of a color from gray (McLaren, 1980)] an extremely variable pattern of changes during heating in the temperature range of 40-100°C was reported (Palombo and Wijngaards, 1989b). Therefore, construction of such a model with the procedure used here is not readily attainable.

The present study is based on a limited volume of experimental data collected from a specific and well defined processing procedure. The effect of the number of replicates of data sets and the range covered by them on the model formulation is well documented (Draper and Smith, 1981; Rand, 1983). Nevertheless, this study

demonstrates that intermediate and end point values of lightness can be reasonably well predicted for time-temperature combinations within the range used for the construction of the model. Hence the results presented here, can serve as a basis for further development of predictive models during meat processing and storage.

ACKNOWLEDGEMENT

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REFERENCES

See at the end of the thesis.

PART 2

**COLOR AND RELATED STRUCTURAL
PROPERTIES OF CURED PORCINE
BATTERS**

6. INTRODUCTION

The work performed during the first part of the study was mainly based on the empirical approach of kinetic analysis and mathematical modeling of processes in food production and storage (Palombo and Wijngaards, 1989b,c). Color, determined by reflectance measurements, was then used merely as a suitable parameter although the problems, complexity and hence the limitations of its use were consciously considered. At that stage of the study the aim was to describe changes in color using attributes which are as visually meaningful as practically possible. In doing so, a compromise was sought between simplicity and accuracy for a phenomenological study which demands as frequent sampling as possible along the process under investigation.

In this part of the study, we have chosen to follow a more mechanistic approach, i.e., to try to explain experimental findings (some of which were gained during the previous stage of the study) by using known relevant physical and chemical principles (see Chapter 1). In addition, the scope has been extended to include some additional physical properties of meat batters.

From a study aimed at the characterization of changes in psychometric color attributes of comminuted porcine lean meat during processing, Palombo and Wijngaards (1989a) concluded that changes in L^* can be essentially related to changes in physical traits of the PLMBs. Based on this conclusion, a principal choice was made to orient the investigational efforts towards this attribute. This consideration is the rationale for the mechanistic study on changes in L^* of PLMBs during processing and subsequent storage at 15°C reported in Chapter 7. This work was followed by a study on the influence of surface rheological properties of PLMB on the behavior of entrapped air bubbles and on the corresponding changes in L^*

during phase 2 (Chapter 8). Finally, a study of the influence of air pressure during chopping and of formulation on color, rheology and fracture of some porcine batters is reported in Chapter 9.

7. MECHANISTIC STUDY ON CHANGES IN L^* OF PLMBs DURING PROCESSING AND SUBSEQUENT STORAGE AT 15°C

7.1 Introduction

Fig. 7.1 shows the results of a typical experiment, performed during the previous part of the study, dealing with changes in L^* of a porcine lean meat batter (PLMB), chopped under atmospheric air pressure (AAP), during chopping and subsequent

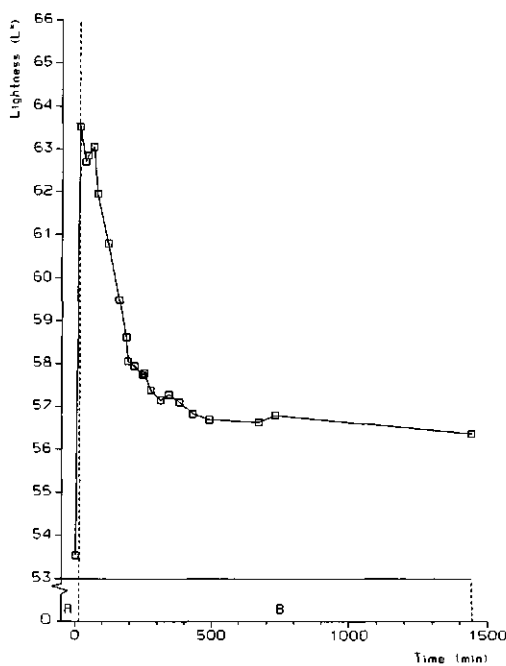


Fig. 7.1: Changes in lightness of porcine lean meat during chopping and subsequent storage at 15°C. A = Phase 1, B = Phase 2.

storage at 15°C. As has been pointed out by Palombo and Wijngaards (1989b) one can clearly speak of two distinguishable phases:

Phase 1. An increase during the chopping stage and

Phase 2. A decrease approximating to a plateau, which takes place during storage at 15°C for the period between "end of chopping" and "24 h".

The marked effect of air pressure during chopping on changes in L^* of PLMBs during these two phases has been characterized (Palombo and Wijngaards (1989a)) and kinetically analyzed (Palombo and Wijngaards (1989b)). In the latter publication it was clearly shown that for the chopping stage significantly higher L^* values were obtained for chopping under AAP than for chopping under reduced air pressure (RAP). On the other hand, the derived rate constant for changes in L^* during phase 2 was significantly lower for the system chopped under AAP versus that chopped under RAP. Data collected from the same study for temperatures of 30°C and 40°C were further analyzed to obtain information about the temperature dependence of the rate constants. The same model used for describing the decreasing phase (phase 2) in L^* (Palombo and Wijngaards, 1989b) was used for the analysis of the corresponding decreasing phase during storage at 30°C and 40°C. Table 7.1 presents

Table 7.1: Rate constants (C) and apparent energy of activation (E_a) for the changes in lightness

Temperature (°C)	Chopping under reduced air pressure ($C \times 10^2 \text{ min}^{-1}$)	Chopping under atmospheric air pressure ($C \times 10^2 \text{ min}^{-1}$)
15	1.5	0.8
30	22.8	4.6
40	124.0	14.0
Energy of activation (Kcal/mol)	31.8 (0.999) ^a	19.8 (0.999) ^a

^a Numbers in brackets are adjusted linear correlation coefficients of $\ln(C)$ vs $1/T$

the calculated rate constants for the three temperatures for two experiments representative of the two processing conditions, i.e., chopping under AAP and chopping under RAP. For AAP treatment at all temperatures the rate constants are lower. Using the Arrhenius model (Palombo and Wijngaards, 1989b) for describing

the temperature dependence of these rate constants resulted in an excellent fit (Fig. 7.2), which supports the adequacy of this model for the analysis (Saguy and Karel, 1980). Calculation of the apparent activation energy (E_a) for each of the conditions revealed a markedly lower value for the system chopped under AAP (Table 7.1).

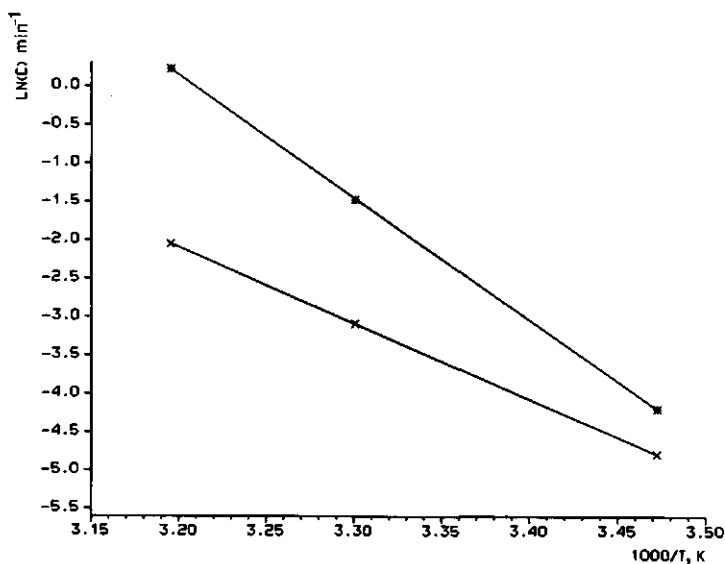


Fig. 7.2: Arrhenius plot of derived rate constants for chopping under atmospheric air pressure (x-x) and under reduced air pressure (x-→).

In both publications (Palombo and Wijngaards, 1989a,b) some lines of attack are presented for explaining this dramatic effect of air pressure during chopping on the behavior of L^* during the two phases. Essentially, two different types of processes are suggested to be responsible for the observed changes in L^* . One type concerns the transitions in scattering properties of the meat batter matrix. The other type concerns the changes in the absorption characteristics of their pigment myoglobin (Mb). However, no detailed relevant mechanisms responsible for the typical pattern of changes in L^* and for the strong effect of air pressure on it, neither evidence for their possible occurrence are provided.

In this chapter, we present results of a study aimed at:

- (1) Elucidation of the importance of some physical and chemical events in explaining the observed changes in L^* during phases 1 and 2.
- (2) Some mechanistic explanation, on the basis of the findings obtained from 1, of

the marked effect of air pressure during chopping on changes in L^* during phase 2 and on the corresponding changes in the E_a values.

First, a theoretical introduction will be given regarding: (1) The interaction between light and object and its relevance for our study; (2) The various physical and chemical events possibly affecting the behavior of L^* during processing. Based on this introduction working hypotheses for this study will be formulated. Subsequently, results pertaining to the effects of the absorption traits of the PLMB, salt and phosphate and entrapped air on the behavior of L^* will be reported separately. This part of the thesis will be concluded with an assessment of the extent to which our working hypotheses are confirmed or rejected.

7.2 Theoretical considerations

There has been an abundance of research work on the transitions taking place during processing of comminuted meat products (Hamm, 1975; Kotter and Fischer, 1975; Acton et al., 1983; Hermansson, 1986, 1988; Smith, 1988; Whiting, 1988). Basically, one can speak about five major physicochemical interactions occurring between the four components of the used system namely: (1) Protein-water; (2) Protein-protein; (3) Protein-fat; (4) Protein-air, and (5) Fat-air. As has been described by Palombo and Wijngaards (1989a,b), the meat batter system for which changes in L^* are presented in Fig. 7.1 consists of porcine lean meat (about 2.5% fat) to which no fatty tissue has been added. The processing procedure included addition of salt (containing nitrite) and phosphate. Accordingly, the protein-fat and the fat-air interactions may be of less relevance to our system.

The raw comminuted product obtained at the end of chopping is a disperse system consisting of a continuous, aqueous, and viscous sol-like matrix of sarcoplasmic and extracted myofibrillar proteins in which some muscle tissue fragments, fat particles and air bubbles are embedded (see also Chapter 1). It has been well established on the basis of aspects related to the light-object interaction that, this system is a translucent medium (MacDougall, 1982, 1984). As outlined previously, in the present part of the study a more mechanistic approach has been chosen, i.e., to try to explain experimental findings by known relevant physical and chemical phenomena. This approach demands much deeper understanding of the analytical procedures used. To provide a better insight into the possible impact of

the aforementioned physicochemical interactions on the changes in L^* (Fig. 7.1), the following theoretical introduction is indispensable.

7.2.1 Light object interaction

When light strikes an object the following may occur (Hunter, 1975):

- (1) *Reflection from the surface*: (1) Smooth surface: Mainly specular reflection (this mirror-like reflection occurs at 90° from the incident light and is mainly responsible for gloss). (2) Rough surface: Mainly diffuse reflection (this reflection occurs at 45° from the incident light and is mainly responsible for the color).
- (2) *Transmission into the object*: The ray of light penetrates the object after being refracted at its surface.
- (3) *Refraction into the object*: (1) Through the surface, (2) Through internal surfaces of numerous particles within the object (resulting in a backward diffuse reflection).
- (4) *Absorption within the object*: Selective absorption by the pigments.

In general, one can divide objects into three main types according to their interaction with the incident light (Billmeyer and Saltzman, 1981; Francis and Clydesdale, 1975):

- (1) *Transparent*: Objects that allow most of the light to pass through them with very small loss due to refraction at their surfaces.
- (2) *Opaque*: Objects that do not allow transmission of light but only reflect, absorb, and scatter the incident light (see below).
- (3) *Translucent*: Objects that allow some transmission of light and also reflect, absorb and scatter the incident light.

Since raw comminuted meats are translucent materials, it is apparent from this somewhat simplified classification that their interaction with light is far more complex than that of the other two types. Thus, further explanation of their different modes of interaction with light is merited.

Through the interaction between light and a raw meat batter the following may occur:

- (1) *Reflection from the surface*. From a rough surface the light is diffusely reflected. The wetness of a meat batter, in addition to the roughness of the surface, promotes some specular reflection (gloss) as well (MacDougall, 1984).
- (2) *Absorption*. While traveling through the object, part of the light is selectively

absorbed by the pigments of the material and gives rise to the color appearance of the object.

(3) *Transmission into the object.* The depth to which the light penetrates, directly depends on the degree of translucency and the thickness of the object.

(4) *Internal diffusion.* After having penetrated the surface the light beam encounters the surfaces of internal particles. It is partially (about 4%) reflected at each surface. When many of these particles exist in the system, the multiple refraction and reflection greatly diffuse the light and return most of it to the surface, where it leaves as diffusely reflected light. In our PLMB, being a disperse system, three important factors influence the process of internal diffusion, i.e., refractive index, overrun and particle size.

Refractive index. At every boundary between two materials of different refractive index e.g., aqueous matrix versus air bubbles or fat particles, light changes its speed and part of it is reflected. This process promotes diffusion of light and is called "scattering". Principally, at a certain wavelength, the larger the differences in refractive index between two components of a measured system the higher is its scatter (Francis and Clydesdale, 1975).

Overrun. In aerated systems, this term refers to the volume ratio (expressed as a percentage) between embedded gas bubbles and the continuous matrix. The effect of overrun on scattering is obvious. In case of low overrun the beam of light meets fewer number of interfaces on its way through the medium, and the extent of reflectance due to scattering becomes relatively small.

Particle size. The impact of particle size on light scattering and reflectance is more complex than that of the refractive index since it depends not only on the wavelength of the light but may involve also a resonance phenomenon (Gall, 1971). However, for a constant wavelength and a given refractive index of the particles and the medium the situation becomes simpler. In such conditions, as the particle size becomes smaller the scattering increases with the inverse of the square of the particle diameter to a maximum. This maximum is reached at about $0.1\ \mu\text{m}$. From then, as the particle size diminishes the scattering decreases with approximately the third power of the particle diameter (Francis and Clydesdale, 1975).

7.2.2 Kubelka Munk (K-M) analysis

Reflectance is defined as the ratio of reflected to incident radiation (Hunter, 1975). Basically, it is a surface property, but for translucent material due to the multimode of its interaction with light, it is not exactly so. In such a turbid medium, because of the internal transmittance and internal diffusion, both absorption and scatter affect the reflected light. The Kubelka-Munk (K-M) analysis is the most commonly used technique for separating the relative contributions of the absorption and the scatter to reflectance. The method of applying this analysis to translucent media is described by Francis and Clydesdale (1975). A prerequisite for performing such an analysis in meat systems, is the possibility to slice the material thin enough (1-5 mm) in a reproducible manner and to measure its thickness accurately. Additionally, in order to calculate the absorption (K) and the scatter (S) coefficients, one should measure reflectivity (R_∞ -reflectance from an infinitely thick sample, i.e., a sample in which no change in reflectance occurs due to a further increase in thickness) and the reflectance of thin layers of the material on black and white backgrounds. Several quantities may be calculated from this analysis, but the most commonly used one is:

$$K/S = (1-R_\infty)^2/2R_\infty \quad (7.1)$$

where:

R_∞ = reflectivity

K = absorption coefficient

S = scatter coefficient

Essentially, this equation states that the ratio of light absorbed by the pigments to that scattered by the matrix in which they reside, decreases with increasing reflectivity.

7.2.3 Relevant physical and chemical events

Individual physical and chemical events originating from the five interactions mentioned at the beginning of this section and having some bearing upon changes in L^* of our PLMB are outlined here separately for each of the defined processing

phases, i.e., Phase 1. An increase during the chopping stage; Phase 2. A decrease taking place during the storage at 15°C between "end of chopping" and "24 h". Additionally, the specific expected influence on L^* of each of the events is discussed using educated guesses based on the literature and on previous results.

7.2.3.1 Phase 1

(1) *Size reduction of the muscle tissue.* Basically, due to the creation of many new surfaces, this process is expected to cause an increase in light scattering and a corresponding increase in the L^* of the PLMB (see Section 7.2.1). However, with regard to the myofibrillar fragments, due to a small difference between their refractive index and that of the aqueous proteinaceous matrix, only a small increase in scatter and L^* can be expected. This point is supported by Birth (1978), who stated that for high-moisture food products contrary to the situation in dry powder systems, particle size has no obvious meaning. On the other hand, for optically distinguishable particles, e.g., air bubbles or fat particles, due to large differences in refractive indices, a marked increase in scatter and in L^* can be expected.

(2) *Mechanical liberation of cellular proteins resulting from the decomposition of the muscle tissue.* This process is expected to form a sol- like matrix mainly consisting of sarcoplasmic proteins. Such a matrix can induce a decrease in light scattering of the meat due to smaller differences in refractive indices between myofibrillar fragments and sarcoplasm in the final batter. Thus, the translucency of the PLMB is expected to increase with attended decrease in L^* .

(3) *Entrapment of air.* Using the classification suggested by Prins (1988), the comminution process can be considered as a foam-making process in which a given amount of semisolid material is aerated in an unlimited amount of air. During the initial stage of chopping the air is brought into the system in the form of big bubbles which are subsequently reduced in size due to the work of the cutting knives. At the end of chopping, finely distributed air bubbles are dispersed within the continuous proteinaceous matrix of the meat batter (Kotter and Fischer, 1975). Due to the differences in refractive indices of the air and the matrix, air bubbles act as scattering elements. Higher scatter is associated with higher L^* (Francis and Clydesdale, 1975).

(4) *Transitions in the state of muscle proteins on the air-water interface.* This process is shown to take place on the air-water interface during the whipping of egg albumin

and is partly responsible for the opacity of the produced foam (Halling, 1981). Although no evidence for its occurrence during the comminution of meat systems could be found in the literature, Dickinson et al. (1988) suggest accelerated aggregation and precipitation of myosin, in the form of "wispy threads", on an oil-water interface under specific conditions. Protein films on oil-water and air-water interfaces can be considered to behave similarly (Tantikarnjathep et al., 1983). So, it is felt that this possible event should be mentioned since in case it occurs during chopping of the meat, an increase in the scattering properties of the PLMB with a corresponding increase in L^* can be expected.

7.2.3.2 Phase 2

(1) *Salt-and phosphate-induced swelling of myofibrillar fragments and myofibrillar proteins.* This process (Offer and Trinick, 1983; Wilding et al., 1986) is expected to increase the translucency of the system and to induce a corresponding decrease in L^* (Jenkins, 1984; MacDougall, 1984).

(2) *Disproportionation of entrapped air bubbles.* This process causes a shift in the bubble size distribution towards higher size classes (Prins, 1988). Scattering properties of the PLMB are expected to decrease with an attended decrease in L^* (see Section 7.2.1).

7.2.3.3 Phase 1 and phase 2

(1) *Salt-and phosphate-induced extraction, solubilization and depolymerization of myofibrillar proteins* (also called salt-soluble proteins; Solomon and Schmidt, 1980; Acton et al., 1983). As explained under 1 in Sections 7.2.3.1 and 7.2.3.2, this process is expected to cause a decrease in L^* .

(2) *Changes in the absorption characteristics of the main PLMB pigment, myoglobin (Mb).* As is well documented in the literature (MacDougall, 1977), a dynamic equilibrium among the various forms of this pigment exists during the processing of the comminuted meat products. In particular for cured products shifts in this equilibrium can be large (Palombo and Wijngaards, 1989a,b). Examination of the reflectance spectra of Mb, nitric oxide Mb (NOMb) and metmyoglobin (MMb) (Reith and Szakally, 1967; Francis and Clydesdale, 1975), together with the corresponding curve of the standard observer (Billmeyer and Saltzman, 1981), makes

clear the possible shift in the tristimulus Y value, and consequently in L^* , that can be expected whenever the equilibrium among the Mb forms changes favoring the formation or reduction of MMb.

7.2.4 Approach used and working hypotheses

Fig. 7.3 summarizes the proposed principal effects of the various physical and chemical events on the observed changes in L^* . Basically, it is suggested that the overall changes observed in L^* during each of the processing phases is the sum of the assumed corresponding individual effects induced by each of these events. A study on the impact of any of these various events on changes in L^* is complicated by the fact that they may occur simultaneously and occasionally are interdependent. Moreover, their relative relevance in affecting L^* can vary during the different phases of the process. Owing to this complexity, it is obvious that the defined objectives of the study (Section 7.1) cannot be accomplished using the exactness of a purely mechanistic approach exercised in certain branches of physical chemistry. Consequently, we decided to adopt the empirical approach for purpose of this investigation. Practically, this implies that some chosen relevant factors of the process are varied while the response in L^* and other closely related parameters is monitored. The analysis of the response is used to deduce the relative importance of the related physical and chemical events in explaining the changes in L^* . The two stages approach, i.e., exploratory and confirmative was employed. This means that the influence of a factor was further investigated, only if the effect found for it during the exploratory stage (which includes review of closely related literature, previous results, and small scale-experiments) was sufficiently large to merit embarkation on the confirmative stage (in which the effect is further substantiated and, whenever possible, quantified).

The experimental efforts were concentrated on studying the influence of three factors, namely:

- (1) Absorption traits of the muscle pigment,
- (2) Salt and phosphate.
- (3) Entrapped air, and

Accordingly, the working hypotheses were:

- (1) Changes in the absorption traits of the muscle pigment are an important factor influencing the changes in L^* during phase 2.

Physical and chemical events

Expected effect on L^*

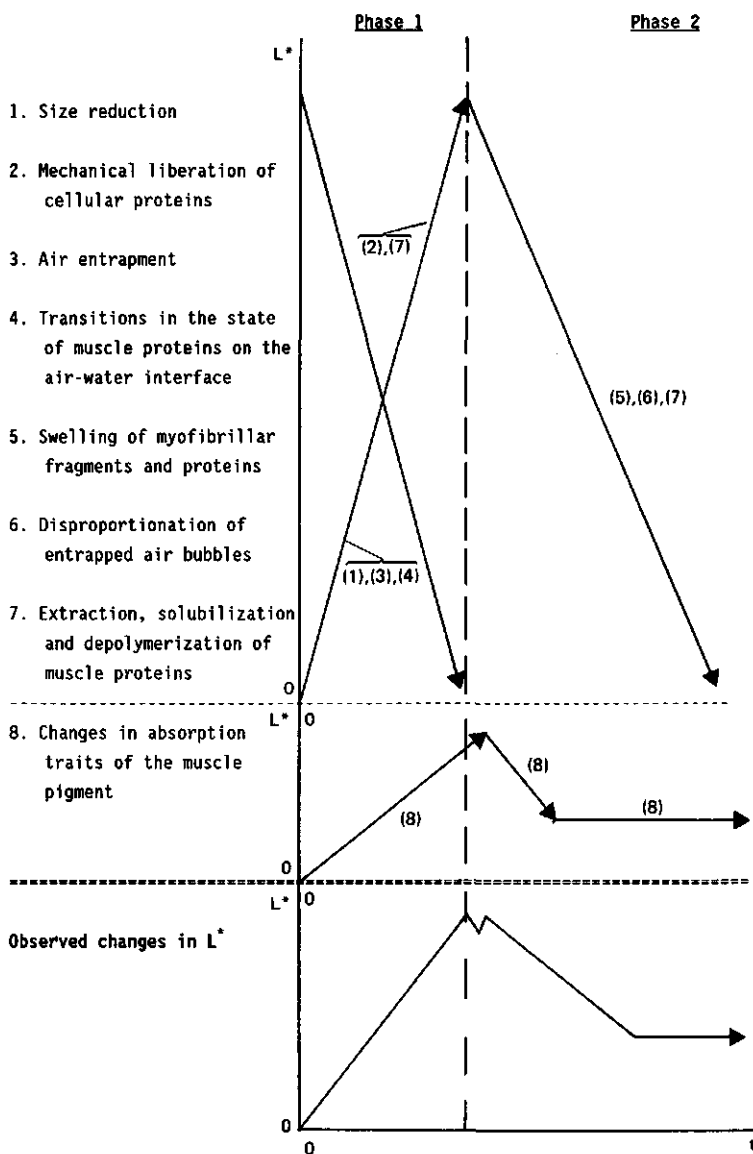


Fig. 7.3 : Expected effect of various physical and chemical events on the behavior of L^* during phase 1 and 2.

(2) Events induced by salt and phosphate are an important steering factor influencing the scattering properties of the PLMB and thus changes in its L^* during phase 2.

(3) The extent and behavior of entrapped air in PLMB strongly affect its scattering properties and consequently the changes observed in its L^* during phases 1 and 2.

7.3 Influence of changes in absorption characteristics of the PLMB

7.3.1 Introduction

Little (1964) worked with a translucent model system consisting of agar (to ensure internal transmission), cellulose (for light-scattering effects) and stable yellow dye (to regulate color differences among samples). Results of color measurements for this model system, were expressed in the Hunter L, a and b values. For all modes of measurement, including the deep layer which is of relevance to our meat batter system, she could clearly demonstrate that increasing the pigment concentration resulted not only in a shift in a and b values but also in the L value. In a comprehensive study, MacDougall (1982) presented the complex interactive effect of muscle pigment concentration and the K-M scatter coefficient (see Section 7.2.2) on the color of oxygenated bovine muscle using the psychometric attributes L^* , h^* and C^* . He demonstrated that an increase in L^* can be achieved either by an increase in scatter or by a decrease in pigment concentration. Such an increase is accompanied with an increase in hue towards yellow and a rather small effect on chroma. Palombo and Wijngaards (1989a) showed how the presence of nitrite can influence the changes in L^* of PLMB during processing and storage at 15°C. Two distinguishable phases were analyzed separately:

Phase 1. An increase during the chopping stage, and

Phase 2. A decrease approximating to a plateau which takes place during storage at 15°C between "end of chopping" and "24 h".

For phase 1 a marked effect of nitrite on the pigmentation state at the end of chopping was reported. In the system containing nitrite the predominant form of Mb was MMb, whereas for the system without nitrite the predominant form was OxyMb. These dramatic differences could easily be detected visually and were also monitored by the corresponding values for h^* and C^* . The system without nitrite had the typical

bright pinkish color of bloomed meat (low h^* and high C^* values) whereas the system with nitrite had the typical brow-gray color of oxidized Mb (high h^* and low C^* values). The reason for not detecting an influence of the pigmentation state differences on the L^* value at the end of chopping can be the relatively high scattering properties of the batters at this stage (As was suggested in Section 7.2.3, this high scatter can be accounted for by the entrapment and subsequent size reduction of air bubbles during comminution). This suggestion is further supported by the rationale of the Kubelka-Munk (K-M) analysis (see Section 7.2.2), i.e., with increasing reflectivity the proportion of light scattered by the system increases on account of light absorbed by its pigments. Thus, when the reflectance of a translucent medium is being measured, one may speak of a certain masking effect on absorption by increasing scatter characteristics (Hunter, 1975).

For phase 2, a large influence of the transitions in pigmentation on the behavior of L^* was detected. In the system containing nitrite a steeper decrease and consistently lower values until 24 h storage at 15°C were obtained for L^* . This event corresponded closely with the marked decrease in h^* , which was mainly caused by the formation of NOMb. Thus, compared to the situation in phase 1, during storage at 15°C - presumably due to a decrease in scatter - a larger effect of absorption changes on L^* is observed.

From the above review and from the introduction given in Chapter 2 and in Section 7.2, it is conceivable that in a meat system a shift in concentration, and/ or form, of myoglobin (Mb) have consequences on both its measured reflectance spectrum and calculated lightness (L^*) hue (h^*) and chroma (C^*) values. Additionally, the relation between lightness and pigment concentration is not linear (MacDougall, 1982). Thus, a simple correction for the absorption component in the values of lightness in order to gain information pertaining only to changes in scatter, is not readily attainable. For this purpose a detailed K-M analysis is needed.

Several studies have used the K-M analysis to separate the contribution of absorption and scatter to the experimental reflectance values of meats (MacDougall, 1970, 1984). The application of this analysis to the present study proved to be difficult, and even practically impossible, because of several problems. First, handling of the meat batter to obtain a sufficiently thin layer with accurately measurable and reproducible thickness (1-5 mm) was hampered by the sticky and inhomogeneous nature of the batter. Second, such handling caused detectable transitions in the surface and microstructure (with strong reference to the entrapped air bubbles) of

the batter. Third, the preparation of such samples took excessively long time periods during which large changes in the state of the pigmentation and the entrapped air bubbles (see Section 7.5) took place.

In view of these problems a choice has been made to obtain a better insight into the effect of the pigmentation state on changes in L^* during phase 2 by fixation of the pigmentation state. Carbonmonoxide (CO) is known to form an extremely stable covalent complex with Mb called, carboxymyoglobin (COMb) (Lanier et al., 1978). This complex is cherry red in color, resembling the color of the oxygenated myoglobin (OxyMb) which is appreciated by consumers. The extremely stable absorption characteristics of COMb stimulated studies on the use of CO in controlled-atmosphere packaging and storage (Francis and Clydesdale, 1975) as well as during blending of mechanically separated poultry meat (McNeill et al., 1987). Even at a low concentration (1-10%) of this gas a marked preservative and stabilizing effect on color of meat has been shown (McNeill et al., 1987). Additionally, CO contrary to CO₂, is an inert gas which doesnot impose changes in the proteinaceous matrix, and thus in scatter, due to pH alteration. Also, its solubility is comparable to that of nitrogen thus excluding any side-effect on a possible disproportionation of entrapped gas bubbles during phase 2. Hence, the main traits of the batter affected by CO is its absorption.

In this study, we used CO in order to fix the absorption properties of the PLMB and thus to learn about the validity of our first working hypothesis, i.e., changes in the absorption traits of the muscle pigment are an important factor influencing the changes in L^* during phase 2.

7.3.2 Materials and methods

Meat raw materials

The preparation and composition were essentially as described by Palombo and Wijngaards (1989a). To achieve better homogeneity of the PLM raw material an additional preparative step was incorporated in this procedure. This step included coarse chopping of the meat pieces for 20 s in a Kilia bowl-chopper as described by Palombo and Wijngaards (1989a).

Experimental procedure

The thawing procedure was also as described by (Palombo and Wijngaards,

1989a). In order to perform the chopping under a controlled atmosphere and because of safety considerations related to the use of CO, the mixer (Moulinette, Paris, France) had to be placed in a special ventilated chamber. An additional consequence of this constraint was the use of smaller quantities of porcine lean meat (PLM) than those used in previous parts of the study (Palombo and Wijngaards, 1989a,b,c).

In each experiment 200 g of this pre-comminuted PLM was placed in the bowl of the mixer and 2% NaCl, 0.1% commercial phosphate mixture, 0.05% sodium ascorbate (see Palombo and Wijngaards, 1989a) and 0.05% dithionite (Merk, Darmstadt, W. Germany) were added dry. Dithionite was added to extend the conversion of MMb, if present in the PLMB, to COMb (Fransham and Walters, 1981). Then the cover of the mixer, having an inlet for a gas flow, was placed and tightened. To have a CO atmosphere in the headspace of the mixer at start of the chopping, a flow of CO was regulated to achieve a 0.02 bar overpressure which was maintained for 15 seconds before the onset of chopping and during chopping. Then the meat was chopped for three 15-second runs which were interrupted by breaks of 30-second for temperature measurement and for scraping the walls of the bowl. Based on work reported by Fransham and Walters (1981), using such a chopping set-up, almost all pigments were in the COMb form at the end of chopping. (This was further checked by preliminary experiments in which the meat was saturated with CO by spreading it in a thin layer on large perforated Petri dishes and storing it for 24 h at 0°C in a desiccator containing a CO atmosphere. Chopping of this CO-saturated PLM in the aforementioned procedure resulted in color changes which were very similar to those obtained for a system not saturated with CO). Subsequently, the batter was transferred to two 100 g cans. Still being under CO flow a Petri dish cover was placed on top of the batter of each of the two cans and sealed with adhesive tape. This system is named the CO-system. The control experiment for this treatment was performed using the same experimental procedure but with chopping under atmospheric air pressure. This system is named AAP-system. All the taped cans were stored at 15°C in the dark till 24 h. At various time intervals the color of each can was measured as described next.

Color measurement: Owing to an organizational problem, we had to use another colorimeter than the Hunter D25M-9 used in the first part of the study, i.e., the Minolta tristimulus colorimeter model CR-110. The measuring conditions were the same as used with the Hunter. The instrument gave the CIE 1976 L^* , a^* and b^*

(CIELAB) values (for the 2° position of the "standard observer" and a "C"-type light source) from which the psychometric values lightness (L^*), hue (h^*) and chroma (C^*) were calculated (Wyszecki and Stiles, 1982). The color of the surfaces of two replicate cans was measured separately through the Petri dish covers.

Several preliminary experiments showed that the pattern, but not the magnitude, of the changes in color of the PLMB during processing was similar to that obtained using the Hunter colorimeter. The main cause of the difference in the absolute values is the fact that the Minolta colorimeter unlike the Hunter colorimeter includes the specular reflectance.

7.3.3 Result and discussion

A preliminary study showed that color changes during phase 2 for AAP-systems containing or not containing nitrite were similar to those obtained in corresponding large-scale experiments performed in a previous stage of the study (Palombo and Wijngaards, 1989a). Thus, one can use the present set-up to study changes in color during this phase. However, this preliminary study disclosed that the use of nitrite-containing salt in the CO-system resulted in an initial oxidation of the Mb to MMb thus hampering its complete conversion into COMb. Hence, fixation of the pigmentation state in a nitrite-containing system was not possible and a direct evidence of its role in affecting changes in L^* during phase 2 was not attainable.

In light of these findings it was decided to check the effect of a CO atmosphere in a system not containing nitrite. Results of changes in L^* , h^* and C^* during phase 2 in CO and AA systems are presented in Fig. 7.4a, b and c respectively. At the end of chopping a clear difference in the color of the two systems could easily be perceived visually. The CO-system had a dark cherry red color whereas the AAP-system had the typical light pink color of bloomed meat. With storage time the AAP-system, as expected (Palombo and Wijngaards, 1989a), initially became somewhat grayish but with longer storage gradually turned red. In contrast, the CO-system remained constantly dark red without visually perceived changes. These observations are confirmed by the monitored changes in h^* and C^* . The largest relative changes are observed for C^* in the AAP-system. These can be mainly attributed to the formation of MMb and its gradual reduction by the endogenous reducing systems and to the added sodium ascorbate and dithionite (Giddings, 1974; Watts et al.1966).

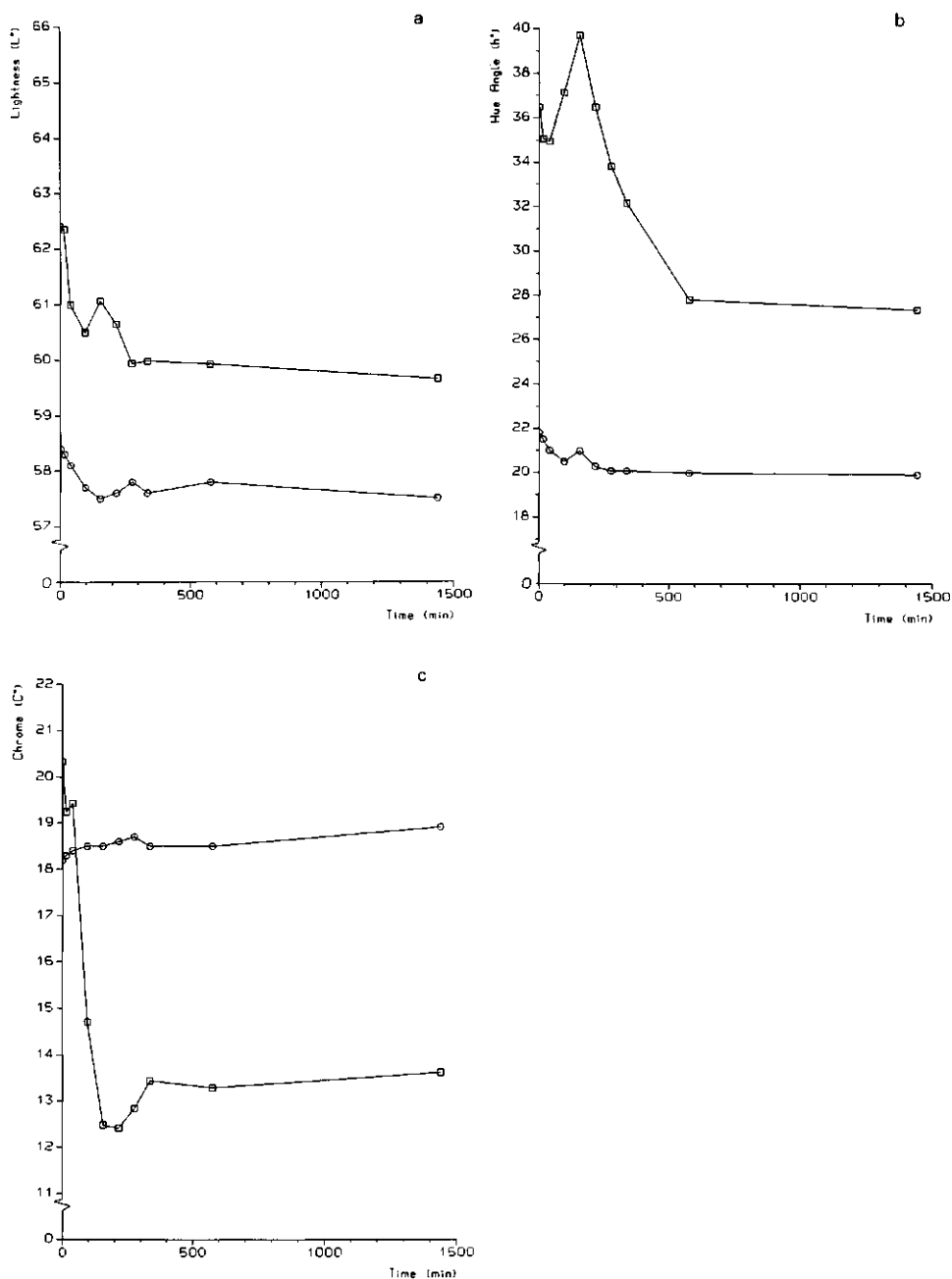


Fig. 7.4 : Changes in lightness (a), hue angle (b) and chroma (c) of porcine lean meat batters during storage at 15°C for system chopped under air atmosphere (□-□) and under CO atmosphere (○-○), (both batters not containing nitrite). 0 time is the time of end of chopping.

These transitions in the absorption traits have a definite effect on the measured L^* in the AAP-system. Closely paralleling changes in h^* and C^* , a clear increase and decrease in L^* is observed. Conversely, for the CO-system the almost constant h^* and C^* values are clearly reflected by a very small decrease in L^* and a subsequent plateau.

The different behavior of the two systems can also be explained by using the relationship between absorption (K) and scatter (S) coefficients as defined by the K-M analysis of reflectance (see Section 7.2.2, Eq. 7.1). Following the approach used by Little (1964) and Francis and Clydesdale (1975) the tristimulus Y value or L^* can be substituted for reflectivity at a certain wavelength (R_λ). Since the two systems are processed identically, S values of both can be assumed virtually identical. Consequently, the only cause of the difference between the two systems with respect to changes in L^* is the different changes in the absorption coefficient, K.

A closer examination of the very first changes in L^* (Fig. 7.4a) reveals that for both systems a small but definite decrease takes place. This initial decrease, immediately after the end of chopping, was always encountered in replicate experiments and also in similar experiments in which sodium nitrite was added during processing. A possible explanation for its occurrence may be the disproportionation of entrapped air bubbles (see Fig. 7.3). This suggestion will be worked out in more details in Section 7.5.

The findings presented in this section provide clear qualitative evidence in favor of the working hypothesis stating that transitions in the absorption characteristics of our PLM system are an important factor affecting changes in its L^* during phase 2. Due to the dynamic and complex nature of the various transitions in the batter system (see Section 7.2.3) a quantitative estimation of this effect experimentally is very difficult.

7.4 Influence of salt and phosphate

7.4.1 Introduction

It is well documented that the empirically determined water-holding capacity of processed meats is positively affected by addition of salt and phosphate (Hamm, 1971; Offer and Trinick, 1983; Hermansson, 1986; Wilding et al., 1986; Smith, 1988).

Comminution destroys the integrity of the muscle tissue. The resulting homogenate consists of a continuous aqueous proteinaceous phase which contains fragments of muscle fibers, myofibrils, sarcolemma and other subcellular particles as well as particles of intramuscular fat and collagen and elastin from connective tissue (see Section 7.2.3). In such an aqueous sol-like system, the presence of salt and phosphate, producing an ionic strength of about 0.6, causes extraction, solubilization and depolymerization of myofibrillar proteins (Acton et al., 1983). Another important effect of the salt and phosphate is the swelling of myofibrils and their fragments. In an extended study on the mechanism of water holding in meat Offer and Trinick (1983) suggest that the difference in light scattering between PSE (pale, soft, and exudative) and DFD (dark, firm, and dry) meats can be explained by the variation in swelling and shrinkage of their myofibrils. They suggest that shrinkage of the myofibrils may increase the difference between their refractive index and that of the sarcoplasm, inducing an increase in scattering properties and lightness or paleness of the meat. However, it is felt that a more important factor causing the pale appearance of PSE meat is a low pH induced protein denaturation (Honikel and Kim, 1986).

Schmidt (1984) has used light, transmission electron and scanning electron microscopy to study the microstructure of comminuted meat products. He states that the type and level of additives such as salt, phosphate, and pH of the system, greatly affect the microstructural characteristics of the final meat batter. Hermansson (1986) has stressed the importance of microstructural studies in understanding the transitions in the water-holding capacity of comminuted meat systems. In light of this information we used microstructure (studied by light microscopy) as an indicative parameter for checking our second working hypothesis, i.e., events induced by salt and phosphate (Fig. 7.3) are an important steering factor influencing the scattering properties of the PLMB and thus changes in its L^* during phase 2.

Theoretical considerations: Results reported by Palombo and Wijngaards (1989a,b) clearly demonstrate the large influence of air pressure during chopping on the behavior of the psychometric color attributes of PLMB during processing. Based on these studies it may be assumed that the air overrun as well as the size distribution of the entrapped air bubbles have a strong impact on the scattering properties and hence on the L^* of the PLMB (This hypothesis will be investigated in Section 7.5). Addition of salt and phosphate is known to markedly increase the apparent viscosity

of muscle homogenate and meat emulsions (Hamm, 1975). A relation between bubble size and viscosity of a liquid or a semisolid system that is being whipped or aerated states that, the higher is the viscosity, the smaller is the size of the entrapped air bubbles (Prins et al., 1986). Further, a finer and more stable distribution of air during foaming of meat batters is attributed to the action of added phosphates (Kotter and Fischer, 1975). Therefore, measurement of the effect of salt and phosphate on changes in L^* during the chopping phase, simply by their addition or elimination, is complicated by the fact that other relevant factors change as well. Consequently, the present study will deal with the effect of salt and phosphate on changes in L^* only during phase 2. However, also for this phase a potential complication has been outlined in Section 7.3, i.e., the influence of transitions in the state of pigmentation on L^* . Thus, if one wishes to examine the pure effect of salt and phosphate, accompanying changes in the absorption traits of the system should be reduced to a minimum. To approach these prerequisites the following experimental procedure was used.

7.4.2 Materials and methods

Experimental procedure

For each of the two experiments (both performed on the same day), 5 kg of PLM (see Section 7.3.2 for its preparation and thawing procedure) was placed in a Stephan bowl chopper (model A-120, Almelo, The Netherlands) and coarsely chopped for 1 min at knife and bowl speeds of 3000 and 18 rpm respectively (these speeds were applied throughout the whole chopping stage). Then 0.5% NaCl (containing 30 ppm sodium nitrite) and 0.05% sodium ascorbate were added dry. Chopping was continued for another 2 min and was followed by a 1-min break for temperature measurement and for cleaning the wall of the bowl. This was followed by 0.5-min chopping after which the batter was transferred to a Hobart mixer (model A-12, London, England). Then 1.5% NaCl and 0.1% commercial phosphate mixture (see Section 7.3.2) or none of these were added dry. The batters with and without added salt and phosphate were designated +sp and -sp respectively. Subsequently, each of the batters was mixed at a rod speed of 40 rpm in two 1-min runs interrupted by a 1-min break for temperature check and for cleaning the wall of the mixer. The final batters were transferred to 100 g cans which were sealed and stored in a water-bath at 15°C.

This experimental procedure resulted in batters having the same characteristics for the two treatments at the end of chopping. The subsequent moderate mixing stage is expected to distribute the dry additives (when added) evenly into the batter, but to have little influence on the air content, nor presumably on the air distribution as compared to the immense effect of the high-speed chopping phase (which will be further discussed in Section 7.5).

Microstructural examination: Samples for microstructural examination were taken at four time points of the process, namely, end of chopping, end of mixing, and 3 and 24 h from the start of chopping. Samples were embedded in paraplast. One block from each sampling time was sectioned at 5 μm thickness using an American Optical rotation microtome (model 820, New-York, USA) and stained with toluidine blue as described by Swasdee et al. (1982). The stained sections were examined by light microscopy for identifying morphological changes in the microstructure of the batters.

Density measurements: The batter content of two cans was immersed in a 250 ml measuring cylinder filled with water and positioned on a digital balance. The volume of displaced water and the recorded weight (after correction for added salt (2.1 g/ml)) were used for calculation of the density.

Color measurements: Was done as described in Section 7.3.2. For every "time-point" measurement two replicate cans were opened and the color of their surfaces was measured separately through Petri dish covers.

7.4.3 Results and discussion

Changes in L^* during the various processing phases for the systems +sp and -sp are presented in Fig. 7.5a, b. For both systems a similar pattern of changes can be seen. This pattern includes an increase during chopping followed by a small decrease during mixing. Then a small increase commences followed by a gradual decrease until a plateau is reached at about 7 h from the start of chopping. The L^* values are continuously lower for the +sp system than for the -sp system. However, this difference diminishes during the storage period from 3 h to 24 h. An examination of the microstructural traits of the two systems at the end of chopping reveals a very similar appearance (Fig. 7.6a). Due to the low salt content for both systems a grainy appearance can be observed. Some fragments of muscle fibers in which the myofibrils can be easily distinguished are embedded in a grainy matrix of

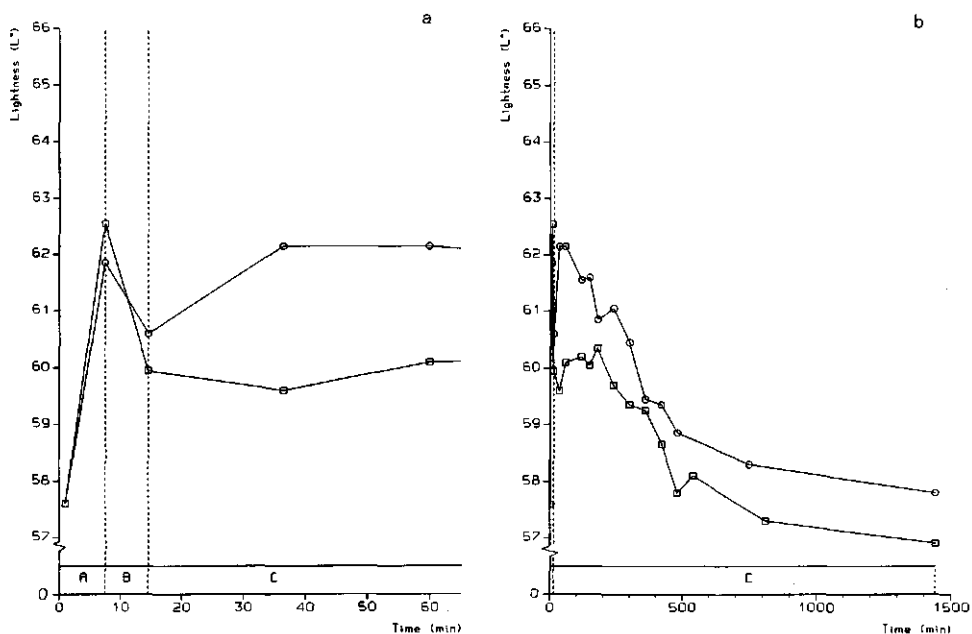


Fig. 7.5 : Changes in lightness of porcine lean meat batters during processing and storage at 15°C for system with (□—□) and without (○—○) addition of salt and phosphate at the stage of mixing. A = Chopping, B = Mixing and C = Storage at 15°C. a = Changes until 60 min; b = Changes until 24 h.

mechanically liberated sarcoplasmic and myofibrillar proteins. At the end of mixing, an extremely different microstructure is observed for the two systems (Fig. 7.6b) The -sp system still maintains the same grainy appearance, whereas the +sp system shows a smooth and dense matrix containing fiber fragments and having a diffuse appearance (in which no distinct myofibrillar structure can be seen). This difference is explained by the well documented influence of salt and phosphate on solubilization and extraction of myofibrillar proteins and partly on swelling of myofibrillar fragments (Section 7.4.1). The same difference in appearance persisted until 24 h at 15°C.

The densities (in g/ml) of the two batters were 1.043 ± 0.008 (n=5) and 1.047 ± 0.009 (n=5) for the +sp and -sp systems respectively. These results support the assumption that the moderate mixing stage would not have much impact on the air overrun of the batters.

The marked difference in microstructure between the two systems is paralleled,

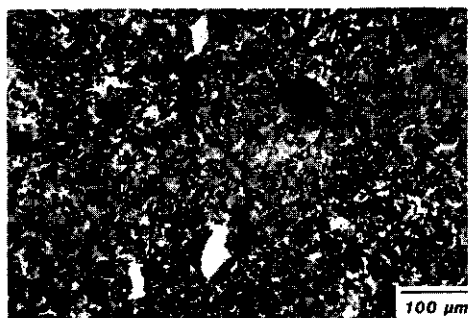
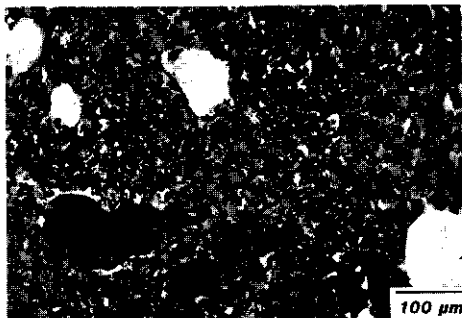
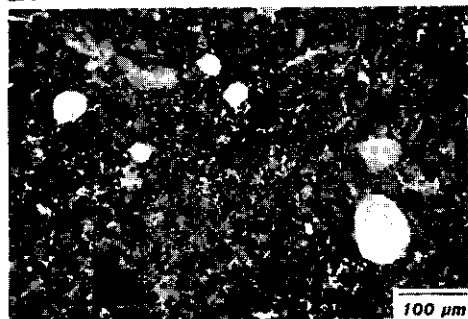
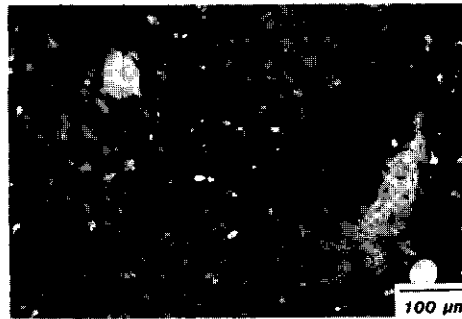
A1**A2****B1****B2**

Fig. 7.6 : Microscopical appearance (x100) of porcine lean meat batters at the end of chopping (A) and at the end of mixing (B). 1 and 2 stand for systems without and with the addition of salt and phosphate at the end of mixing respectively.

in particular during processing time up to 3 h, by a small but consistently lower absolute position of the L^* plot for the +sp system. This finding suggests that the salt-and phosphate-induced solubilization, extraction, depolymerization and swelling of the microcomponents of the batter causes a small increase in the translucency of this batter.

In case these transitions would have had a large and continuous decreasing impact on the translucency of the +sp batter all along phase 2, a definite difference between the corresponding courses of changes in L^* of this system and that of the -sp system should have been obtained. However, as can be observed in Fig. 7.5b, from 3 h until 24 h, the plots for the two treatments have a similar decreasing course.

Additionally, it should be noted that a decreasing phase in L^* immediately after chopping occurred also in similar experiments in which no salt and phosphate were

added at any stage and in experiments in which salt and phosphate were added but the mixing stage was replaced by a corresponding waiting time. It is suggested that this decrease is to be attributed to transitions in entrapped air bubbles. This hypothesis will be dealt with in Section 7.5 when we will also attempt to provide some explanation for the subsequent small increase in L^* .

Based on the evidence obtained from these exploratory experiments, it can be suggested that, if there is any effect of salt and phosphate on the behavior of L^* during phase 2, it occurs mainly during the initial stage of this phase. Due to these findings any further quantification of the effect of this factor was not undertaken.

7.5 Influence of entrapped air

7.5.1 Introduction

The study described in Section 7.1 demonstrates the great effect of the air pressure during chopping on the behavior of L^* during the two defined processing phases. The marked inhibitive effect of oxygen on the chemical reactions ultimately leading to the formation of the cured meat pigment NOMB during phase 2 has been discussed by Palombo and Wijngaards (1989a). Also, a considerable effect of changes in the state of pigmentation on the behavior of L^* during phase 2 is demonstrated in Section 7.3. So, an effect of entrapped air on L^* via a chemical pathway was established.

Another mode through which air can influence the behavior of L^* is a physical one. The first evidence for the existence of this mode was obtained from the following exploratory experiment. Quantities of PLMB (produced under atmospheric air pressure as described by Palombo and Wijngaards, 1989a) in which the pigments were mainly in the NOMB state were deaerated by placing each of them in a nylon polyethylene laminate bags and sealing the bags in vacuum (0.05 bar). Changes in color were measured using the Minolta tristimulus colorimeter (see Section 7.4.2). Removal of most of the entrapped air bubbles, as confirmed by the determination of the percent of entrapped air (6.6% and 0.3% for aerated and de-aerated PLMB respectively; $p < 0.001$), caused a large and significant decrease in L^* (L^* values of 58.9 and 56.8 for aerated and de-aerated PLMB respectively; $p < 0.001$). The time needed for performing the vacuum sealing was rather short and the absorption by

the pigments can be considered constant. Thus, the change in L^* can be satisfactorily explained by the withdrawal of most of the entrapped air bubbles, scattering elements affecting the scattering properties of the PLMB.

In this section we try to verify our third working hypothesis, i.e., the extent and behavior of entrapped air in PLMB strongly affect its scattering properties and hence the changes observed in its L^* during phases 1 and 2. For the sake of clarity, results and discussion will be presented separately for each of the two phases.

7.5.2 Phase 1

If the extent and behavior of entrapped air have important bearing upon the dramatic changes in L^* during this phase it may be expected that imposing a large interference in the behavior of the former will be reflected in the corresponding behavior of the latter. In this section, the validity of this assumption is checked by application of aeration and deaeration steps during the processing of PLMBs. In addition to measurement of L^* we monitored the corresponding changes in several air parameters. Comparison between the behavior of the latter with that of L^* was done with the aim of revealing a possible cause and effect relationship.

7.5.2.1 Materials and methods

Meat raw materials

In each experiment 10 kg of PLM (see Section 7.3.2) were used.

Experimental procedure

Basically, the experimental procedure employed was as described in Palombo and Wijngaards (1989a). A mixing stage subsequent to chopping was incorporated using a Stephan mixer (model UMM-25, Almelo, The Netherlands) in which the cutting knife was replaced by a vertical arm revolving at 24 rpm. The reduced air pressure of 0.05 bar at the start of mixing, was obtained by a vacuum pump connected to the lid of the mixer. Two mixing intervals under 0.05 bar, i.e., 3 and 4.5 min, were sequentially performed. Thus, identical effective chopping and mixing time periods were used.

Air determination: Percent of entrapped air was determined using a SMRAT air tester (Stork, Oss, The Netherlands). An illustration of the instrument is given in

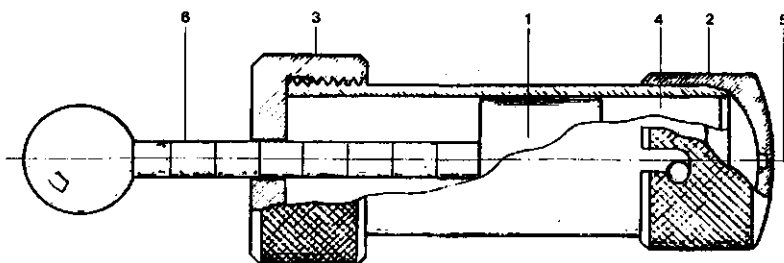


Fig. 7.7 : SMRAT (Sausage Meat Residual Air Tester) instrument. (1) Piston; (2) Front cap; (3) Back cap; (4) Space for a meat batter sample; (5) Hole (1 mm diameter); (6) Calibrated stem.

Fig. 7.7. A meat batter sample is filled under water into the space marked in Fig. 7.7. The back and front caps are screwed and the piston is pressed onto the batter to allow a proper reading of the stem length (water entrapped during filling of the tester is allowed to escape through a 0.1 mm clearance between the piston and the cylinder and through a 1 mm diameter hole in the front cap). Thereafter, the tester is placed in a large transparent container and a reduced air pressure of 0.05 bar is created by an oil vacuum pump. If the batter contains air it expands and pushes the stem outward. The stem length is read once more. The whole determination procedure is performed at 15°C.

The following equation, based on Boyle's ideal gas law, is used for calculating the % air entrapped within the batter:

$$\% \text{air} = ((L_2 - L_1) / L_1) * (P_2 / (P_1 - P_2)) * 100 \quad (7.2)$$

where:

L_1 = exposed stem length at barometric pressure

L_2 = exposed stem length at 0.05 bar

P_1 = barometric pressure

p_2 = 0.05 bar

Two measurements were done for each determination.

Microstructural examination : At various stages of the process, 6 sample units, 1

cm³ each, were taken at random. They were mounted on small cork disks, wrapped with aluminum foil and frozen in isopentane cooled with liquid nitrogen. The samples were stored at -80°C until further handling. Shortly before the microscopical examination sections, 6 µm thick, were cut in a Cryostat (type HR, Slee, London, UK) set at -20°C. One representative section was taken from each sample unit for microscopical examination. Employing the dark-ground microscopy (Drury & Wallington, 1980), air bubbles could be easily distinguished from the meat matrix (see Fig. 7.10). Three sections from 3 different sample units were used for counting the number of bubbles per field of view (NB) at a magnification of x100. For each section, the number of bubbles in each of 15 randomly selected fields of view was counted. The results for the 3 sections were averaged and used for further analysis. Information about the size distribution of the bubbles' diameter (BSD) was obtained using a light microscope (Zeiss, Oberkochen, W. Germany) equipped with a projection head (magnification of x100). One similarly prepared section from each of the other 3 sample units was systematically screened to permit, when possible, at least 100 bubbles to be measured in a section. Assuming the observed bubbles (Fig. 7.10) to be perfect spheres the BSD can be used as a reliable indication for the real bubble size distribution.

Color measurements: Was done as described in Section 7.4.2.

Experimental design

This included four sequential combinations of the following processing steps: (1) chopping (Chop.); (2) mixing under reduced air pressure of 0.15 bar (V.mix.); (3) waiting time at 15°C (Wait.). Each of these steps had an effective duration of 7.5 min. Step 1 was used for aeration of the system, step 2 for de-aeration and step 3 for controlling the effect of changes occurring when neither step 1 nor step 2 were applied.

The combinations were:

1. Chop.1 - V.mix. - Chop.2 (CVC)
2. Chop.1 - V.mix. - Wait. (CVW)
3. Chop.1 - Wait. - Chop.2 (CWC)
4. Chop.1 - Wait. - Wait. (CWW)

Each of the combinations was checked in a separate experiment. At various

stages of processing, measurements of color and percent entrapped air were performed for all the experiments and microstructural examinations only for the CVC and CWC experiments.

Remark: About the same temperatures at the end of each of the two chopping cycles were obtained by either keeping the batter at 0°C (CWC system) or cooling the mixer with ice water (CVC system) during the preceding stage.

7.5.2.2 Results and discussion

As can clearly be observed in Fig. 7.8 for all four combinations similar increase in L^* takes place during the first chopping cycle. The subsequent V. mix. or Wait. steps induce a large or moderate decrease in L^* respectively. An additional chopping cycle however, results in a large or a moderate increase when the preceding stages are V. mix. or Wait. respectively. The corresponding Wait. periods causes a

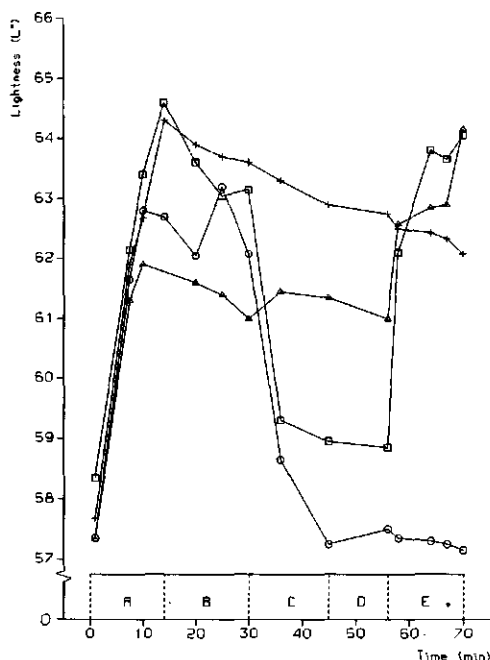


Fig. 7.8 : Changes in lightness of porcine lean meat batters during processing. (□-□) CVC (Chop.1 - V.mix. - Chop.2) system; (○-○) CVW (Chop.1 - V.mix. - Wait.) system; (△-△) CWC (Chop.1 - Wait. - Chop.2) system; (+-+) CWW (Chop.1 - Wait. - Wait.) system. A = Chop. 1; B,D = Transfer; C = V.mix. or Wait.; E = Chop. 2 or Wait.

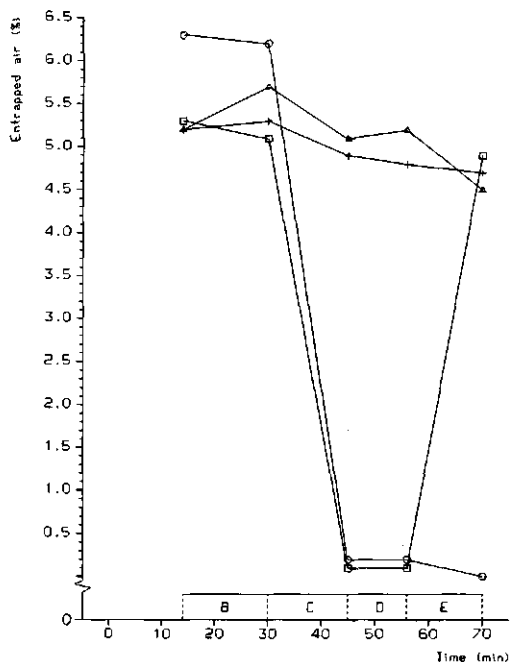


Fig. 7.9: Changes in mean values of % entrapped air of porcine lean meat batters during processing. (□-□) CVC (Chop.1 - V.mix. - Chop.2) system; (○-○) CVW (Chop.1 - V.mix. - Wait.) system; (△-△) CWC (Chop.1 - Wait. - Chop.2) system; (+-+) CWW (Chop.1 - Wait. - Wait.) system. B,D = Transfer; C = V.mix. or Wait.; E = Chop. 2 or Wait.

moderate or no decrease in L^* when the preceding stages are Wait. or V. mix. respectively.

Results of percent of entrapped air for the same processing steps show a pattern of changes which is highly associated with that obtained for L^* (Fig. 7.9). Essentially, a higher percent of entrapped air corresponds to a higher L^* value and vice versa.

A typical microscopic appearance of a PLMB at the end of Chop.1 and at the end of V. mix. is shown in Fig. 7.10. Due to the V. mix., a definite decrease in number of bubbles in a microscopic field of view can be observed. A quantitative substantiation of this finding is provided by the results pertaining to NB (Table 7.2). V. mix subsequent to Chop.1 causes a tremendous decrease in NB. A corresponding Wait. step still results in a considerable decrease in NB. In both systems Chop.2 induces an increase in NB which is clearly much larger for the CVC system.

Changes in BSD at the same processing steps (Fig. 7.11) show that a large and

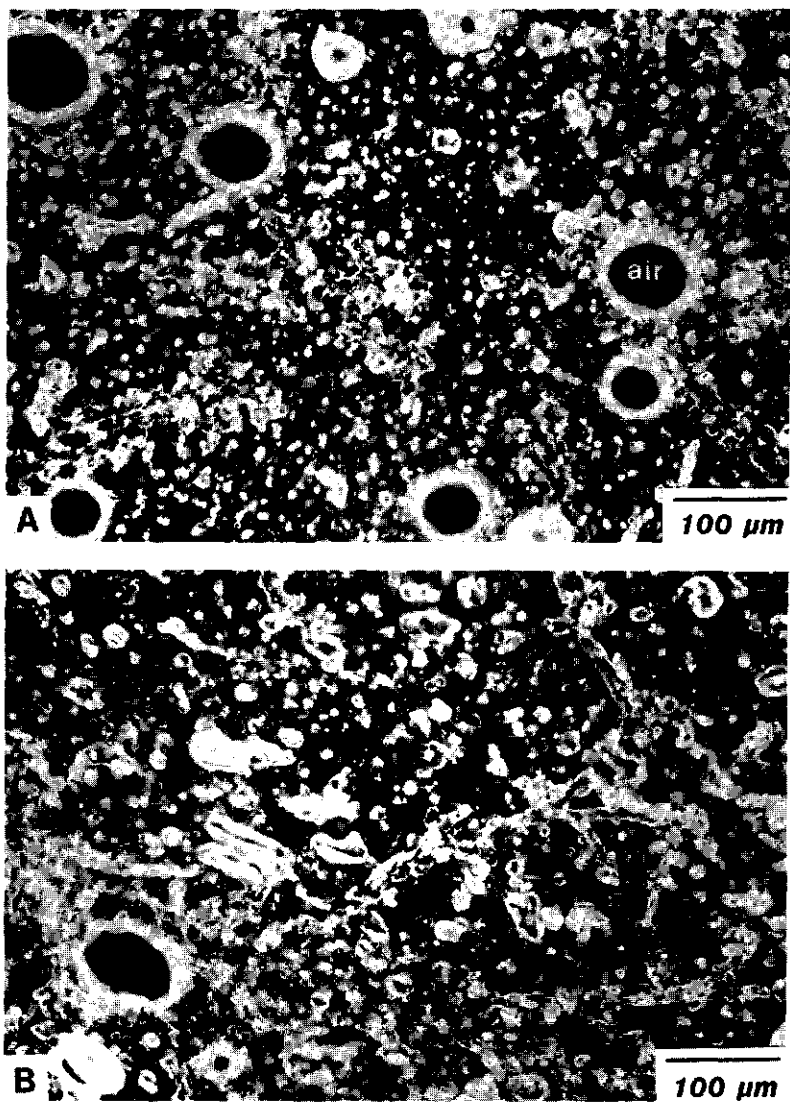


Fig. 7.10 : Typical microscopical appearance (using dark-ground microscopy (x100)) of a porcine lean meat batter at the end of chopping (A) and at the end of mixing under reduced air pressure, 0.15 bar (B).

moderate decrease in NB due to V. mix. and Wait. respectively is associated with a large and moderate shift in the BSD towards higher size classes. Similarly to the changes in the NB, in both treatments Chop.2 almost restores the situation seen at the end of Chop.1.

Table 7.2 : Mean \pm S.D. of number of bubbles in a microscopical field of view (NB) at various processing steps for CVC (Chop.1 - V.mix. - Chop.2) system and CWC (Chop.1 - Wait. - Chop.2) system

<u>Processing step</u>	<u>CVC - system</u>	<u>CWC - system</u>
End of chop. 1	24.0 \pm 5.0	30.0 \pm 5.0
end of V. mix.	0.3 \pm 0.5	-
End of Wait.	-	16.0 \pm 4.0
End of chop. 2	30.0 \pm 6.0	32.0 \pm 7.0

Confronting these changes with the corresponding changes in L^* reveals that: (1) An increase in L^* is associated with an increase in NB and a shift in BSD towards lower size classes; (2) A decrease in L^* is associated with a decrease in NB and, a shift in BSD towards higher size classes. Linear regression analyses between L^* and each of the parameters, percent of entrapped air, NB and the percent of bubbles in the size class $< 50 \mu\text{m}$ resulted in rather high correlation coefficients (0.8, 0.88 and 0.84 for percent entrapped air, NB and percent BSD respectively; ($n=11$)). This implies that a large percentage of the variation in L^* can be explained by the variation in each of the parameters related to the air entrapped in the PLMB. Moreover, the slopes of the regression lines were all positive, which is in a complete accordance with previously described relations between L^* and the other parameters.

Finally, some additional points have to be mentioned:

(1) V. mix. subsequent to Chop.1 almost restores the original L^* values (i.e., L^* after 1 min of chopping). Chop.2 results in L^* values which are very similar to those obtained at the end of Chop.1. Further, for all three systems - CVC, VWC, and CWW - the values of L^* at 70 min and thereafter until 24 h (data not shown) are similar. These findings suggest that the hypothesis stating that an irreversible surface coagulation of meat proteins on the air-water interface affects the behavior of L^* during phase 1, is less likely to be true (see Section 7.2.3).

(2) As was demonstrated by Palombo and Wijngaards (1989a), the changes in absorption characteristics of a PLMB during the first 70 min of processing are very small. This holds true even for a system chopped under reduced air pressure. Thus, absorption-induced changes in L^* are unlikely to have a strong negative bearing on

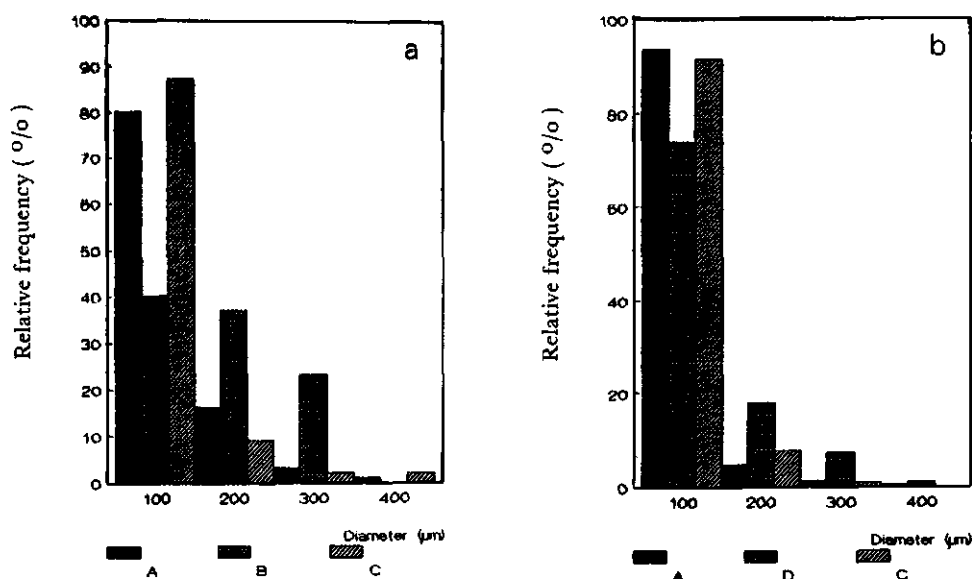


Fig. 7.11 : Size distribution of entrapped air bubbles (BSD) at various processing times for CVC (Chop.1 - V.mix. - Chop.2) system (a); and CWC (Chop.1 - Wait. - Chop.2) system (b). A = End of Chop. 1; B = End of V. mix.; C = End of Chop. 2; D = End of Wait.

the determined air effect on L^* .

(3) Subsequent to Chop.1, not only V. mix. but also a corresponding Wait. step induced a decrease in L^* . However, when V. mix. was followed by a Wait. step no decrease in L^* occurred (Fig. 7.8). These findings together with the corresponding findings regarding the NB and the BSD, substantiate the previous findings in the sense that L^* of the PLMB is affected not only by the mere entrapment or withdrawal of air but also by transitions in number and size distribution of the bubbles.

In fact, the observation that the NB, BSD and L^* change considerably also during the Wait. steps was the first evidence for the possible occurrence of disproportionation among the air bubbles as proposed in Section 7.2.2. Moreover, this also served as an incentive for the study regarding the effect of entrapped air on changes in L^* during phase 2. This will be reported in the next Section.

Based on these findings, it can be concluded that the behavior of L^* of a PLMB during phase 1 can, to a large extent, be explained by the changes in parameters

related to the air entrapped in it. This furnishes the basis for accepting our third working hypothesis stating that the extent and behavior of entrapped air are strongly responsible for the behavior of L^* during phase 1.

7.5.3 Phase 2

Disproportionation is a physical process that can take place in a dispersion when bigger particles are growing on the cost of smaller particles. This process is driven by the Laplace pressure difference (ΔP) over a curved particle surface.

$$\Delta P = 2\gamma/R \quad (7.3)$$

where:

γ = surface tension (N/m)

R = particle radius (m)

According to this equation, the smaller the bubble the higher the gas pressure within it. Henry's law states that the solubility of a gas is directly proportional to its pressure. Consequently, a gas diffusion from small bubbles to neighboring bigger bubbles will take place. Monitoring the changes in a unit volume of an aerated system undergoing disproportionation, reveals a shift in the bubble size distribution towards higher and lower size classes. Additionally, this process is self-accelerating since as bubbles get smaller the driving force increases. Thus, parallel to the shift in bubble size distribution, also the number of bubbles in a unit volume decreases since smaller bubbles ultimately disappear (Prins, 1988). The rate of this process depends, among other variables, on the solubility of the dispersed gas in the system and the bubble size distribution. In the preceding section, it is clearly shown that also during the Wait. steps considerable changes in the NB and BSD take place. There it is suggested that the disproportionation of entrapped air bubbles is the process responsible for those transitions. Further, our third working hypothesis (Section 7.2.4) suggests that, through alteration of the scattering properties of the PLMB, the behavior of entrapped air during phase 2 strongly affects the changes in L^* during the same phase. Accordingly, the aim of the study reported in this Section is twofold.

(1) To check if indeed disproportionation is the process responsible for the transitions in NB and BSD during phase 2;

(2) To examine the importance of the transitions in NB and BSD in explaining the behavior of L^* during this phase.

Point 1 was approached by monitoring NB and BSD at various time points along phase 2. Also, sequential picturing of a fixed stereomicroscopical field of view was used for monitoring transitions in individual bubbles. Point 2 was approached by checking the effect of chopping the PLM under N_2O on the behavior of its L^* during phase 2. The rationale of this approach was: The solubility of N_2O in water is about 50 times higher than that of N_2 . In case disproportionation of entrapped gas bubbles is a dominant steering factor influencing the change in L^* during phase 2, replacing the air in the bubbles with N_2O will result in a substantial acceleration of the disproportionation process and subsequently in a considerable change in the behavior of L^* during this phase. The use of this gas is advantageous in that it is an inert one, i.e., it does not induce any other changes e.g., change of pH in the system.

7.5.3.1 Materials and methods

Meat raw materials

In each experiment 5kg of PLM (see Section 7.3.2) were used.

Experimental procedure

Essentially, with the exception of using the bowl chopper described in Section 7.4.2 the experimental procedure described in Palombo and Wijngaards (1989a) was used (the batter thus produced was named 'air system'). To replace most of the air surrounding the PLM during chopping with N_2O (' N_2O system'), a constant flow of the latter (at overpressure of 0.6 bar) was allowed shortly before and during the whole chopping stage (by locating the outlet of a tube connected to a N_2O cylinder in the vicinity of the chopping blades).

Microstructural examination: Basically, this was done as described in Section 7.5.2.1. For the determination of BSD we employed a morphometrical processor (mini-MOP, Kontron, Munich, W. Germany). In comparison to the system used in the previous section, the advantages of using this computerized image analysis system were the ease in performing the measurements and the ease of data analysis.

Stereomicroscopical examination: Immediately after the end of chopping a quantity of PLMB was transferred to a 100 g can. A Petri dish cover was placed on top of the batter and sealed with adhesive tape. Using a stereomicroscope (Zeiss,

Oberkochen, W. Germany), fitted with a camera, a fixed field of view was photographed sequentially. This enabled us to follow changes in the size of individual bubbles during storage at 15°C.

Color measurements: Was done as described in Section 7.4.2.

Experimental design

This included two treatments: chopping under air atmosphere ('air system') and chopping under a continuous flow of N₂O ('N₂O system'). Several replicate experiments were performed for each treatment.

7.5.3.2 Results and discussion

Point 1

The typical pattern of changes in L* during phase 2 (described in Section 7.1) was obtained for the air system (Fig. 7.12b). Changes in NB (Fig. 7.13) and BSD

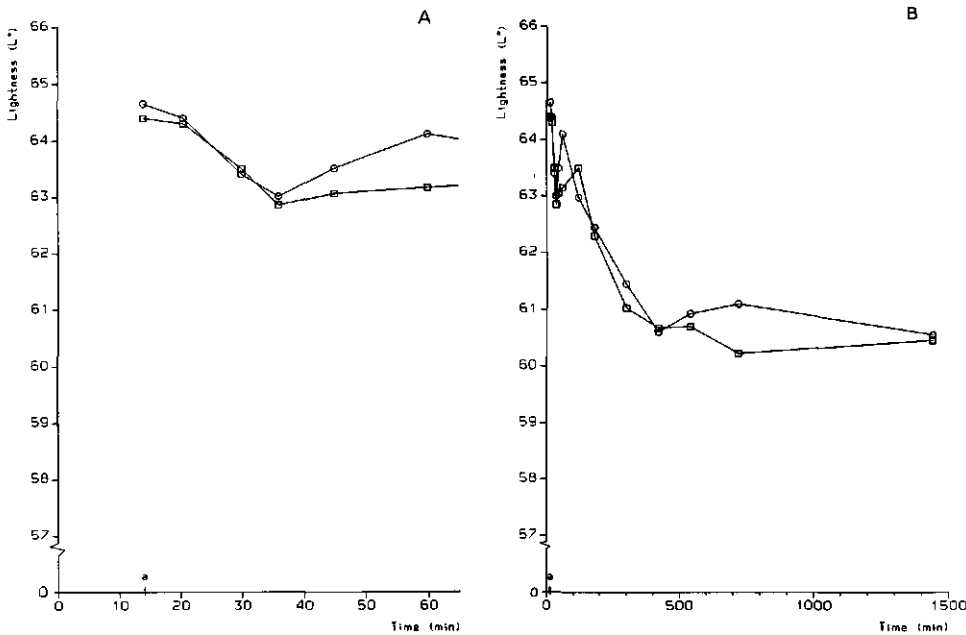


Fig. 7.12 : Changes in lightness of porcine lean meat batters during storage at 15°C for a system chopped under air atmosphere (○-○) and a system chopped under N₂O atmosphere (□-□). a = End of chopping. A = Changes until 60 min; B = Changes until 24 h.

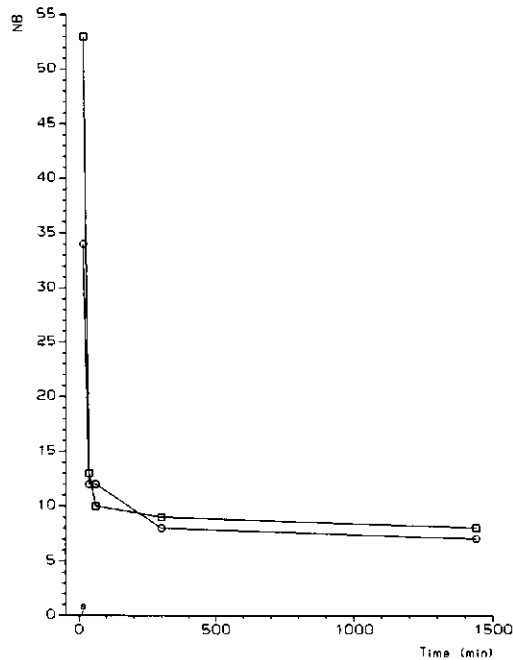


Fig. 7.13 : Mean of number of bubbles per field of view (NB) of porcine lean meat (PLM) batters at various storage times at 15°C. (□-□) PLM chopped under air atmosphere; (○-○) PLM chopped under N₂O atmosphere. a = End of chopping.

(Fig. 7.14a) of the same system show a large decrease in NB and a concomitant shift of BSD towards higher size classes. Further, the magnitude of these transitions is larger during the first 60 min and gradually diminishes with prolonged storage time. This observation strongly suggests that a disproportionation process indeed takes place during this process phase. A more direct evidence for its occurrence was obtained from the sequential picturing of a fixed stereomicroscopical field of view. Fig. 7.15 presents a streomicroscopical field of view shortly after the end of chopping (A) and after 24 h storage at 15°C (B). A side-by-side comparison of these pictures reveals a massive disappearance of smaller bubbles and an extremely different size distribution after 24 h at 15°C. Although more difficult to be quantified, also the expansion of bigger bubbles was observed in pictures taken between these time points. Further analysis of the transitions in the bubbles as observed from these pictures substantiated the finding of BSD and NB, i.e., shrinkage of small bubbles and growth of bigger bubbles occurred all along phase 2 but had higher rate at the

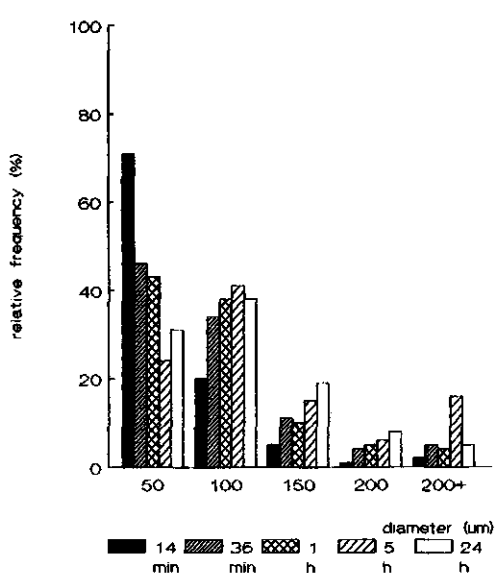
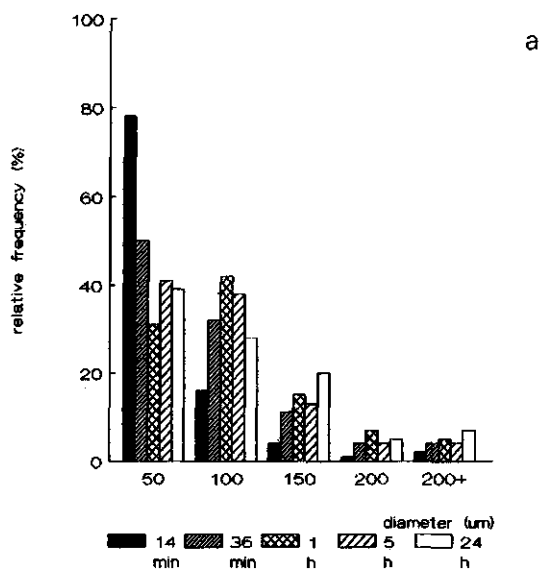


Fig. 7.14 : Size distribution of entrapped air bubbles (BSD) at various storage times at 15°C for a system chopped under air atmosphere (a) and a system chopped under N₂O atmosphere (b).

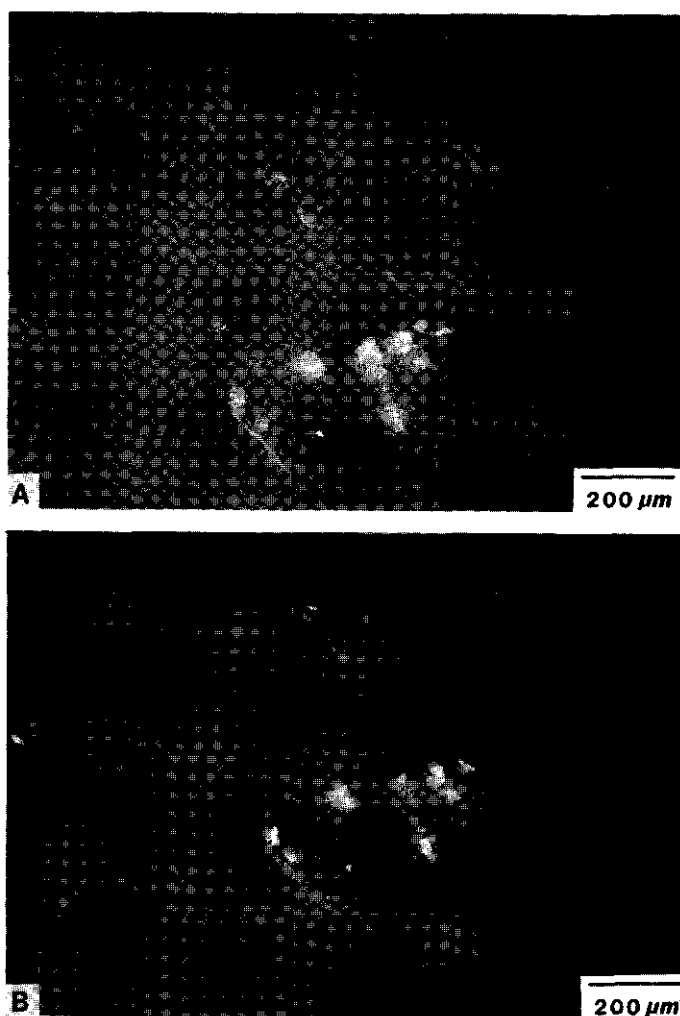


Fig. 7.15 : Appearance of the same stereomicroscopical field of view (x40) of a porcine lean meat batter chopped under air atmospher at the end of chopping (A) and after 24 h storage at 15°C (B).

first 60 min of the process. From then, the rate decreased with process time.

Additionally, from the abovementioned evidence and the finding that the air overrun in the PLMB didnot exceed 10%, it was very unlikely that coalescence of air bubbles took place during phase 2.

Based on these findings, it is concluded that disproportionation is the mechanism responsible for the changes in the entrapped air bubbles during phase 2. In Chapter 8 additional support for this conclusion will be presented.

Point 2

Preliminary experiments in which the usefulness of the experimental setup was examined revealed the following findings. For both batters similar densities were determined: 1.0402 ± 0.0091 ($n=5$) and 1.0413 ± 0.0084 ($n=5$) for the air and N_2O systems respectively. This indicated that both systems had the same overrun. On the other hand, determination of the percent entrapped gas using the SMRAT resulted with markedly different values for the two systems, i.e., 5.9 ± 1.1 ($n=5$) and 9.5 ± 1.2 ($n=5$) for the air and the N_2O system respectively. This apparent difference in the gas overrun is obviously due to the higher solubility of N_2O and in fact indicates that the air was indeed replaced by N_2O in the N_2O system (note that the percent gas determined by the SMRAT (see Section 7.5.2.1) was affected by both, the entrapped gas and the dissolved gas). Additional support for the successful replacement of air by N_2O was obtained from monitoring the change in percent entrapped gas of PLMBs in open cans exposed to air atmosphere and stored until 24 h at $15^\circ C$ (the cans were kept in a container at high humidity to avoid drying). For the air system the values remained the same whereas for the N_2O system they decreased to almost 50% of the initial value.

The plots for changes in L^* during phase 2 for the air and the N_2O systems overlap (Fig. 7.12a,b). However, at the end of chopping the air system has a definitely higher NB value (Fig. 7.13) as well as a higher proportion of the bubbles in size class $< 50 \mu m$ (Fig. 7.14). Hence, at this processing step the air system contains more and considerably smaller bubbles than the N_2O system does. Some explanation for this finding may be provided by the "football" theory (Prins, 1988) which states that aeration of a system under a well soluble gas versus a poorly soluble one results with larger gas bubbles in the former. Further inspection of the histograms shown in Fig. 7.14 reveals that the above difference is in fact the main one. For both treatments the shift in the BSD with storage time has a similar pattern which is mainly characterized by larger changes during the first 60 min. A comparable behavior is obtained also for NB (Fig. 7.13). Here, for both systems marked decrease in NB values is over after about 36 min. These findings were confirmed by results of several replicate experiments. a possible explanation for the similar behavior of the air and the N_2O systems is the following: according to Eq. 7.3 the driving force of disproportionation increases with decreasing bubble size. Therefore, it is expected that the overall rate of disproportionation will increase as BSD shifts towards lower size classes. Thus, it may be suggested that the expected

effect of the differences in solubilities of air and N_2O on the rate of disproportionation is counteracted by the effect produced by the difference between the two systems, in the BSD and NB, at the end of chopping. Consequently, similar rates of disproportionation result as indeed monitored by NB and BSD.

For both systems, confronting these results with the corresponding changes in L^* suggests that the short decrease in L^* until 36 min can be attributed to corresponding shifts in NB and BSD (see below). From 36 min on only a small decrease in NB accompanied with a gradual shift in BSD toward higher size classes takes place. For the L^* values however, a large decrease occurs between 1 and 5 h and from then the plots approximate to a plateau (Fig. 7.12b). Hence, changes in L^* during the period 1 h until 5 h can not be explained by the corresponding changes in NB and BSD. Further, linear regression analysis between L^* on one hand and NB or the median of histograms of BSD for the individual time points on the other hand, using experimental data from the whole time range of phase 2, results in rather low r values: 0.68 and - 0.67 ($n = 24$) for NB and the median of BSD respectively. However, restricting the data points for the regression analysis to those only from the time period until 36 min results in a remarkable increase in r value: 0.80 and -0.97 ($n = 13$) for NB and the median of BSD respectively.

Summarizing, strong evidence for the occurrence of disproportionation between the air bubbles entrapped within the PLMB are provided. However, this process cannot be readily used to explain the behavior of L^* during the whole duration of phase 2. Yet, it can be used to explain the small decrease in L^* shortly after the end of chopping.

7.6 General discussion

In this chapter results pertaining to the effects of changes in the absorption traits, salt and phosphate and entrapped air on the behavior of L^* during processing are presented. To evaluate the extent to which our working model (Fig. 7.3) is confirmed by these findings each of the two well defined process phases will be referred to separately. Additionally, at the end of the discussion for phase 2, an attempt will be made to provide some mechanistic explanation for the effect of air pressure during chopping on the behavior of L^* and on the corresponding apparent activation energy (E_a) values for this phase (see Section 7.1).

Phase 1

Based on the results reported in Section 7.5.2 it is concluded that the main event that is responsible for the increase in L^* during chopping is the entrapment and the subsequent size reduction of air bubbles. Thus, strong evidence are provided in favor of the part of our third working hypothesis referring to this phase .

Phase 2

From the results regarding to the effect of salt and phosphate we conclude that events associated with their action in the PLMB, have a little impact on the behavior of L^* during this phase. Disproportionation of entrapped air bubbles appears to have considerable bearing on the behavior of L^* only for a short period after the end of chopping. For the whole time span of this phase it was shown to be of less relevance. Changes in the absorption traits of the muscle pigment, however, were demonstrated to strongly affect the changes in L^* during this phase.

Based on these findings it is concluded that the predominant event steering the changes in L^* are the chemical reactions ultimately leading to the formation of NOMb.

To further visualize our view in relation to the events responsible for the unique pattern of changes observed for L^* during this phase (Fig. 7.3), the following stepwise occurrence is proposed. Shortly after the end of chopping, two events having an opposite impact on L^* govern its course of changes: the chemical reactions leading to the formation of MMb, and the process of disproportionation.

The first process commences at the moment of addition of nitrite to the PLM (after 1 min of chopping). As discussed by Palombo and Wijngaards (1989a), after the end of chopping the shift in the absorption characteristics of the PLMB is governed by dynamic equilibria among the various forms of Mb. Depending on the process conditions these equilibria are shifted to favor the formation of a specific form of Mb. This form will be of major importance in determining the color appearance of the PLMB. The time period needed for the shift in the predominant Mb form, from MMb, to NOMb with the attended visually detectable shift from gray to red, exceeds the time period of the chopping stage. Consequently, if the changes in absorption would have been the single event influencing the behavior of L^* the increase in the latter should have continued after the end of chopping (Fig. 7.3)

The second process has been shown to start immediately after the end of chopping and to be effectively over after 36 min. It is expected to induce a decrease

in L^* (Section 7.2.3).

The observed changes in L^* during the period between end of chopping until about 60 min are governed by the balance between the effects of each of these processes on L^* . At the initial decreasing stage the effect of disproportionation predominates. Then, the concomitant formation of MMb takes over to induce a temporary increase. The subsequent gradual decrease in L^* is mainly due to the shift in the absorption traits, i.e., the formation of NOMb.

The findings disclosed in the present study stimulated a further attempt to obtain a better insight into the mechanism responsible for the effect of air pressure during chopping on the behavior of L^* and on the corresponding E_a values (reported by Palombo and Wijngaards (1989b) and further discussed in Section 7.1). To this end, we repeated this experiment and, besides L^* , also checked the air overrun, NB and BSD (see Section 7.5). The results for L^* (Fig. 7.16) were very similar to those obtained by Palombo and Wijngaards (1989b). For the air overrun the following values were obtained (in % v/v): 6.3 ± 0.7 and 1.3 ± 0.3 (mean \pm

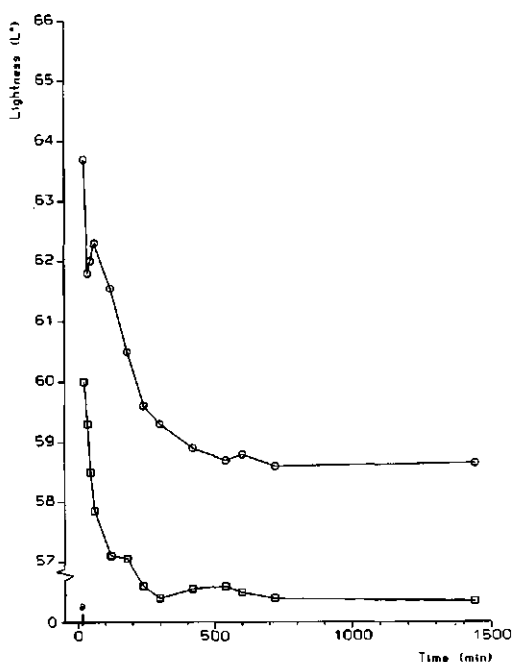


Fig. 7.16 : Changes in lightness of porcine lean meat (PLM) batters during processing and subsequent storage at 15°C. (\circ - \circ) PLM chopped under atmospheric air pressure; (\square - \square) PLM chopped under reduced air pressure. a = End of chopping.

S.D.) for PLMB chopped under atmospheric air pressure (AAP) and reduced air pressure (0.15 bar; RAP) respectively (It is worthy of note that the ratio between the air overrun of the AAP system versus the RAP system was in the same magnitude as the ratio between the corresponding air pressures. Boyle's law could explain this observation.). Changes in the mean values of NB as a function of storage time at 15°C, for the two systems, are presented in Fig. 7.17. For the AAP system, results similarly to the those reported in Section 7.5.3 for the air system (Fig. 7.13), from the end of chopping until 36 min a steep decrease in NB takes

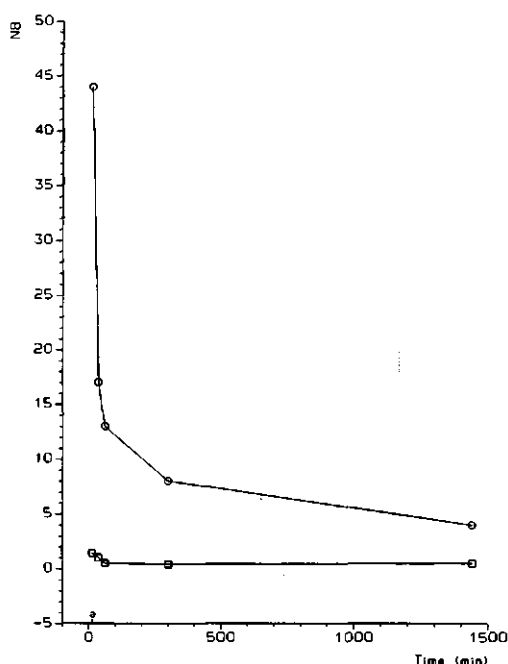


Fig. 7.17 : Mean of number of bubbles per field of view (NB) of porcine lean meat (PLM) batters at various storage times at 15°C. ($\circ-\circ$) PLM chopped under atmospheric air pressure; ($\square-\square$) PLM chopped under reduced air pressure. a = End of chopping.

(Fig. 7.13), from the end of chopping until 36 min a steep decrease in NB takes place. Thereafter, only moderate changes occur. For the RAP system very low values are obtained at the end of chopping. From then a very small decrease commenced and was followed by a near constant value until 24 h. For the AAP system regarding the BSD, results similar to those reported in Section 7.5.3 for the air

system (Fig. 7.14a) were obtained. For the RAP system, the extremely low NB values as well as the rapid disappearance of the air bubbles (probably due to a considerable undersaturation of PLMB) hampered the construction of reliable histograms and the detection of shifts in BSD during this phase.

In light of these findings the balance between the relative contributions of disproportionation and the formation of NOMb to the overall changes seen in L^* can be used to explain the marked difference between the rate constants obtained for L^* in the two chopping conditions, i.e., AAP and RAP. In the batter chopped under RAP the contribution of disproportionation to the overall decreasing rate in L^* is very small. On the other hand, the rate of NOMb formation is markedly accelerated due to the lower proportion of entrapped oxygen. Thus, the rate of this process will predominantly steer the rate of the observed decrease in L^* . In the batter chopped under AAP, the contribution of the disproportionation to the overall rate of decrease in L^* is masked by the decelerating effect induced by the retarded rate of NOMb formation (due to the inhibitive effect of entrapped oxygen). Thus, a lower overall rate of decrease in L^* results.

Following the same line of reasoning a hypothesis for the difference in E_a can be offered. Activation energy indicates how sensitively changes in properties or components of food systems respond to temperature changes. A shift in E_a due to a specific treatment, might suggest a change in the physicochemical properties of the system. If we assume that disproportionation and the reactions responsible for the formation of NOMb have different E_a values, that the E_a for the latter process is higher and that during chopping under RAP the process with the higher E_a controls, then a steeper slope will be obtained for the Arrhenius plot as indeed resulted from our analysis (Fig. 7.2).

Summarizing, the finding reported in this chapter pertaining to the behavior of L^* during the process studied allow us to conclude that:

- (1) The main event responsible for the changes in L^* during phase 1 is the extent and behavior of the entrapped air.
- (2) The main event responsible for the behavior of L^* during the first stage of phase 2 (from end of chopping until 40 min) is disproportionation of entrapped air bubbles. Thereafter, the main steering factor is the transitions in the absorption traits of the PLMB.

8. INFLUENCE OF THE SURFACE RHEOLOGICAL PROPERTIES OF PLMBs ON THE BEHAVIOR OF THE ENTRAPPED AIR BUBBLES DURING PHASE 2 AND ON THE CORRESPONDING CHANGES IN L^*

8.1 Introduction

The study of surface properties of meat proteins has been mainly connected with investigations pertaining to their emulsifying capacity as well as to the emulsion stability of oil-in-water emulsions produced from them (Acton and Saffle, 1970; Schut, 1976). Since the salt-soluble proteins are known to be superior in emulsifying fat, most of these studies used this fraction (Acton and saffle, 1972; Schut, 1976) or even a pure preparation of myosin (Dickinson et al., 1987). One of the most important findings emerged from these studies is that, similar to films of lysozyme and bovine serum albumin (Dickinson, 1988), myosin film exhibits a viscoelastic behavior on the oil-water interface. This finding has been obtained from measurements of surface shear viscosity of myosin films.

A computerized literature search (FSTA database) on the surface rheological properties of meat proteins at the air-water interface and their impact on the behavior of the air fraction entrapped within meat emulsions or meat batters has not revealed a single study. The only reference to this theme, still in an indirect way, was the work reported by Kotter and Fischer (1975). They reported that foaming of actomyosin in air in the presence of diphosphates resulted in a very voluminous solution which on heating turned into a stable aerated mass. The authors claimed that this effect of the diphosphates cannot be explained by reduction of the surface tension. The dissociation of actomyosin into actin and myosin was suggested as an explanation for this behavior.

In Chapter 7 strong evidence were provided for the occurrence of disproportionation among the entrapped air bubbles in the studied PLMBs

immediately after chopping. This process was shown to have detectable influence on changes in L^* only during a short period from the end of chopping. The rate of this process in gas-containing aqueous food systems is known to be dependent not only on well documented physical factors enumerated by De Vries (1958) but also on the topology of the bubble, the gas composition inside and outside the bubbles and the surface rheological properties of the continuous phase. The latter factors were recently studied and reviewed by Prins (1988) and Ronteltap (1989).

The objective of the study to be reported in this chapter was to examine the following working hypothesis: The surface rheological properties of the matrix of the studied PLMBs have a strong impact on the behavior, during phase 2 of the process, of air bubbles entrapped within it and on the corresponding behavior of their L^* .

Theoretical considerations and the approach used

One of the more successful models for describing the decrease in the radius of a disproportionating bubble as function of time is that of De Vries (1958).

$$R_t^2 = R_0^2 - (4R'TDS\gamma/p_0\Theta)t \quad (8.1)$$

where:

R_t = bubble's radius at time t (m)

R_0 = bubble's radius at $t = 0$ (m)

R' = gas constant ($J \text{ mol}^{-1} \text{ K}^{-1}$)

T = temperature (K)

D = diffusion coefficient ($m^2 \text{ s}^{-1}$)

S = gas solubility ($\text{mol m}^{-3} \text{ Pa}^{-1}$)

γ = surface tension ($N \text{ m}^{-1}$)

P_0 = atmospheric pressure (Pa)

Θ = film thickness (m)

t = time (s)

This model has been developed during a study on the effect of gas diffusion on the stability of foams. In the course of derivation it has been assumed that the gas transport from a smaller bubble to a bigger one is caused by the Laplace pressure difference (see Eq. 7.3) between the bubbles and is governed by diffusion. Further, the model simply states that the square of the radius of a shrinking bubble situated

in the neighborhood of a bubble with infinite radius of curvature and separated by a matrix film with a thickness Θ is linearly related to time. These conditions define the topology of the bubble. Based on this model, the effect of gas solubility on the disappearance time of disproportionating bubbles has been demonstrated by Prins (1988). For two gas bubbles, in a liquid system, both having identical initial dimensions, one filled with CO_2 and the other with N_2 , the calculated disappearance times are 55 and 3100 s respectively.

The De Vries model assumes constant surface tension during the shrinking process of a disproportionating bubble. For most food systems this assumption is not valid (Prins, 1986b; van den Tempel, 1977). Due to the presence of surface active molecules on the air-water interface the surface tension decreases during compression. Consequently, the driving force of the process diminishes (see Eq. 7.3) and the process slows down. Since shrinking of a bubble's surface is a dynamic process it is obvious that in order to learn about the mechanism involved, the surface dynamic rheological properties of the continuous phase should be considered. An equation, that describes the changes in surface tension as a function of the surface expansion or compression rates, defines a quantity named the surface dilational viscosity (η_s):

$$\eta_s = \Delta\gamma(\text{dln}A/\text{dt})^{-1} \quad (8.2)$$

where:

$\Delta\gamma$ = the change in the surface tension with respect to the equilibrium value.

$\text{dln}A/\text{dt}$ = the relative deformation rate of a surface area A .

This quantity describes the ability of a surface to resist an external disturbance and in fact provides information about its stiffness. In most liquid or semi-liquid food systems the bubble's surface behaves viscoelastically (Prins, 1986a). That implies that they show both viscous and elastic behavior to an extent which is dependent on the time scale of the experiment. For such rheological behavior it has been empirically established that the power law can be used to describe the dependence of the η_s on the relative rate of surface deformation (Prins, 1988; Ronteltap, 1989).

$$\log_{10}\eta_s = m\log_{10}(\text{dln}A/\text{dt}) + n \quad (8.3)$$

Where m and n are constants characteristic of the system. For milk, typical values of these parameters are -0.99 and 0.6 respectively (Prins, 1988). The negative value for m indicates that the surface is 'shear thinning', i.e., the value of η_s decreases with increasing rate of deformation. The n value describes the absolute value of η_s . As is schematically shown in Fig. 8.1, the existence of a finite η_s implies that an inflection

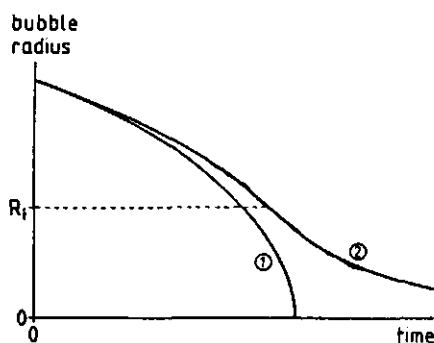


Fig. 8.1 : Schematic presentation of the effect of surface stiffness on the course of disproportionation. The calculated bubble's radius vs. time is presented for the case of constant surface tension (1) and the case where the surface stiffness is taken into account (2). R_i is the bubble's radius at the inflection point (Prins, 1988).

point (R_i) appears on the plot describing the decrease in the radius of a shrinking bubble with time (Prins, 1986a).

Westerbeek (1989) showed that addition of GLP (Glycerol lacto palmitate) to whippable emulsions greatly changed their surface rheological properties. The accumulation of this material on the air-water interface induced an increase in the stiffness of the surface, i.e., the surface became much more elastic. This finding was used to provide an explanation for the greater stability of air bubbles in GLP-containing emulsions against disproportionation. On the basis of this information, we decided to use the GLP as a probe for checking our working hypothesis.

8.2 Materials and methods

Experimental procedure

The preparation and thawing of meat raw materials and the experimental procedure for producing GLP-containing PLMB (+GLP system) and PLMB not

containing GLP (-GLP system) were similar to that described in Section 7.5.3.1. for the 'air system'. For the +GLP system, 1.0% (w/w) GLP was added in the form of spray-dried powder (DMV, Veghel, The Netherlands). The powder consisted of a mixture of GLP, maltodextrin, and sodium caseinate in a ratio of 6:3:1 respectively. In the -GLP system only maltodextrin and sodium caseinate in the same quantities as used in +GLP system were added. The powders were added to the batter with the other dry additives after 1 min of chopping.

In addition to the aerated samples, immediately after the end of chopping, 300 g portions of batter from each of the systems were de-aerated by sealing them under vacuum as described in Section 7.5.1. Then the samples were transferred to 100 g cans, each covered with a Petri dish and sealed with adhesive tape. These samples, stored at 15°C, were used for monitoring the contribution of the air fraction to changes in L^* .

Color measurement, % entrapped air determination, and microscopical and stereomicroscopical examinations: These were performed as described in Section 7.5.3.1.

Surface rheology: The surface rheological properties of the PLMBs were determined on dispersions prepared from them. The steps in preparing the dispersions were:

- (1) 1 g of PLMB was homogenized with 50 ml demineralized water using an Ultra Turrax homogenizer. This was done at low speed and at short intervals to avoid foaming of the dispersion.

- (2) Under continuous stirring the volume of the dispersion was brought to 2 liters using stock solutions prepared from the NaCl and the phosphate mixture used in the preparation of the batters. Before use, the pH of the phosphate solution was brought to 6.0 using 1.0 M HCl. The concentrations (g/v) of the PLMB, salt and phosphate mixture in the final dispersion was 0.05% , 2.0% and 0.1% respectively.

Both equilibrium and dynamic surface properties were determined using a Langmuir trough equipped with a caterpillar belt described by Prins (1976). The temperature during measurements was 15°C. Preliminary experiments revealed that an equilibration time of 1 h was enough to reach a stable equilibrium surface tension. Only after reaching that stage the measurement of the dynamic surface properties commenced. To imitate the conditions prevailing during the compression of the bubble's surface along the disproportionation process single compression tests were performed. These were carried out by a single barrier attached to the

caterpillar belt in a set up described by Ronteltap (1989). A surface area of 315 cm^2 was compressed to a surface area of 195 cm^2 (further referred to as the compression stage). The relative compression rates RCR (s^{-1}) used were: 1.04×10^{-3} , 1.03×10^{-2} and 1.24×10^{-1} . In addition to the compression stage, the subsequent relaxation stage (while the surface was still in the compressed state i.e. at a surface area of 195 cm^2), was studied during a period of 4 min. Three consecutive tests were done for each compression rate .

8.3 Results and discussion

A typical pattern of changes in the surface tension (ST) during the single compression tests, characteristic of both -GLP and +GLP systems, is presented in Fig. 8.2. One can clearly observe the sharp decrease in ST with increasing

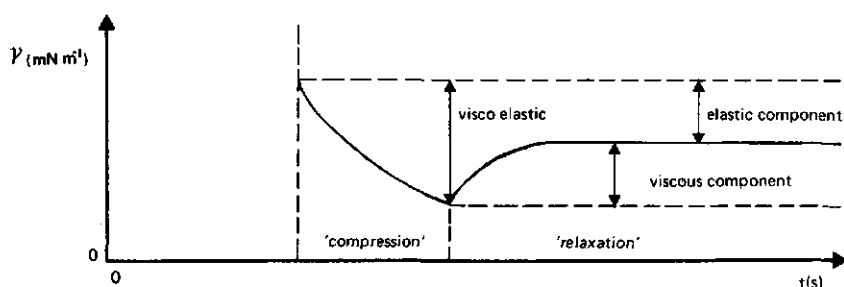


Fig. 8.2 : Typical pattern of changes in the surface tension of a PLMB dispersion during single compression and relaxation measurement.

compression. A minimum value is reached at the end of this stage. Thereafter, during the relaxation stage an increase in ST takes place. A phenomenological interpretation of this pattern of changes, with the knowledge of the viscoelastic nature of the surface, includes the following. During compression, surface active-components adsorbed at the surface are forced closer to each other (elastic or energy-storing component), but in parallel they can rearrange or desorb from the surface (viscous or energy-dissipating component) (Prins and van 't Riet, 1987; Prins 1988). The fact that ST increases during the relaxation stage indicates that indeed surface active components rearrange or desorb from the surface. Since the initial ST value is not restored during the time scale of this phase, one speaks also of an

elastic component of the surface rheological behavior.

Changes in ST during the compression stage (RCR of $1.03 \times 10^{-2} \text{ s}^{-1}$) for -GLP and +GLP systems are presented in Fig. 8.3. The equilibrium ST (ST at 0 % compression) is markedly lower for the +GLP system. For both systems a decrease in ST, being much more pronounced for the +GLP system, takes place during

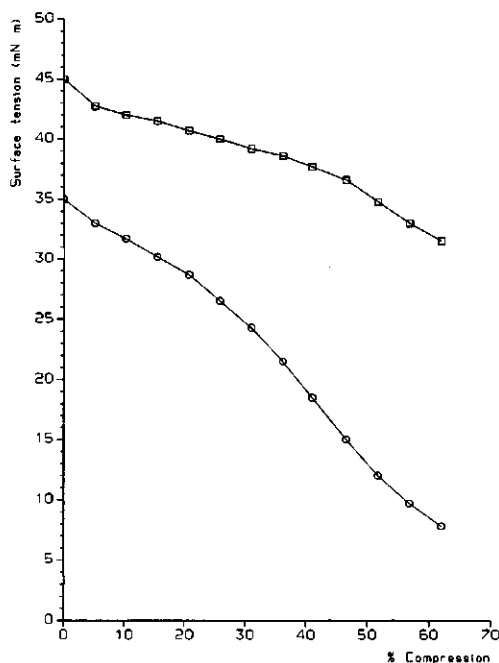


Fig. 8.3: Changes in surface tension of PLMB dispersions during a single compression measurement at a relative compression rate of $1.03 \times 10^{-2} \text{ s}^{-1}$.

(□-□) Dispersion not containing GLP; (○-○) dispersion containing GLP.

compression. GLP has a great effect not only on the value obtained at the end of compression but also on the rate of decrease in ST. Further, the increase in ST after a relaxation period of 4 min for the +GLP system is half as much as that measured for the -GLP system (data not shown). Hence, the values of ST in the +GLP system versus the -GLP system become lower during compression and also remain lower during the subsequent relaxation stage. In Table 8.1 values for the apparent surface dilational viscosity ($a\eta_s$), calculated using Eq. 8.2, for the different relative compression rates are presented. Before discussing these results, it should be stressed that a proper determination of η_s requires the application of a constant

Table 8.1: Apparent surface dilational viscosities ($a\eta_s$) at different relative compression rates for dispersions of PLMBs not containing and containing GLP (-GLP and +GLP system respectively)

$d\ln A/dt$ (s^{-1})	-GLP system ($mN\ s\ m^{-1}$)	+GLP system ($mN\ s\ m^{-1}$)
1.04×10^{-3}	1.3×10^4	2.7×10^4
1.03×10^{-2}	1.4×10^3	2.6×10^3
1.24×10^{-1}	1.1×10^2	2.2×10^2

RCR as well as steady-state conditions (van Voorst Vader et al., 1964). In our experimental set up, because of the linear movement of the barrier, the RCR ($d\ln A/dt$) increases during compression and no steady state is accomplished. Thus, a true η_s cannot be calculated from our experiments. In spite of these limitations, for the sake of further analysis and for relative comparison of the surface dynamic properties of different systems, we calculated an averaged value for the relative compression rate and used it in Eq. 8.2. Consequently, the derived values were termed $a\eta_s$.

As is clearly observed in Table 8.1 for both systems, the $a\eta_s$ decreases with increasing RCR. This indicates that the surfaces have a 'non-Newtonian' behavior and may be classified as 'shear thinning' systems (Prins, 1986b). More importantly, for all three RCR the values of $a\eta_s$ of the +GLP system versus -GLP system are about two times higher. Thus, GLP renders the surface stiffer, i.e., its ability to resist an external disturbance increases.

Now we turn to examine the effect of these alterations in the dynamic surface properties of the PLMBs on the disproportionation of bubbles entrapped within them. The decrease in the bubble's radius as a function of storage time for two bubbles having almost the same initial radius and topology (i.e., situated in the neighborhood of a bubble with an infinite radius of curvature and separated by a matrix film)-the one embedded in the -GLP system and the other in the +GLP system-is presented in Fig. 8.4 (These results were obtained using the stereomicroscopical setup). Also presented in this graph is the calculated radius vs. time plot, using the De Vries model (Eq. 8.1) which assumes constant surface

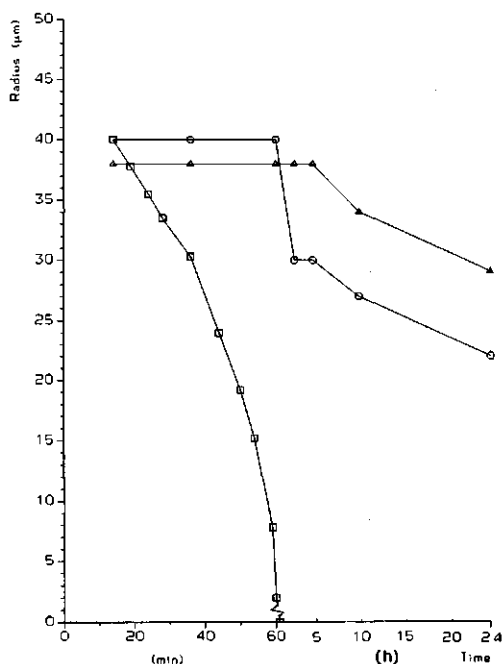


Fig. 8.4 : Measured decrease in bubble's radius vs storage time at 15°C for bubbles in a -GLP system (○-○) and a +GLP system (△-△) having the same topology. (□-□) Calculated decrease in radius vs storage time (using Eq. 8.1) for a bubble under the conditions prevailing in the -GLP system.

tension, for a bubble having the same initial radius and being in the same situation as the one prevailing for the bubble of the -GLP system. As has been argued previously and is well documented for food systems (Prins, 1988; Ronteltap, 1989), the tremendous difference between the measured and calculated rate of decrease in the bubble's radius for the -GLP system is mainly attributable to the existence of a finite $a\eta_s$ (Table 8.1). In the same line of reasoning, the slowest rate of decrease in radius vs. time in the +GLP system can be explained by the experimentally established higher $a\eta_s$ for it.

The association between the observed effect of GLP on the changes in the course of the radius vs. time plots for individual bubbles in the original PLMBs and the observed corresponding impact on the $a\eta_s$ of the dispersions prepared from them, is taken as evidence in favor of our working hypothesis stating that the dynamic surface properties of the meat matrix constitute an important factor

affecting the disproportionation of the entrapped air bubbles.

Changes in lightness during phase 2 for the -GLP and the +GLP systems are shown in Fig. 8.5. GLP causes a dramatically higher value of L^* at the end of chopping in fact the highest value ever obtained in the whole study for a raw PLMB. From then in both systems a gradual decrease commences and is much more rapid for the +GLP system. All along this process phase the L^* values are higher for the +GLP system than for the -GLP system.

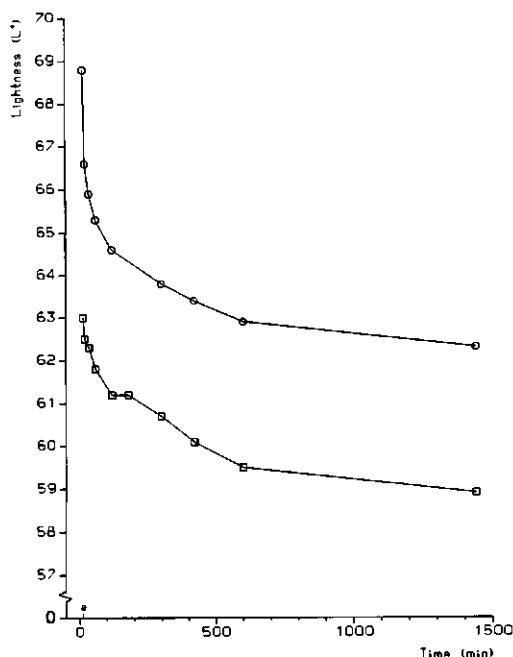


Fig. 8.5: Changes in lightness during storage at 15°C for a PLMB not containing GLP (□-□) and a PLMB containing GLP (○-○). a = End of chopping.

The % entrapped air (v/v) in both batters was very similar: 7.6 ± 0.4 and 7.4 ± 0.6 ($n = 4$) for -GLP and +GLP respectively. Thus, the large effect of GLP on L^* cannot be explained by an increase in air overrun of the PLMB but must be attributed to other scatter-promoting factors.

The behavior of NB and BSD for both systems is presented in Figs. 8.6 and 8.7 respectively. At the end of chopping the +GLP system versus the -GLP system contains much more (higher NB value) and markedly smaller air bubbles. These findings can be used to explain the corresponding difference in L^* values (see also

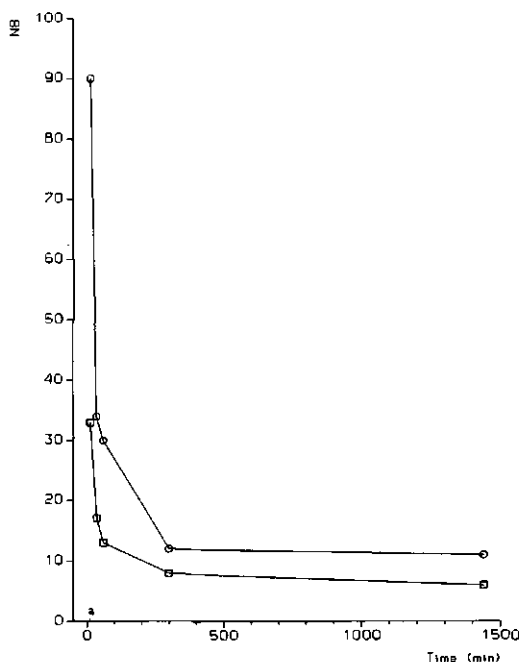


Fig. 8.6 : Mean of number of bubbles per field of view (NB) PLMBs at various storage times at 15°C. (□-□) -GLP system; (○-○) +GLP system. a = End of chopping.

Section 7.5.3). For both systems, the subsequent sharp decrease in the NB concomitant with an increase in bubble size, as is evident from the large decrease in the proportion of bubbles in the size class $< 50 \mu\text{m}$, coincides with the corresponding decrease in L^* . Thereafter, except for continuously higher absolute L^* values for the +GLP system, both batters have the same course of changes. This finding is in a complete agreement with the results obtained in Section 7.5.3 namely, the behavior of entrapped air bubbles can be used to explain the changes in L^* only during the first stage of phase 2. From then the main steering factor is the changes in absorption traits of the PLMB.

The cause of the continuously higher absolute position for the L^* plot of the +GLP system becomes evident from the results described in Fig. 8.8. Here, changes in the L^* of the de-aerated samples of both systems are presented. Clearly, GLP exerts a distinct whitening effect (also visually detected) by inducing a higher scatter which is not accounted for by the entrapped air bubbles (evacuated by the vacuum sealing treatment).

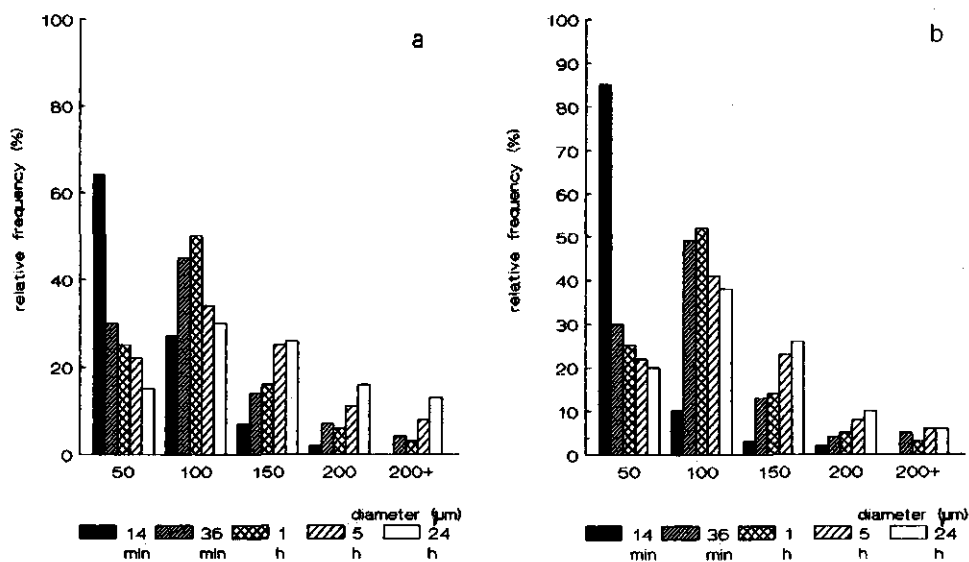


Fig. 8.7 : Size distribution of entrapped air bubbles (BSD) at various storage times at 15°C. a = -GLP system; b = +GLP system.

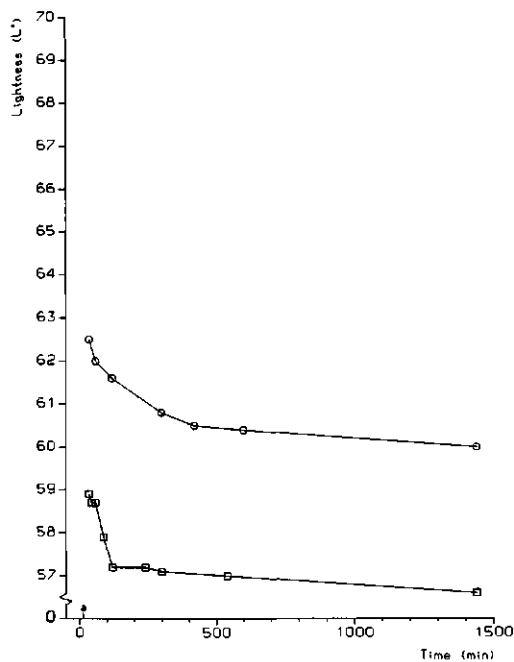


Fig. 8.8 : Changes in lightness during storage at 15°C for PLMBs de-aerated immediately after the end of chopping. (□-□) -GLP system; (○-○) +GLP system.

From these results one may conclude that no detectable stabilizing effect of GLP on the behavior of entrapped air, which is also reflected in the behavior of L^* , can be established.

A discrepancy between these findings and the previously established stabilizing effect of GLP on the shrinking process of individual bubbles becomes obvious. An explanation for it can be approached by referring to the combined effect of the viscoelastic character of the bubbles' surface and the initial bubbles' size distribution. At the end of chopping the size of the entrapped air bubbles in both systems covers a wide range of values. Set by the detection limit of the analytical method, the smallest detectable bubble has a radius of about $3\text{ }\mu\text{m}$. According to equation Eq. 7.3 the Laplace pressure within this bubble is $15\,000$ or $11\,666\text{ N m}^{-2}$ when it exists in the -GLP or the +GLP system respectively. These very high pressures, being the driving force for disproportionation, cause high rates of surface compression. In Table 8.1 the 'shear thinning' nature of the surface of the PLMB dispersions was shown, i.e., the higher the compression rate the lower the value of $\alpha\eta_s$. Thus, because of their very small size, any stabilizing effect of the bubble's surface stiffness is easily outweighed by the very high counteracting Laplace pressure. Hence, very small bubbles disappear in very short time. Conversely, for a bigger bubble say one having a radius of $40\text{ }\mu\text{m}$ the Laplace pressure is 1000 or 875 N m^{-2} for the -GLP or the +GLP system respectively. The corresponding rates of the bubble's surface compression are much lower and consequently the surface stiffness is relatively higher. This exerts a stabilizing effect on the shrinking process and a relatively longer persistence of the bubble.

The suggested explanation finds support in the results obtained from the comparison between the measured disappearance time (using the stereomicroscopical setup) and the calculated one (using the De Vries equation, Eq. 8.1), for a wide range of bubbles' sizes ($3\text{ }\mu\text{m} < r < 100\text{ }\mu\text{m}$). It revealed that the disagreement between the two values increased dramatically with increasing bubble size, i.e., the measured time became progressively longer than the calculated one. Since the De Vries model does not account for the surface stiffness of the bubbles, this finding is taken as evidence for the diminishing effect of the latter on genuinely small bubbles.

Making the step back to the results obtained for the NB and BSD, we suggest that the extremely rapid dissolution of small bubbles masks any detectable stabilizing effect of GLP on larger air bubbles in the PLMBs. Consequently, no pronounced scatter-induced effect of GLP on the behavior of L^* is observed.

Summarizing, we managed to demonstrate that the presence of GLP in the PLMB have a strong bearing on the shrinking process of medium-sized individual entrapped air bubbles and on the surface rheological properties of the dispersions prepared from the batter. This was taken as evidence for accepting the part in our working hypothesis pertaining to the important role of the dynamic surface rheological properties in affecting the behavior of the entrapped air bubbles during phase 2.

9. INFLUENCE OF AIR PRESSURE DURING CHOPPING AND OF FORMULATION ON COLOR, RHEOLOGY AND FRACTURE OF SOME PORCINE BATTERS

Studies pertaining to the introduction of vacuum application during the processing of comminuted meat products started already in the sixties (Tauber and Simon, 1963; Simon et al., 1965). Generally, it was concluded to be an important factor which led to considerable improvement in the functional properties of these products. The advantages in using vacuum included, higher emulsifying capacity, higher cook yield (Tantikarnjathep et al., 1983), higher extraction of salt soluble proteins (Solomon and Schmidt, 1980), increased product stability, improved storage stability, improved flavor and consistency (Jones and Mandigo, 1981; Wirth, 1973, 1978) and better color (Wirth, 1986). The microstructural basis for the last four of these positive actions can be easily visualized. For example, consider the increase in the contact area between air and the meat matrix as a result of chopping in air of a cube of meat having dimensions of 1 cm^3 placed in an open vessel with the same dimension (the contact area meat-air is 1 cm^2). Assuming 10% air overrun, and an average bubble diameter of $30\text{ }\mu\text{m}$ (see Chapters 7 and 8) a 200 times increase in the contact area is calculated.

Literature on the effect of formulation on the functional and quality properties of comminuted meat systems is wide spread (Kramlich, 1971; Schut, 1976; Acton et al., 1983; Ambrosiadis and Wirth, 1984; MacDougall and Allen, 1984; Hermansson, 1986). In particular, much research work has been devoted to the role of the proteinaceous fraction of these systems in affecting the stability (water and fat holding), rheology, and color of the raw and the cooked comminuted meat systems. The latter topics were reviewed recently by Schmidt (1988), Smith (1988), Whiting (1988) and MacDougall et al. (1988).

As stated in the introduction (Chapter 6) the predominant premise of this thesis

is that the exploitation of modern technologies in the production of comminuted meat products, with uniform and constant quality properties requires extensive basic knowledge concerning the effects of their formulation and of the applied processing conditions on them. Three of the most important quality attributes of these products are color, rheology and fracture properties. From a review of the literature pertaining to these quality marks (see below), it appears that although considerable research has been done on the effect of formulation and of low pressure during the processing of comminuted meat systems on them, there is still a paucity of basic and systematic information. In particular, no studies could be found in which the effects of vacuum processing on the quality characteristics of these products are investigated for a variety of meat batters formulations in a systematic way.

The aim of this study was to gain more fundamental knowledge regarding the effects of formulation and of air pressure during the chopping in the preparation of porcine batters on their color, rheology, and fracture properties. For this purpose the following topics were investigated:

1. The effect of air pressure during chopping on color changes during processing and a subsequent storage at 15°C of four batter formulations. The formulations were systematically varied in a design which enabled the examination of the individual effects of each of their major components i.e. lean meat, fatty tissue, and water. The color of the cooked batters was also studied. Further, for batters chopped under atmospheric air pressure (AAP), the behavior of the entrapped air was examined.

2. The effect of air pressure during chopping on the rheological and fracture properties of the cooked batters, prepared from the four formulations, as determined by uniaxial compression tests.

This chapter starts with an introduction that includes a literature review on the effect of vacuum chopping and formulation on the behavior of color, rheology and fracture of meat batter products. This will be done separately for color, and for rheological and fracture properties. Color will be discussed first. The review on rheological and fracture properties is preceded by a theoretical introduction of some basic rheological concepts and is followed by a description of the compression test chosen to be used in this study. Following, a detailed description of the materials and methods is presented. Finally, the results are reported and their significance is discussed.

A comment related to terminology should be mentioned. In the literature the terms vacuum, low-pressure, and even reduced air pressure are usually used

interchangeably to convey essentially the same processing condition. In the present review these terms will be used in the same manner.

9.1 Introduction

9.1.1 Color

Vacuum can be applied at various stages during the processing of comminuted meat products, i.e., during chopping, during a subsequent mixing stage and during stuffing of the batter into casings or cans. Most research on the effect of vacuum on color of meat batters has been restricted to the application of vacuum during the chopping or mixing stages. Further, most of the studies surveyed are characterized by the use of a frankfurter batter as a typical and representative meat system for cooked batter products.

Tauber and Simon (1963), and Fox et al. (1967) studied the effect of vacuum treatment after the chopping stage in the production of frankfurters. Both studies reported a considerable positive effect on the color of the cooked sausages. The latter study also reported a faster formation of cured meat color during prolonged storage at 38°C. In a more recent experiment, Klettner and Ambrosiadis (1980) studied the effect of vacuum chopping and vacuum stuffing on the color of frankfurters. They showed that compared to non-vacuum treatment, both vacuum chopping and stuffing resulted in lower L^* and higher a^* values, i.e., darker and redder color, for the cooked sausages. Yet, the effect of vacuum stuffing was much lower than that of vacuum chopping. Jones and Mandigo (1981), and Tantikarnjathep et al. (1983) conducted extensive studies on the effect of vacuum chopping on the functional properties of cooked frankfurter batters. The former investigators reported minor differences between the color of vacuum chopped and non-vacuum chopped cooked sausages. The results of the latter study disclosed an improvement in the color of the cooked sausages due to vacuum chopping, i.e., they had a darker and redder color. This positive effect was further associated with the possibility of reducing the level of nitrite needed for a satisfactory and uniform cured color formation. Wirth (1986) reviewed the effects of vacuum application during the processing of frankfurter-type sausages on their color. He concluded that only vacuum chopping resulted in sufficient withdrawal of entrapped air from the comminute and consequently led to the largest improvement in the color of the

cooked sausages.

The only study, found during this literature survey, reporting a systematical examination of the effect of composition on the color of comminuted meat products was that of MacDougall and Allen (1984). In their extended study they varied the percentage of added fatty tissue (i.e., pig back fat) and of water from 0 to 30 and from 10 to 40 respectively. Changes in color were described by mathematical models and visualized by contours within equilateral triangles for each of the psychometric color attributes L^* , h^* and C^* . Models were constructed for both raw and cooked sausage homogenates. The main findings for the raw batters were: (1) Addition of fat caused an increase in the opacity of the batters due to increase in light scattering. The effect on color was an increase in L^* and h^* , and a decrease in C^* . (2) Addition of water increased the translucency of the homogenates. This caused a decrease in L^* and C^* and an increase in h^* . Interestingly, the magnitude of the effect of fat was far more superior over that of water. This finding was explained by the fact that fat is highly scattering and to a certain extent also absorbing whereas water is not. These findings were in accordance with the rationale of the Kubelka-Munk analysis (see Section 7.2). Generally, similar trends to those obtained for raw homogenates were reported for the cooked homogenates. However, due to the massive denaturation of muscle proteins and the attended large increase in scattering a much smaller magnitude for the corresponding changes in L^* , h^* , and C^* was obtained.

From this literature survey it can be concluded that an agreement exists regarding the positive effect of low pressure during chopping on the color of cured cooked comminuted meat products (CCCMP). However, none of the reviewed reports examined the effect of air pressure during chopping and of formulation on the continuous changes in color of meat batters during processing. Moreover, none of the investigations combined the analysis of both factors in an experimental design which could enable the detection of possible interactions between them.

Strictly limited to a well defined 100% PLM system, Palombo and Wijngaards (1989a) characterized the effect of air pressure during chopping on the behavior of its color during processing. In a later publication (Palombo and Wijngaards, 1989b), they provided a kinetical analysis for this effect. These studies demonstrated a profound effect of the air pressure during chopping on the behavior of the three color attributes L^* , h^* and C^* during storage at 15°C until 24 h. Interactive effects of time and temperature on the behavior of these attributes were disclosed during

heating. More important, the effect of the air pressure during chopping on the color values at the end of the most severe thermal treatment (3 h at 60°C) was far more moderate compared to the corresponding effect on the color of raw batter. In Chapter 7 a mechanistic study on the changes in L^* , of still 100% PLM system, during processing and storage at 15°C was reported. We provided strong evidence for the superior effect of air entrapped within the batter on the changes in L^* during the chopping stage. For the subsequent storage at 15°C its effect was restricted to only a short period after chopping.

Equipped with this knowledge in the present study, we extended the batter formulation to include also fatty tissue and water and delved into the effects of air pressure during chopping and of formulation on the behavior of color during processing.

9.1.2 Rheological and fracture properties

Following Reiner (1971), rheology can be defined as the study of the deformation of materials in relation to the stress (force per unit area) employed and the time scale of the measurement. According to this definition it is possible to divide all materials into three groups namely, elastic materials, viscous materials and viscoelastic materials. Materials which belong to the first two groups show deformation which is not time scale dependent. When stress is applied on a linearly elastic material it will instantaneously and finitely deform when a stress is applied on it. When the stress is released it will instantaneously return to its original dimensions. Thus, the added energy is completely stored and released under stressed and unstressed conditions respectively. For such material a constant, which is derived from the ratio between the stress and the deformation, may be defined and is called the modulus (N m^{-2}). A linearly viscous material will deform at a certain rate (s^{-1}) as a reaction to an applied stress. On removal of the stress, the material remains completely in the deformed state. Hence, the added energy is completely dissipated through flow of the material. For such material the ratio between the applied stress and the rate of deformation is constant. This ratio is called the viscosity ($\text{N m}^{-2} \text{ s}$) and in fact reflects the amount of dissipated energy. For viscoelastic materials the deformation due to the applied stress is associated with both elastic and viscous behaviors (Ross-Murphy, 1984). The relative contribution of each of these

components to the overall viscoelastic behavior depends on the time scale of the experiment. At short time scales more bonds are permanent, over the considered time scale, contribute so elastically to the reaction of the material to the stress; more energy can be stored in them. Thus, more elastic-like behavior will be observed. At long time scales due to bond breakage energy may be dissipated. Hence, more viscous-like behavior is witnessed.

A study of the literature related to the rheology of solid food materials reveals two distinct approaches in the evaluation of their rheological and fracture properties. The first one uses empirical or imitative tests like, shear press tests, penetration tests, and the Warner-Bratzler shear tests. The second approach uses fundamental rheological tests such as uniaxial compression or tension tests, and bending tests (Voisey et al., 1975; Rao and Skinner, 1986; Dobraszczyk et al., 1987). During the execution of the empirical tests the material is exposed to complex, unpredictable, and continuously changing stress and strain (defined as the relative deformation in a certain point) conditions. Consequently, the information obtained depends completely on the conditions of measurement e.g., instrument, sample size and shape, rate of deformation etc. Their main use have been to provide some information about the mechanical properties of the tested material that correspond or can even replace the sensory evaluation. Consequently, many of them proved to be advantageous for rapid quality control measurements during food processing operations. The fundamental tests, however, are used with the aim of providing information pertaining to mechanical properties that are more inherent to the material and less dependent on the experimental method (Luyten, 1988). This is usually done by using a well defined dimension of the test piece and by applying a known or predictable stress and rate of deformation. Such conditions enable classical analysis of fundamental rheological properties such as Young's and shear modulus, relaxation times etc. Further, these tests provide a better possibility for replicating measurements and verification of rheological results obtained from different investigations on the same food. They may also offer a better insight into the microstructure and the interaction between the various components of the tested food sample.

Literature review

A literature search on the effect of vacuum chopping and formulation on the rheological and fracture properties of cooked meat batters revealed reports in which

only empirical or imitative tests were used. Simon et al. (1965) studied the effect of vacuum chopping on the texture of frankfurters using an Instron tensile tester and a Carbide penetrometer equipped with a tooth shaped puncture probe. They defined, as a working parameter, the ratio between the force and the compression at puncture as the modulus at puncture. A clear increase in both parameters (force and modulus at puncture) due to vacuum chopping was reported. Klettner and Ambrosiadis (1980) employed penetration and compression measurements to examine the effect of vacuum chopping on the firmness and density of frankfurter sausage. With both methods, they were able to demonstrate that vacuum chopped versus open bowl chopped frankfurters had a higher "firmness". This higher firmness was deduced from higher values for maximum force during compression and significantly lower penetration values. Further, by density measurements, they managed to show that vacuum chopped frankfurters also had higher density. Jones and Mandigo (1981) were able to detect only minor differences between the "Instron textural properties" of frankfurters prepared from vacuum chopped and non-vacuum chopped sausage emulsions. Similarly, nonsignificant effects of vacuum chopping on the shear values of poultry meat bologna were reported by Raymond et al. (1983). The most recent, as well as the most extensive, study on the use of vacuum during the formation of meat emulsions, encountered during this literature review, was the one reported by Tantikarnjathap et al. (1983). Their results show that vacuum chopping versus open-bowl chopping caused a significant increase in the frankfurters density. However, they failed to establish the expected corresponding firmer texture by measurements of Warner-Bratzler shear values.

These conflicting data on the effect of vacuum chopping on the texture of the cooked meat products may be due to the use of different empirical tests in the different studies. Clearly, the subject warrants further study.

We now turn to examine the literature on the effect of batter formulations on the texture of cooked meat batter products. Simon et al. (1965) showed that the forces and the "Instron moduli" at puncture of frankfurter sausages increased when the protein to fat ratio increased (moisture content was kept constant). They used this finding to conclude that formulations with a greater proportion of muscle protein result in firmer sausages. Generally, similar trend was reported by Singh et al. (1985). Employing texture profile analysis, they reported that for samples with a higher protein and lower moisture content higher values for all the studied texture parameters were obtained. In an extensive study on the effect of composition on the

texture and color of cooked meat sausages, MacDougall and Allen (1984) used a punch and die technique to measure the shear force needed to shear a sausage disk. Their modeling study included a systematic evaluation of the effects of the three major components in meat batters, i.e., lean meat, fatty tissue, and water, on the texture of the cooked products. The findings substantiated previous observations regarding the role of meat proteins content. More important, they found that an increase in water content at constant fat content, was more effective than elevating the fat content at constant level of water, in diminishing the shear values.

Summarizing, this literature survey discloses that a little if any research has been conducted pertaining to the effect of air pressure during chopping on the rheological and fracture properties of cooked meat batters using fundamental rheological parameters. Further, conflicting results exist concerning the significance of the effect caused by this processing factor. An increase in added water or fat causes a decrease in the empirically measured textural properties of cooked sausages. Increase in water content versus increase in fat content has a much stronger diminishing effect on their textural properties.

Many types of fundamental tests are available for studying the rheological and fracture behavior of foods (Whorlow, 1980; Luyten, 1988). For the present study, we decided to use the uniaxial compression test in order to analyze the effect of air pressure during chopping and of formulation on some fundamental rheological and fracture properties of the cooked meat batters. This method was chosen mainly because of the simplicity in its performance. Although it has some inherent drawbacks (Luyten, 1988) they are outweighed by the latter consideration especially when the experimental setup and the nature of the tested material require a large number of measurements to be done in a relatively short period. In the following paragraphs, a concentrated theoretical background pertaining to the uniaxial compression test and fracture theory is provided.

Uniaxial compression test

Compression tests have been widely used in the study of textural properties of processed meat products (Voisey, 1975; Payne and Rizvi, 1988; Singh et al., 1985; Lee et al., 1987; Siripurapu et al., 1987). The major aim of most research studies reported in the literature was to analyze the effect of formulation or processing

conditions using objective textural parameters that could be related to sensory quality of the product under investigation. Usually, the objective parameters were based on the interpretation of force-deformation relationships. However, such relationships supply limited information of the fundamental rheological properties of the material. The main reason for this is the difficulty of separating the effects contributed by the test conditions from those contributed by the mechanical properties of the material. The conversion of the force-deformation relationships to true stress-strain relationships enables better insight into the fundamental rheological properties of the tested food. In a rigorous review on the basis of solid food rheology, Peleg (1987) demonstrated that by such transformations it is possible to distinguish between foods exhibiting rheological character that is predominantly compressible (those with a foam-like structure), yielding, elastic and the combination of the last two types. The only report employing such an approach in the study of the rheology of a meat emulsion product is the one by Calzada and Peleg (1978). Based on analysis of the true stress-strain relationships together with complementary relaxation and compressibility data, they suggested a two factors mechanism for the explanation of the stress levels during uniaxial compression tests. One factor was the internal fracture which induces a decrease in strength of the material (material strength is defined as its resistance to break (Peleg, 1987)) and results in a decreasing slope of the curve. The other was compaction of the sample (having a foamy structure) which caused an increase in its strength and an increasing slope in the true stress-strain curve.

The conversion of force-deformation curves obtained from uniaxial compression test to true stress-strain relationships and the derived rheological parameters.

Stress σ (N m^{-2}) is defined as the force F (N) per unit area A (m^2) on which it is applied,

$$\sigma = F/A \quad (9.1)$$

It should be realized that the calculated stress is an average value. The real stresses in the material during deformation may have a more complex internal distribution and may also vary in type (e.g. compression, shear, tension etc.)

depending on the uniformity of the material. However, for most practical purposes and also for our analysis, this is a satisfactory and convenient parameter whenever the test sample is bigger than the inherent inhomogeneity of the material.

Since we used uniaxial compression in which large deformation was exercised on the specimen, its cross-sectional area increased considerably with increasing deformation. Knowledge about this increase is necessary in order to calculate the true stress at any moment of deformation. Calzada and Peleg (1978) measured these changes at any applied strain. In our experimental setup, this measurement proved to be difficult and we used the following formula to calculate the area A_t at any time t along the compression process,

$$A_t = (H_0 * A_0) / H_t \quad (9.2)$$

where:

H_0 = the initial sample height (m)

A_0 = the initial cross-sectional area (m^2)

H_t = the sample height at time t (m)

The assumption in using this equation is that the specimen retains its cylindrical shape and that its volume remains constant during compression. Visual inspection showed that most of the specimens retained their shape during compression (probably also because of the application of mineral oil between specimen and plates (see also Section 9.2)). Samples chopped under AAP contained air (see Table 9.5) and small changes in volume will occur during compression. Principally, it is possible to compensate for it. However, due to the relatively small air content this volume change will be rather small. Based on this consideration, we concluded that this assumption is not far from reality and can be adopted. Thus, true stress σ_t is calculated by,

$$\sigma_t = F_t / A_t \quad (9.3)$$

Where F_t and A_t are the actual force and cross-sectional area at time t .

For large deformations the natural or Hencky strain ϵ_h (-) is usually used for describing the true strain in the sample,

$$\epsilon_h = \ln H_t/H_0 \quad (9.4)$$

For large deformations when a constant compression rate V (m s^{-1}) is used the Hencky strain rate $\dot{\epsilon}_h$ (s^{-1}) is:

$$\dot{\epsilon}_h = V/H_t \quad (9.5)$$

Again, as stated for the stress the calculated strain value is only an average or overall value. Depending on the uniformity of the specimen the local three dimensional strain and strain rate can vary considerably (van Vliet et al., 1990).

Young's modulus E (N m^{-2}) is defined as the ratio between stress and strain. It is constant for linear elastic materials. As can clearly be seen in Fig. 9.7b we obtained an initial linear region in the true stress-strain curve. Because the cooked meat batters are viscoelastic materials (see below) this linear region includes both elastic deformation and flow processes. At relatively large deformations it contains also fracture (see Section 9.3.2). However, assuming that the consequences of non-linearity are small at small deformations the initial slope can be taken as an approximation for the Young modulus. Since it is only an estimate we prefer to call it a "modulus of deformability" E_d (Nm^{-2}) as done by Johnson et al. (1980) for cooked fish flesh. The formula is,

$$E_d = \sigma_t/\epsilon_h \quad (9.6)$$

Basically, this modulus gives an indication about the overall resistance of the material to small deformations.

Fracture of viscoelastic materials

It is beyond the scope of this introduction to elaborate on the present state of knowledge pertaining to the fracture properties of viscoelastic materials. The following discussion is limited to principles of this theory which are the most relevant for the present study.

Fracture or micro-failure always starts at locations where a defect like crack, hole etc., is present (Gordon, 1968). Most of solid food materials are inhomogeneous and often possess a non-uniform structure. Consequently, when a

specimen of such material is compressed the local stress, in different places within it, will greatly vary. Stresses around defects are higher and can initiate local yielding and fracture (Peleg, 1987). Thus one can speak about local stress concentrations of a magnitude which depends on the size and shape of the defect and on the material's rheological properties (Luyten, 1988). Only the elastic or stored energy is available for the spontaneous propagation of a fracture. This may induce formation of additional small cracks in the material until a visually detected disintegration of the whole specimen can be witnessed. Energy dissipated due to viscous flow is not available for the creation of new surfaces. In a viscoelastic material the amount of dissipated energy depends on the deformation rate. Hence, it is conceivable that a theory different from the one used for elastic materials is needed to describe the fracture behavior of viscoelastic materials. Like most solid food systems, cooked meat batters are viscoelastic (see also below). Moreover, at large deformations energy can be dissipated due to flow of internal liquid or movement of structural elements relative to each other. Currently, an established theory for the fracture behavior of such material is not available. However, a qualitative theory was suggested by van Vliet et al. (1990). Essentially, they suggested that a better understanding of the fracture phenomenon of viscoelastic materials can be obtained by considering the energy balance in which the total energy input is related to the sum of the stored strain energy, the dissipated energy not due to fracture, and the energy used for fracture.

In this study, the effects of air pressure, during chopping and of formulation, on the fracture properties of the cooked meat batters was investigated by compressing samples uniaxially until a visually observable gross failure occurred.

9.2 Materials and methods

Meat raw materials

Lean meat from pig leg muscle and pig back fat were trimmed to arrive at a desired proximate composition (Table 9.1). The lean meat was cut into small pieces, tumbled for 10 min and chopped in Kilia bowl chopper (at conditions described in Section 3.3) for 20 s and finally tumbled again for 5 min. At this stage the pieces of meat had a size of about 1 cm³. Quantities of 5 kg were packed under vacuum and stored at -40°C as described in Section 3.3. The back fat pieces were ground through

Table 9.1: Proximate chemical analysis of batters ingredients: PLM = Porcine lean meat; PBF = Porcine back fat

<u>Ingredient</u>	<u>protein</u>	<u>fat</u>	<u>moisture</u>
PLM	21.9	3.2	73.0
PBF	3.1	83.7	13.0

a 3 mm plate using a Svenska grinder (model CN-106, Almelo, The Netherlands) . Quantities of 3 kg were packed under vacuum and stored at -40°C as described in Section 3.3. These stages were necessary in order to obtain a relatively uniform and more homogeneous bulk of meat raw materials.

Experimental procedure

A constant reproducible temperature of the raw materials at the start of chopping was obtained by thawing them in a water bath at 2°C for 12 h. Their temperature at the start of chopping was always about -1°C.

Due to a logistical problem for performing the chopping under a reduced air pressure, we had to use a Stephan chopper (model UMM-25, Almelo, The Netherlands) instead of the Laska bowl chopper which was used in a previous stage of the study. The Stephan chopper was equipped with a 'double wall' bowl and a manually operated 'arm' for scraping its inside wall. An outlet of a vacuum pump was connected to the lid of the chopper thus enabling the application of reduced air pressure during chopping. Different from the Laska chopper, this chopper had horizontally positioned knives. Consequently, as observed in preliminary experiments, the increase in temperature of the batter during chopping was much higher in the latter. Too high temperature at the end of chopping is associated with higher instability of the cooked batters (Schut, 1976; Kramlich, 1971). Accordingly, we changed the chopping procedure (see below) so that homogeneous batters having a temperature of about 20°C at the end of chopping were obtained. Further, the temperature increase during chopping was regulated also by circulating water at a preset temperature (-4°C - 0°C) through the double wall of the chopper's bowl.

In each experiment a 10 kg batch of meat batter was processed. The chopping

started after placing the lean meat in the bowl of the chopper and coarsely chopping it for 1 min at knives speed of 3000 rpm (this speed was used through the whole chopping stage). Then the water and the additives, salt (containing 0.6% sodium nitrite), phosphate mixture, and sodium ascorbate (All additives were identical to those mentioned in Section 3.3.), were added. Salt and phosphate were added in quantities producing the same brine concentration (of 2.7% and 0.14% respectively) in all the formulations. The amounts of added sodium nitrite and sodium ascorbate were calculated to produce in all the formulations the same molar ratio between myoglobin, nitrite and ascorbate. Chopping was then continued for 1 min. Next, the back fat was added. Thereafter, 3 additional chopping periods of 1 min (interrupted by breaks of 3-4 min for temperature measurement and sampling) were performed. The batters were transferred to a Handtmann Vacuum stuffer (model VF-80, Bibrach, West Germany) and filled into 100 and 400 g cans at 0.8 bar (this vacuum stuffer was used in order to withdraw big air pockets from the meat batter). The cans were sealed and placed in water bath at 15°C. After 3 h from the start of chopping, several of the 100 g cans were heated for 3 h in a water bath at 70°C and subsequently cooled for 1 h in a water bath at 0°C. This heat treatment was chosen since it simulates the thermal input used for pasteurization of comminuted meat products (Moerman, 1988).

Color measurements and microstructural examination: These were done as described in Section 7.5.3.1.

% air determination: This was determined using a Vemag air tester (Vemag, Verden, W. Germany). The reason for using this apparatus instead of the SMRAT was the better reproducibility of the determinations with the former. The design of the instrument is visualized in Fig. 9.1. A raw meat batter sample is filled directly

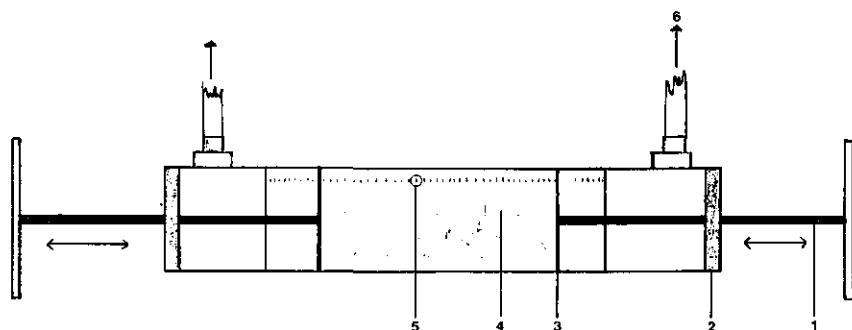


Fig. 9.1: Vemag air tester. (1) Plunger; (2) Cap; (3) Plunger's plate; (4) Meat batter sample; (5) Calibrated scale; (6) Outlet to vacuum pump.

from a 400 g can into the transparent measuring compartment. The plungers are entered from both sides of the cylinder and are fastened to it by the two caps. These are then pressed onto the batter to allow proper reading of the samples length (L_1) from the calibrated scale. Next, a vacuum of 0.05 bar is created by an oil vacuum pump and is maintained for 3 min. During this period the plungers are pushed on and from the batter to enhance the air withdrawal from the batter and through little holes in the plungers plates. Thereafter, air is allowed into the cylinder and the plungers are pushed onto the compressed batter to allow a second reading from the calibrated scale (L_2). The whole determination is done at 15°C. Percent of air content is calculated using the following equation:

$$\% \text{ air} = ((L_1 - L_2)/L_1) * 100 \quad (9.7)$$

Where:

L_1 = Length of meat batter at barometric pressure before exposure to vacuum

L_2 = Length of meat batter at barometric pressure after exposure to vacuum

At least 4 measurements were done for each determination.

Measurement of defect size: The cooked batter contents of each of three cans from each treatment (see experimental design next), was sliced along the longitudinal axis and the defects' (e.g. tissue fragments, air bubbles etc.) sizes were measured by a ruler.

Uniaxial compression tests: All samples were prepared from cooked batter samples present in 100 g cans. During sampling and further test stages, the samples temperature was about 15°C. This was achieved by placing the machine and the samples in a temperature controlled chamber set at 15°C. Using a borer and parallel wires (0.3 mm thick), cylindrical specimens were prepared with the dimensions of 15 mm diameter and 20 mm height. This was done as slowly as possible to minimize the non-flatness or roughness of the surfaces of the cylinders. Before each test the actual dimensions of the samples were measured with a micrometer and used for further analysis of the results.

Compression measurements were done using an Overload Dynamics tension compression apparatus (table model S-100). A 200 N load cell, calibrated with a 50 g weight, was used. The machine consisted of a fixed lower plate and a moving bar

which contained the load cell and an upper plate connected to it. We used a lower metal plate and an upper perspex plate (10 cm diameter). The specimen flat edges were covered with a film of mineral oil before the start of the test. In preliminary measurements, 3 samples from each treatment (see experimental design next) were tested at constant rates of 0.5, 5 and 50 mm min⁻¹ until gross fracture. Only the latter deformation rate was used for quantitative comparisons between treatments. The main consideration was to avoid the drying out of the sample. Ten replicate measurements were done for each determination.

The force-time curves were directly recorded during the compression process. From them the true stress-strain relationships were calculated as described in the Section 9.1.2. The parameters taken from the true stress-strain relationships (Fig. 9.7b) were :

- (1) The modulus of deformability (E_d).
- (2) Stress at fracture σ_f . The maximum stress obtained during the compression coincided with visually detected gross fracture of the sample. This value was taken as an estimate of σ_f .
- (3) Strain at fracture ϵ_f . This was the value of ϵ corresponding to the value of σ_f .
- (4) Apparent toughness aR (J m⁻³). This was derived by calculation of the area below the true stress-strain curve left to the point of σ_f . The value of this parameter indicates the total amount of energy needed to produce a gross fracture in a unit volume of a sample.

Experimental design

Two factors, i.e., air pressure during chopping and formulation with 2 and 4 levels respectively, were studied by means of 8 treatments. The levels of the former factor were: (1) Atmospheric air pressure (AAP), and (2) Reduced air pressure - 0.15 bar (RAP). The levels of the latter factor are shown in Table 9.2. The 8 treatments consisted of 8 combinations in which each level of the formulation factor (A - D) was checked in each of the two air pressure levels (AAP and RAP). The treatment codes are defined in Table 9.3. Each treatment was checked in a separate experiment. Pairs of treatments having the same formulation were checked on the same experimental day. To learn about the magnitude of the day effect only one pair of treatments, i.e., the treatments AAAP and ARAP, was replicated. The results of these experiments indicated that the day effect was sufficiently small to allow comparison between treatments.

Table 9.2: Batter formulations (in %): PLM = Porcine lean meat; PBF = Porcine back fat

Ingredient	Formulation			
	A	B	C	D
PLM	100	85	70	60
PBF	-	-	30	30
WATER	-	15	-	10

Table 9.3: Treatment codes

	Formulation			
	A	B	C	D
Air pressure				
AAP	AAAP	BAAP	CAAP	DAAP
RAP	ARAP	BRAP	CRAP	DRAP

9.3 Results and Discussion

9.3.1 Color

9.3.1.1 Results

Results pertaining to the changes in L^* , h^* and C^* during processing and subsequent storage at 15°C for the eight treatments (Table 9.3) are presented in Figs. 9.2, 9.3 and 9.4 respectively. Generally speaking, for all treatments the course

of changes in the three color attributes is similar to that characterized by Palombo and Wijngaards (1989a) under the study of the effect of air pressure during chopping on the color of 100% PLMB.

For the sake of clarity, the presentation of further results and discussion is done separately for each color attribute. A distinction is also made between two processing phases: (1) Chopping stage, and (2) Subsequent storage at 15°C until 24 h.

Lightness (Fig. 9.2)

Phase 1. For the two levels of air pressure, the effect of back fat addition on the increase in L^* was superior over the effect of added water. The effect of back fat and water addition (formulation D) did not differ markedly from the effect of back fat addition only. The magnitude of difference between the L^* values, at the end of chopping, of systems with and without back fat addition was higher for chopping under RAP.

Phase 2. For both levels of air pressure, the L^* values for the systems with added back fat (formulations C and D) remained extremely high compared to the L^* of the systems without added back fat (formulations A and B). In both pairs the decrease in L^* , subsequent to chopping, existed but this decrease was much more pronounced for the systems without back fat addition. The magnitude of the effect induced by the air pressure on changes in this phase was far more profound for the systems without added back fat.

Cooking of the batters decreased the differences in L^* values between systems with and without added back fat (Table 9.4). In addition, the effect of air pressure on L^* values within each formulation disappeared.

Hue angle (Fig. 9.3)

Phase 1. The effect of back fat addition versus that of water addition on changes in h^* was higher. Chopping under RAP versus chopping under AAP induced a more pronounced difference between the h^* values, at the end of chopping, of systems with and without added back fat.

Phase 2. The effect of back fat addition was still dominant over the effect of water addition. Values of h^* for systems with added back fat were considerably higher. As reported by Palombo and Wijngaards (1989a,b), for 100% PLMB, for all formulations chopping under RAP induced a faster approximation to a final constant h^* value.

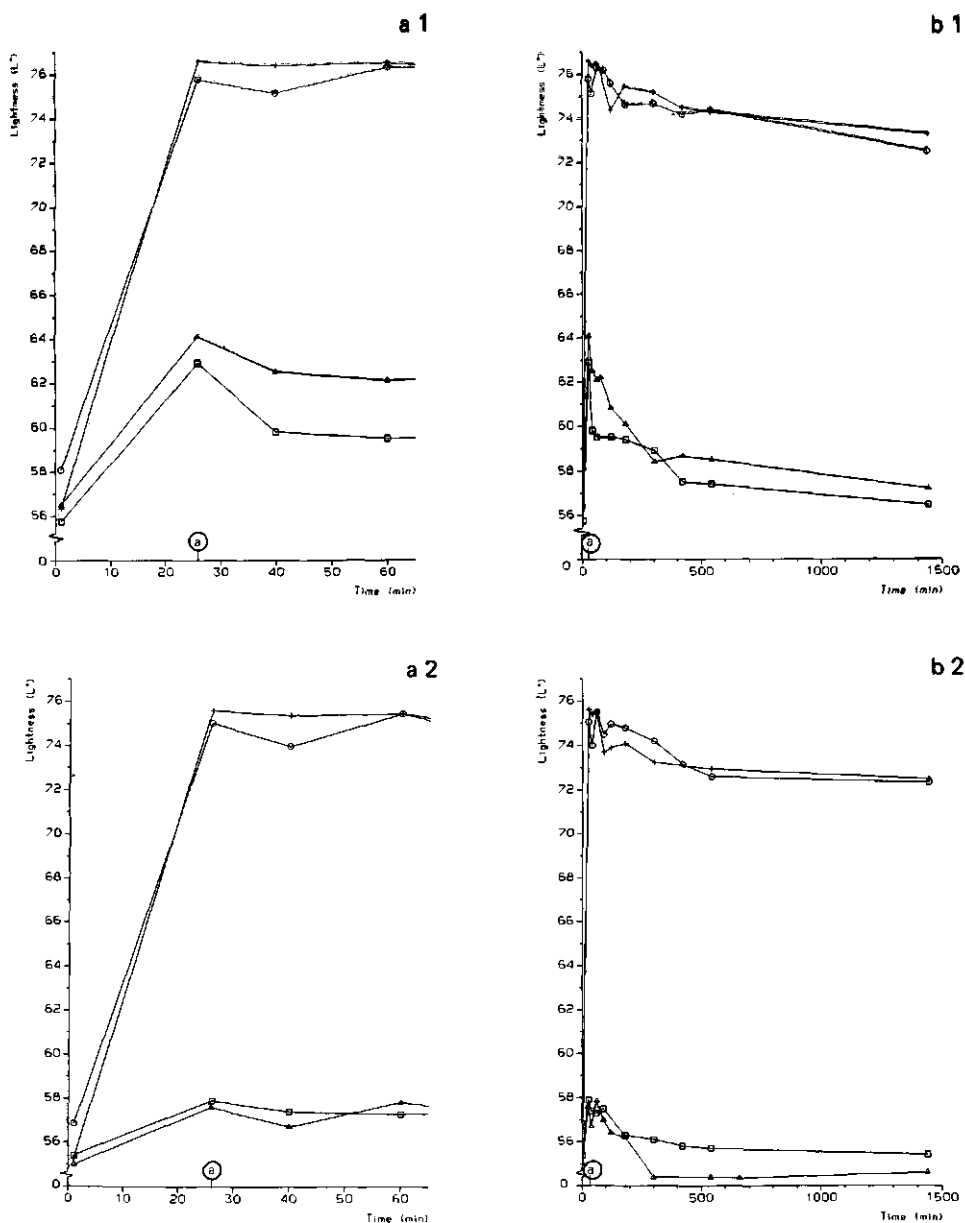


Fig. 9.2: Changes in L^* during chopping and subsequent storage at 15°C for batters chopped under AAP (1) and RAP (2). a stands for 60 min time interval; b stands for 24 h time interval; (a) marks the time of end of chopping; (\square) = Formulation A; (\triangle) = Formulation B; ($+$) = Formulation C; (\circ) = Formulation D.

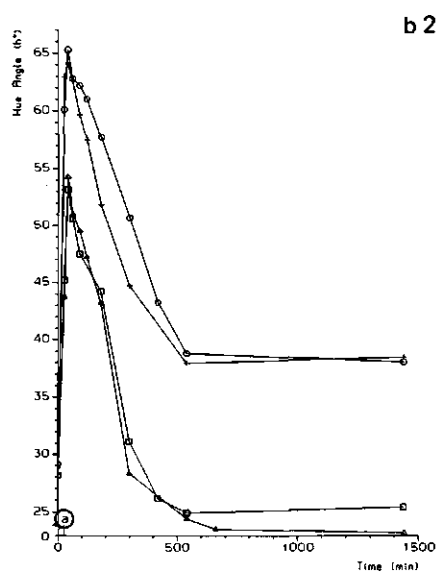
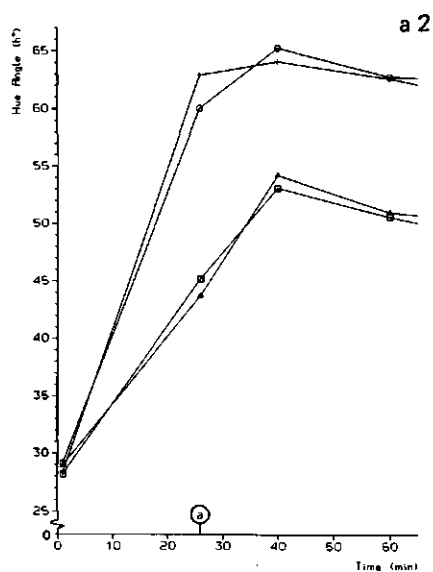
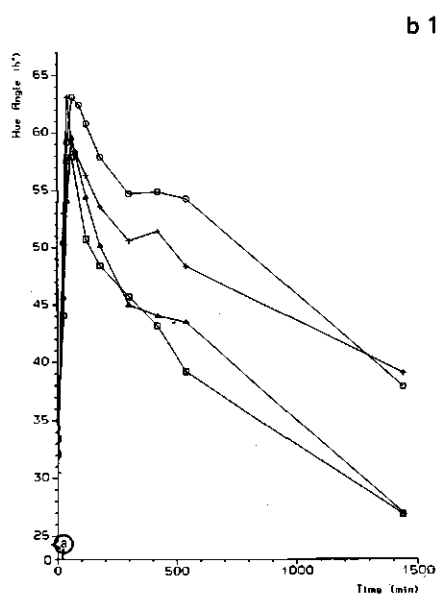
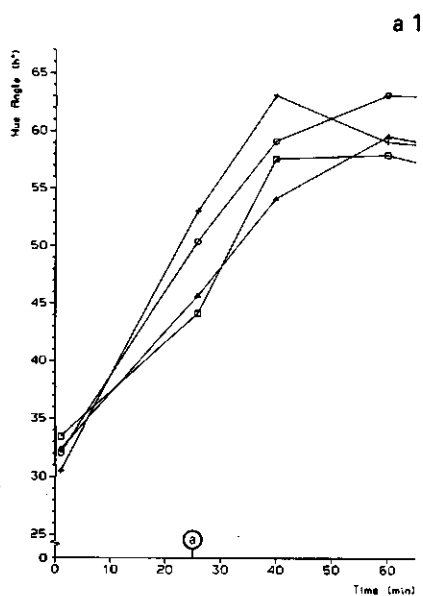


Fig. 9.3: Changes in h° during chopping and subsequent storage at 15°C for batters chopped under AAP (1) and RAP (2). a stands for 60 min time interval; b stands for 24 h time interval; (a) marks the time of end of chopping; ($\square-\square$) = Formulation A; ($\triangle-\triangle$) = Formulation B; ($+-+$) = Formulation C; ($\circ-\circ$) = Formulation D.

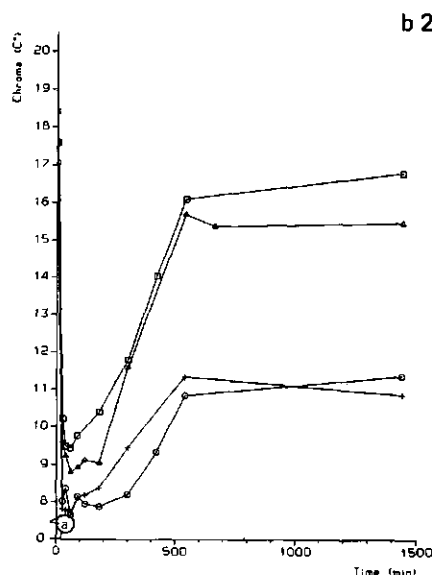
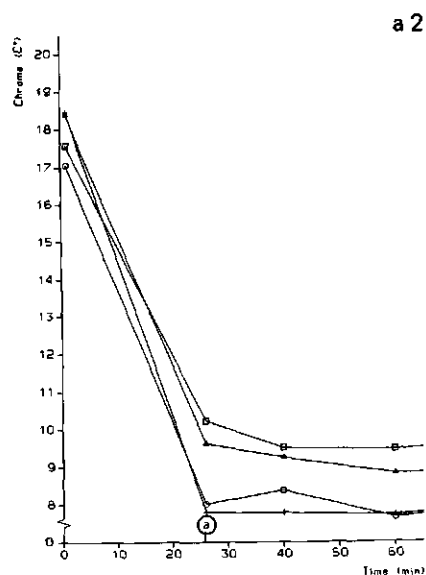
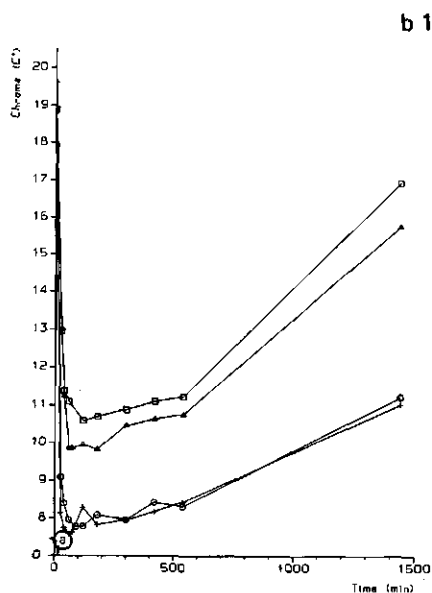
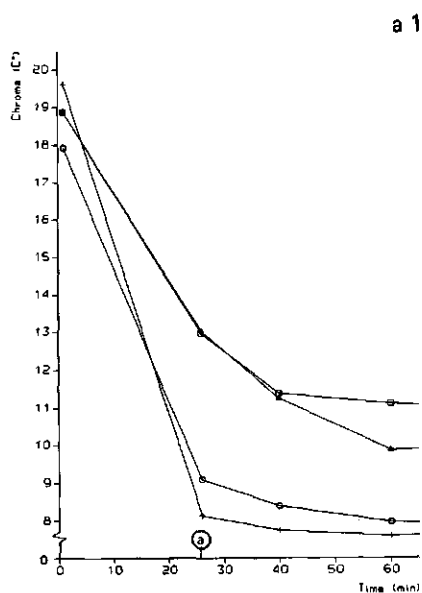


Fig. 9.4: Changes in C^* during chopping and subsequent storage at 15°C for batters chopped under AAP (1) and RAP (2). a stands for 60 min time interval; b stands for 24 h time interval; (a) marks the time of end of chopping; (□-□) = Formulation A; (△-△) = Formulation B; (+-+) = Formulation C; (○-○) = Formulation D.

Cooking the meat batters diminished the magnitude of differences in h^* values between systems with and without added back fat (Table 9.4). The effect of air pressure within each formulation also decreased markedly.

Chroma (Fig. 9.4)

Phase 1. As for h^* and L^* the effect of back fat addition was dominant over that of water addition. Contrary to the observation in L^* and h^* , the magnitude of the difference between the C^* values, at the end of chopping, of system with and without added back fat was lower for chopping under RAP.

Phase 2. A pattern which comprises a mirror image of the results observed for h^* was obtained. For all formulations, a faster and earlier approximation to a final constant value was characteristic of the chopping under RAP (Palombo and Wijngaards, 1989a,b).

As for the L^* and h^* , compared to the situation in the raw batters, cooking of the batters resulted in far smaller differences between the systems with and without

Table 9.4: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the color of the cooked meat batters.

Color attribute	Air pressure	Formulation			
		A	B	C	D
L^*	AAP	68.0	68.5	73.4	73.1
	RAP	68.0	68.2	73.2	74.0
h^*	AAP	19.9	20.6	25.0	25.8
	RAP	18.6	19.4	23.7	24.0
C^*	AAP	11.2	10.8	9.5	9.4
	RAP	11.0	10.6	9.9	9.1

back fat addition. Within each formulation the effect of air pressure could not be detected (Table 9.4).

Entrapped air

% entrapped air: Regardless of back fat addition an increase in the air overrun occurred with the addition of water (Table 9.5). Since we didnot perform any rheological measurements on the raw batters it would be too speculative to provide any explanation for these results.

Table 9.5: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the % entrapped air. Values are Means \pm SD (n = 5)

	Formulation			
<u>Air pressure</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
AAP	6.0 \pm 0.6	8.9 \pm 0.4	5.2 \pm 0.9	8.1 \pm 0.5
RAP	1.4 \pm 0.6	0.0	0.0	0.0
AAP - RAP	4.6	8.9	5.2	8.1

NB: The values of all formulations chopped under RAP were very similar. Consequently, for each processing time the mean value of NB from all four formulations is presented in Fig. 9.5. Systems without added back fat versus systems with added back fat had higher NB values at the end of chopping. From then all four formulations were characterized by a similar course of decrease approximating a constant final value at 24 h.

BSD: The extremely low values of NB for batters chopped under RAP hampered the construction of reliable histograms for them. Histograms presenting the BSD of the four formulations chopped under AAP showed an exceptional histogram for the AAP treatment (Fig. 9.6). Compared to the histograms of the other treatments, a

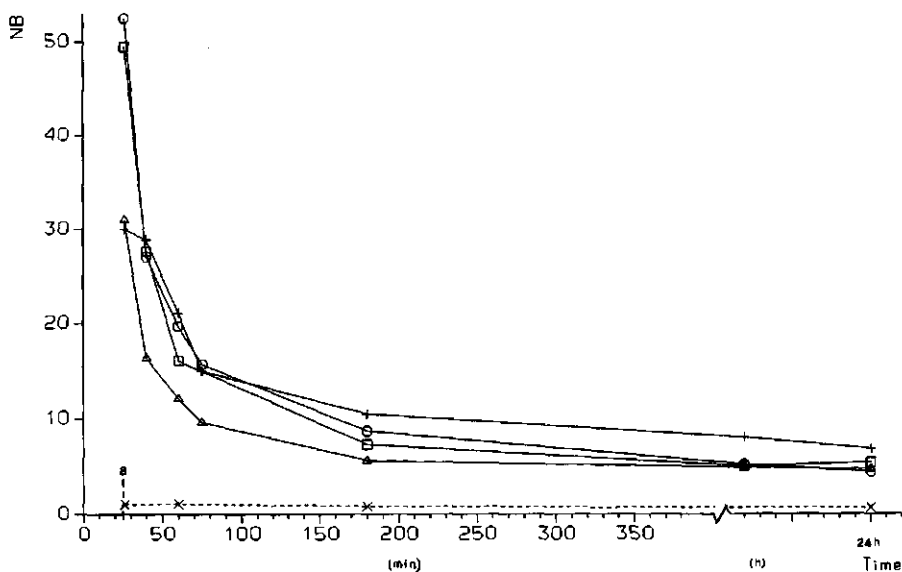


Fig. 9.5: Means of number of bubbles per field of view (NB), for raw batter formulations, at various storage times at 15°C. Batters chopped under AAP: (□-□) = Formulation A; (○-○) = Formulation B; (△-△) = Formulation C; (⋈-⋈) = Formulation D. Batters chopped under RAP: (x-x) = Mean value of all formulations. a marks the time of end of chopping.

markedly higher proportion of bubbles in the size class of $< 50 \mu\text{m}$ was obtained. Hence, addition of water and back fat, alone or together, had a considerable effect on the BSD of the meat batters at the end of chopping.

Finally, it should be noted that any attempt to calculate the air overrun from the data obtained for the NB and BSD is deemed to result in a large under estimation of the percent entrapped air measured. The reason for this is the fact that the bubble size range covered by the microstructural technique used to determine NB and BSD is $6\text{-}400 \mu\text{m}$. However, inspection of slices of meat batters revealed many air bubbles bigger than $400 \mu\text{m}$, reaching up to sizes of $4\text{-}6 \text{ mm}$ (Table 9.10).

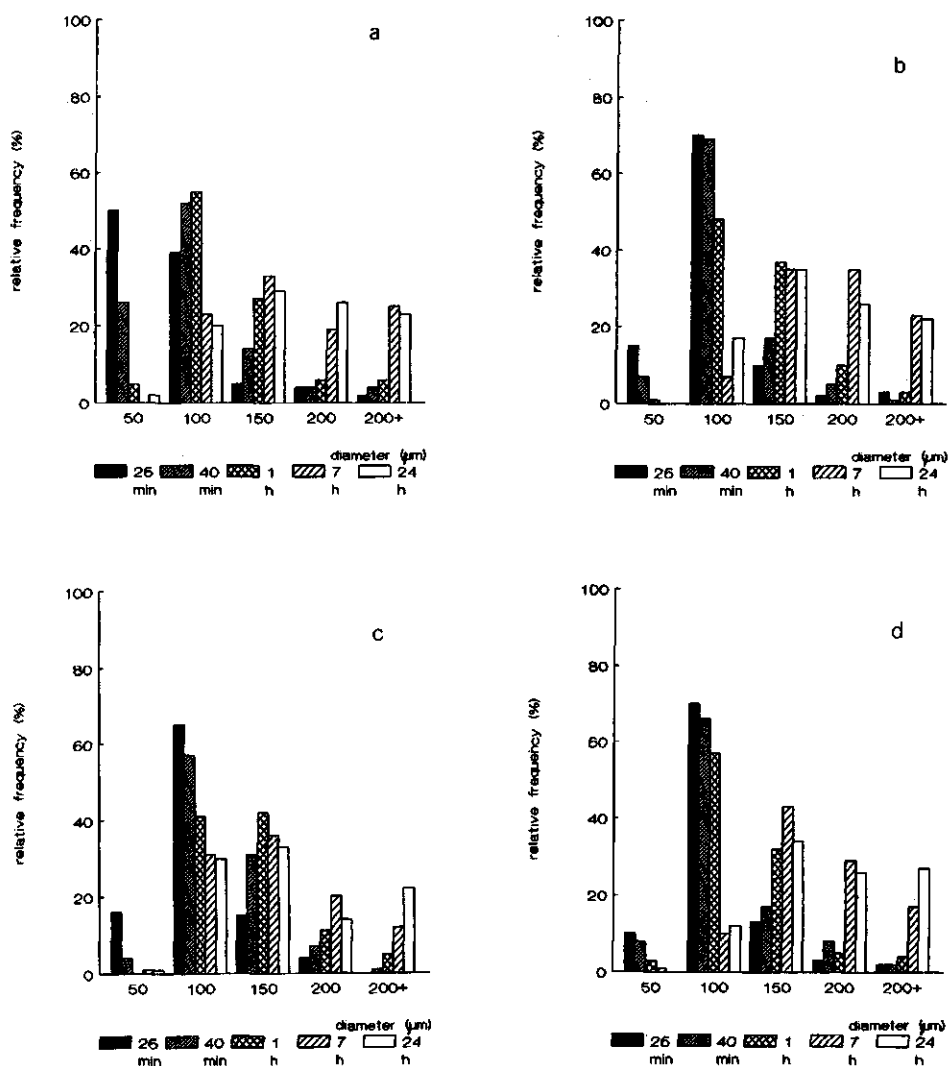


Fig. 9.6: Size distribution of entrapped air bubbles (BSD) at various storage times at 15°C. a, b, c, and d stand for raw batter formulations A, B, C and D respectively. All batters were chopped under AAP.

9.3.1.2 Discussion

Lightness

Phase 1. Clearly, the large effect of back fat addition on the value obtained at the end of chopping (Fig. 9.2) is attributed to the immense light scattering properties of back fat (MacDougall and Allen, 1984). This increase in scatter is also responsible for the minor changes in L^* , due to entrapped air near elimination (Table 9.5 and Fig. 9.5), during chopping of the systems with added back fat under RAP. Increase in scatter due to air entrapment is largely outweighed by increase in scatter due to back fat addition.

For systems without added back fat, however, the previously established entrapped air induced scatter (see Chapter 7) can be witnessed. Further, for the AAP condition of these formulations (treatments AAAP and BAAP) a better insight into the effect of entrapped air can be obtained from the examination of the relevant air parameters. The percent entrapped air is somewhat higher for formulation B (Table 9.5). The values of NB at the end of chopping are similar (Fig. 9.5) but the proportion of bubbles in the size class $< 50 \mu\text{m}$ is much higher for formulation A (Fig. 9.6). It may be speculated that this difference in the BSD is due to viscosity differences between these systems (Prins, 1988). As stated previously, it is very likely that the determined percent entrapped air values can be markedly affected by the existence of air bubbles which are much larger than those affecting the scattering properties of the batters. Accordingly, we think that the difference between the percent entrapped air of these systems has small bearing on the L^* values obtained at the end of chopping. Thus, the similar L^* values for both systems at the end of chopping can be explained by: (1) The similar NB values. (2) Higher translucence of formulation B that counteracts the effect of the higher proportion of small bubbles in formulation A.

Phase 2. In a previous part of the study (Chapter 7) we have shown that the decrease in L^* shortly after chopping can be attributed to the disproportionation process between the entrapped air bubbles. Accordingly, the much faster decrease in L^* for the AAAP treatment versus that of the BAAP treatment can be explained by the large difference in their BSD at the end of chopping (the driving force for disproportionation is higher for smaller bubbles).

In cooked batters without added back fat, the increase in scatter induced by the massive denaturation of muscle proteins induces the dramatic increase in L^*

compared to the corresponding L^* values of the raw batters (Fig. 9.2; Table 9.4). In formulations with back fat addition, however, this effect of muscle protein denaturation, is masked by the already high scatter due to back fat. In formulations without added back fat this protein denaturation completely masks the air pressure effect observed for the raw batters (Fig. 9.2).

Hue angle

Phase 1. The augmenting effect of chopping under RAP on the difference between the h^* values, at the end of chopping and shortly afterwards, of systems with and without added back fat (Fig. 9.3) can be explained as follows: It is well established that the h^* value of raw meat will change with corresponding changes in the Mb concentration and its form (MacDougall, 1982, 1986; Palombo and Wijngaards, 1989a,b). In systems chopped under RAP, both MMb and NOMb are formed during chopping. Conversely, in systems chopped under AAP, MMb is the predominant form produced during chopping (MacDougall et al., 1975). MMb has markedly different reflectance spectrum compared to that of NOMb (Palombo and Wijngaards, 1989a). As demonstrated by MacDougall (1984, 1986) dilution of a system in which the predominant pigment is NOMb causes a large increase in its h^* value. Consequently, it is suggested that the observation that dilution with back fat of the systems chopped under AAP versus systems chopped under RAP results in a larger increase in h^* for the latter can be explained by the difference in the pigments state of both systems (further experiments are planned to confirm this hypothesis).

Phase 2. The effect of dilution with back fat of meat batters containing the NOMb, on their h^* can also be used to explain the larger differences between the h^* values of systems with and without added back fat for the batters chopped under RAP.

Finally, it should be noted that for both phases the superiority of the effect of added back fat over that of added water would have also been obtained when identical percentage of each component (fat and water) were compared (MacDougall, 1984).

In the cooked batters the dilutive effect of added back fat seen in the raw batters persists, but since the cooked meat is opaque (i.e., its S (see K-M analysis; Section 7.2.2) is higher), it is much smaller. Within each formulation the effect of air pressure observed in the raw batters (Fig. 9.3) still exists but is largely reduced (Table 9.4) due to the fact that nitrite was added in excess for the production of cured meat color (see also Palombo and Wijngaards, 1989b).

Chroma

phase 1. Contrary to the behavior of h^* , the difference between the C^* values at the end of chopping for batters with and batters without added back fat diminished due to chopping under RAP (Fig. 9.4). A possible explanation for this finding is the documented observation that C^* is far more affected by changes in scatter than by changes in pigmentation (MacDougall, 1982, 1986). This explanation is supported by the fact that the above mentioned difference diminishes for chopping under RAP mainly due to the decrease in C^* value of the systems without added back fat and not due to changes in systems with added fat. As was also shown for L^* , and not for h^* , the systems without added back fat versus the systems with added back fat are much more affected by the air induced scatter. Hence, this higher sensitivity of systems without back fat to entrapped air induced scatter, can be taken as evidence for supporting this behavior of C^* .

Phase 2. The changes follow a similar pattern to the one observed for h^* and the same line of reasoning can be used to interpret them. The similar behavior to that of h^* is expected since the effect of scatter due to entrapped air is greatly reduced at this phase (see Chapter 7).

The results of the cooked batters C^* pertaining the effect of formulation (Table 9.4) can be explained using the same reasoning employed for explaining the corresponding h^* results.

Summarizing, this study provided clear evidence for the profound interactive effects of air pressure during chopping and formulation on the behavior of color and entrapped air of meat batters during processing and subsequent storage at 15°C. For phase 1, changes in L^* were dramatically affected by back fat addition and, to a much smaller extent, by water addition. These results were in principal agreement with findings reported by MacDougall and Allen (1984) for meat homogenates. Some explanation for the behavior of L^* in formulations without added back fat and chopped under AAP, was offered by referring to the corresponding changes in several air parameters, i.e., percent air, NB and BSD. Changes in h^* and C^* , due to back fat addition, could essentially be explained by referring to the relative effect of absorption (due to the balance between the relative concentration of MMb and NOMb) and scatter (due to entrapped air) respectively.

For phase 2, the behavior of L^* , shortly after the end of chopping, could be explained by referring to the behavior of the air parameters only for systems without

added back fat. For h^* and C^* , for all four formulations, similar effects of air pressure and formulation were observed. Reduced air pressure increased the rate of changes ultimately leading to h^* and C^* values characteristic to NOMb. Back fat addition imposed a tremendous and consistent diluting effect on both color attributes, i.e., an increase in h^* and a decrease in C^* . For all color attributes, due to the extreme increase in scatter caused by back fat addition, batters with and without it could be easily distinguished all along the storage period at 15°C.

The latter finding also hold for the cooked batters but its magnitude was much smaller. For L^* and C^* and to a lesser extent for h^* , the effect of air pressure observed within each formulation of the raw batters almost disappeared in the cooked batter.

9.3.2 Rheological and fracture properties

9.3.2.1 Results

Viscoelastic properties

A typical pattern of a force-deformation curve obtained for the ARAP treatment is presented in Fig. 9.7a. This concave upwards shape was obtained for all treatments. According to Peleg (1987), such a pattern is commonly observed for solid foods. A convex upwards shaped curve will only be obtained when the internal fracture overwhelmingly outweighs the contribution of the increase in contact surface area between specimen and plates, strain and strain rate (Calzada and Peleg, 1978). As can be seen in Fig. 9.7b, the true stress-strain plot (of the same data set) is characterized by a linear region which is followed by a short convex downwards part near the point of failure. This pattern was obtained for batters from all treatments.

The rather long linear region can be interpreted in two ways: One is that the sample is essentially linearly elastic up to a large deformation. The other is that internal local fracture processes, which cause a decrease in the strength of the material, are compensated by structural yielding and friction processes which cause an increase in strength (Johnson et al., 1980; van Vliet et al., 1990). Since we could observe small local fractures at higher strains along this linear region, we suggest that the second interpretation is more suitable for the behavior of the cooked meat batters. Along the subsequent convex downwards phase, even bigger local fracture could be observed suggesting that fracture processes became dominant and indeed

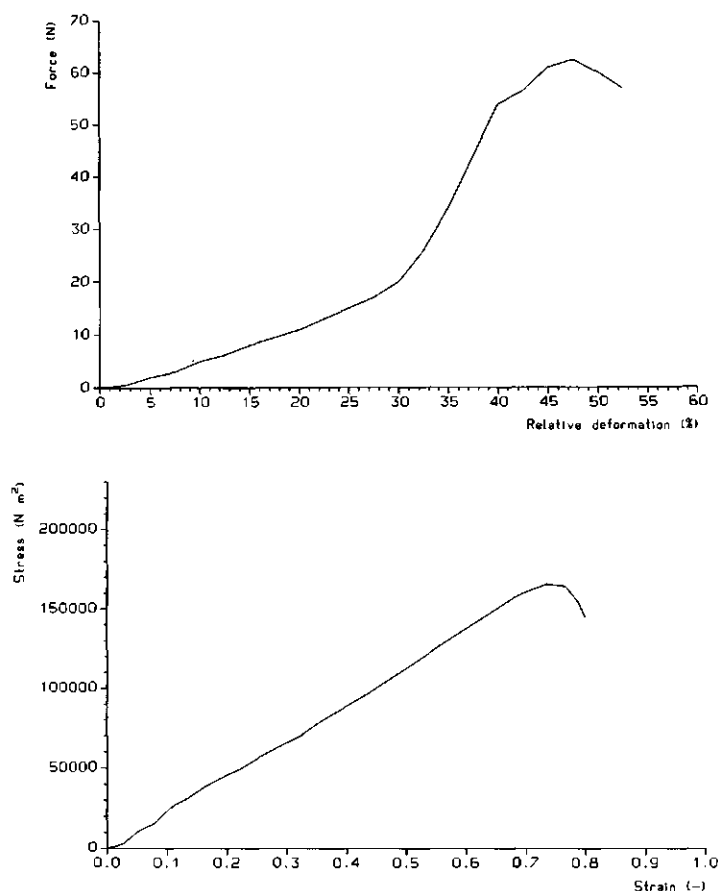


Fig. 9.7: Force - Relative Deformation curve (a) and true strain-stress curve (b) during uniaxial compression test for the same sample. Cooked batter from ARAP treatment; constant compression rate (V), 50 mm min^{-1} .

ultimately led to a gross disintegration of the specimen at the point of maximum stress.

Independent of the treatment, all samples fractured in shear at around 45° to their core axis. This is in agreement with observations on the failure of wiener sausages during compression (Voisey et al., 1975). Basically, this finding shows that in a sample which is compressed uniaxially also shear stresses will be developed which is in agreement with theory (Luyten, 1988). Further, it may be concluded that the magnitude of these shear forces is higher than that of the shear strength of the material and that the material is not very sensitive to the tension stresses which will

also be present in it during uniaxial compression (Luyten, 1988).

The dependency of the mechanical behavior on the deformation rate is shown in Fig. 9.8 for a sample from ARAP treatment. As the deformation rate increases, the slope of the plot and the fracture stress increase. The fracture strain, however, is similar for all rates of deformation. One of the main characteristics of a viscoelastic material is that the stresses developed during compression depend not only on the strain, but also on the strain rate. Generally speaking, the higher the rate of strain the higher the stresses (Luyten, 1988). Our finding indicates that the cooked meat batters are viscoelastic. This is in agreement with several other reports on cooked sausages (Voisey et al., 1975; Calzada and Peleg, 1978; Siripurapu et al., 1987; Payne and Rizvi, 1988).

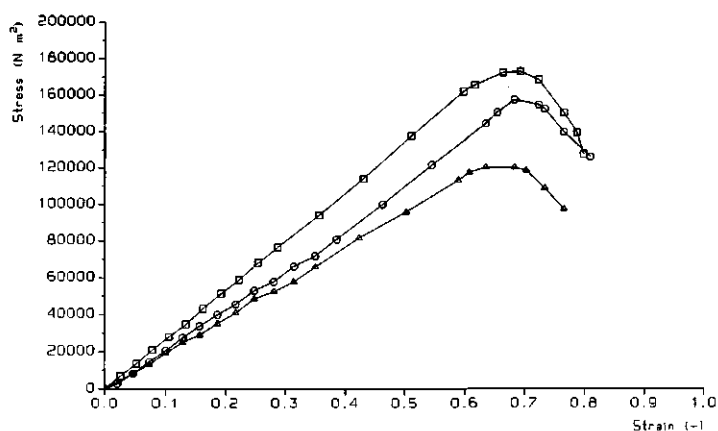


Fig. 9.8 : True stress - strain curves from compression tests performed at constant compression rate of 0.5 (Δ - Δ), 5.0 (\circ - \circ) and 50 (\square - \square) mm min⁻¹ for cooked meat batter from ARAP treatment.

Effect of air pressure during chopping and of formulation

The cooked meat batters may be considered as rigid coagulated protein gels with fat particles dispersed in them. The gel forming proteins build a continuous network which is the main component responsible for the firmness or rigidity of the batters (Acton et al., 1983; Hermansson, 1986; Smith, 1988). Thus, their rheological behavior can be considered as that of a composite material in which water interacts with the matrix proteins and thus decreases the rigidity of the matrix, and fat particles act as a filler (A distinction should be made between the meaning of this

term and that of an identical term used to describe a group of non-meat materials (e.g., wheat flour, corn starch etc.) which are added to improve the water binding capacity of cooked sausages). The entrapped air bubbles can also be considered as a filler component. Following this suggested concept, it is very likely that the air fraction entrapped within the meat batters, as well as the formulation of the latter, will have an important impact on the rheological properties of the cooked meat batters at small and large deformations (Luyten, 1988; van Vliet, 1988). The effects of air pressure during chopping and of formulation were both studied at small and large deformations at a rather high compression rate i.e. 50 mm min^{-1} (A higher rate was avoided because of possible errors due to the recorder pen response). As described in Section 9.2, only the treatments AAAP and ARAP were replicated. This fact hampered a reliable statistical analysis of the results. Accordingly, we will only compare the means of the different treatments. The scatter of the individual results will be indicated by the SD of these means.

Effects at small deformations: For all formulations, chopping under RAP caused an increase in E_d (Table 9.6). This increase appears to have a similar magnitude (defined as the difference between the means for RAP and AAP) for all formulations. The effect of formulation can better be checked by the comparisons between the batters chopped under RAP. Addition of 15% water versus addition of

Table 9.6: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the modulus of deformability E_d (10^5 N m^{-2}). Values are Means \pm SD ($n = 10$)

<u>Air pressure</u>	<u>Formulation</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
AAP	2.35 \pm 0.18	1.47 \pm 0.09	1.71 \pm 0.09	1.17 \pm 0.11
RAP	2.64 \pm 0.23	1.61 \pm 0.18	1.97 \pm 0.23	1.46 \pm 0.21
RAP - AAP	0.29	0.14	0.26	0.29

30% back fat causes a higher decrease in E_d . Addition of both causes the largest decrease in E_d . These findings are qualitatively in agreement with corresponding results obtained with empirical rheological methods reported in literature (see Section 9.1.2).

It is worthy of note that the values of the SD for all the calculated means are rather high. In addition to a high inherent variability between specimens this may also be due to the fact that the ends of the cylindrical specimens, were not completely smooth.

Effects at large deformations: Results for the σ_f , ϵ_f and aR are presented in tables 7, 8 and 9 respectively. For all formulations, chopping under RAP induces an increase in the values of σ_f and aR. The magnitude of these increases is lower for batters with added back fat. Moreover, chopping under RAP induces an increase in the values of ϵ_f only for formulations without added back fat (A and B). The effect of air pressure during chopping is always the largest for formulation B.

Generally speaking, addition of water or back fat causes a decrease in all three parameters. Additions of both water and back fat results in the lowest values.

Table 9.7: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the stress at fracture σ_f (10^5 N m^{-2}). Values are Means \pm SD ($n = 10$)

<u>Air pressure</u>	Formulation			
	A	B	C	D
AAP	1.50 \pm 0.19	0.99 \pm 0.07	0.98 \pm 0.10	0.83 \pm 0.09
RAP	1.77 \pm 0.28	1.44 \pm 0.13	1.12 \pm 0.13	0.93 \pm 0.11
RAP - AAP	0.27	0.45	0.14	0.10

Table 9.8: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the strain at fracture ϵ_f (-). Values are Means \pm SD (n = 10)

<u>Air pressure</u>	<u>Formulation</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
AAP	0.69 \pm 0.04	0.66 \pm 0.06	0.58 \pm 0.03	0.62 \pm 0.05
RAP	0.79 \pm 0.06	0.83 \pm 0.07	0.57 \pm 0.04	0.58 \pm 0.05
RAP - AAP	0.10	0.27	-0.01	-0.04

Table 9.9: Influence of air pressure during chopping (AAP; RAP) and of formulation (A-D) on the apparent toughness aR (10^5 J m $^{-3}$). Values are Means \pm SD (n = 10)

<u>Air pressure</u>	<u>Formulation</u>			
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>
AAP	5.97 \pm 0.99	3.93 \pm 0.61	3.44 \pm 0.28	2.76 \pm 0.41
RAP	7.57 \pm 1.43	6.52 \pm 1.06	3.64 \pm 0.61	2.87 \pm 0.44
RAP - AAP	1.6	2.59	0.20	0.11

9.3.2.2 Discussion

The literature review (Section 9.1.2) revealed no reports that used a similar approach to the one employed in this study on comminuted meat systems. Consequently, the analysis and discussion of the results are mainly based on known concepts or theories pertaining to gel systems and cheese which are treated as composite materials (Luyten, 1988; van Vliet, 1988).

Effects at small deformations (E_d): Depending on the rheological properties of the filler and the matrix, two extreme cases can be distinguished at small deformations:

(1) An interaction between the filler and the matrix exists. In this case the modulus of the composite material increases with increasing volume fraction of the filler given that the filler has a higher modulus than that of the matrix. It decreases if the filler modulus is lower than the matrix modulus.

(2) No interaction between filler and matrix exists. In this case an increase in the volume fraction of the filler always induces a decrease in the modulus of the composite material. The reason for this is that in a material containing such a filler, during deformation of a certain volume of the specimen, a smaller volume of the matrix has to be deformed thus resulting in a larger deformation of that matrix.

In the cooked meat batters, both entrapped air bubbles and fat particles can be associated with the first case. However, the modulus of these fillers differ strongly. That of air is effectively zero, and that of fat is obviously much higher.

Filled gels are a kind of composite materials that may be considered as a model for cooked meat batters. The small but consistent decrease in E_d induced by the entrapped air bubbles (Table 9.6) is, in view of the experimental inaccuracy, in good agreement with the theoretically predicted effect of 8-15%, for a volume fraction of air of 5-9% (Table 9.5) on the modulus of filled gels (van Vliet, 1988).

According to the theory of composite materials, the proteinaceous matrix is suggested to be the main stress carrying component of the cooked meat batters. The addition of water, which implies lowering the protein concentration, renders it less stiff. The decrease in E_d on water addition is in agreement with this mechanism.

The effect of back fat addition is more complex, since the modulus of the fat depends mainly on the temperature at which the measurement is done. Generally, the lower the temperature the larger is the proportion of fat in a crystalline state and the higher is its modulus. Since no measurements of the fat modulus were done

we can only speculate over its real modulus and its influence on the modulus of the composite. At the temperature at which the measurements were performed (15°C) a part of the fat was already in a liquid state (Acton et al., 1983). Accordingly, the observed decrease in the E_d due to back fat addition is suggested to be due to its lower actual modulus compared with that of the matrix. Further, the observation that the lowest value for E_d is obtained when both, water and fat, are added (formulation D) is in agreement with the above discussion.

Effects at large deformations: One of the main factors affecting the fracture properties of food systems is the degree of their inherent inhomogeneity, i.e., the stress concentrations caused by the dimensions and shape of the internal defects (Peleg, 1987). Accordingly, if filler particles contribute to defects that induce higher stress and strain concentrations than those produced by the inherent defects of the matrix, a decrease in the values of the fracture parameters i.e. σ_f , ϵ_f and aR of the composite is expected.

Orders of magnitude for maximum defect size, contributed by the various components of the cooked meat batters, are presented in Table 9.10. The

Table 9.10: Order of magnitude for maximum defects sizes in the meat batters

<u>Component</u>	<u>Scale (mm)</u>
PLM	< 0.5
PBF	2-3
Air	4-6

observation that except, for ϵ_f of formulations with added back fat (C and D), the values of σ_f , ϵ_f and aR were smaller for a higher level of entrapped air (Table 9.5) can be explained by the contribution of the latter to the defect size distribution of the final batters. Tables 9.7 - 9.9 also show that for formulations with added back fat, the effect of reducing the level of entrapped air is smaller than for formulations without added back fat. Possibly, this is due to the larger defects already present in

the former formulations due to the added back fat. This suggested explanation is substantiated by checking the effect of formulation for the batters chopped under RAP. Back fat addition causes a decrease of all 3 fracture parameters. The markedly larger effect of entrapped air on formulation B versus formulation A can be explained by the corresponding results of the percent entrapped air (Table 9.5), i.e., chopping under RAP resulted in a larger decrease in air content for formulation B.

Finally, it should be recognized that in this study we used only compression tests. Due to the viscoelastic character of these batters and the nature of this test (possible side effects due to friction and other energy dissipating processes), the determined parameters supply only partial and limited information over the real rheological and fracture properties of the cooked batters, as well as on the effect of air pressure and meat batter formulation. Together with the limited extent of the experimental evidence obtained from this study, it explains the phenomenological nature of the analysis and discussion. To this end, extending the investigation to include other rheological tests (e.g. tension, bending and cutting) can supply better understanding of the effects of the factors studied.

Summarizing, evidence for the viscoelastic nature of the studied cooked meat batters were provided. The composite material theory was used as basis for the analysis of the effect of air pressure during chopping and the effect of formulation on the rheological and fracture properties of these model products. It was possible to pinpoint and to qualitatively explain several distinct effects of the two factors. At small deformations a higher level of entrapped air induced a decrease in the modulus of deformability, independent of the formulation. The magnitude of this decrease was roughly in agreement with that predicted from existing theory. Water addition caused a decrease in the modulus. This was explained by weakening of the proteinaceous network through dilution. Addition of back fat decreased the modulus. This effect could not be fully explained because of lack of experimental evidence regarding the mechanical properties of the back fat. At large deformations, addition of back fat induced a decrease in all three studied fracture parameters. Entrapped air caused a decrease in σ_f and aR and, only for batters without added back fat, also a decrease in ϵ_f . An explanation for these results was offered by referring to the relative contribution of entrapped air and back fat to the size distribution of the defects in the cooked batters.

9.4 Summary

In this study we examined the effect of two factors, i.e., air pressure during chopping and formulation on the color, rheology and fracture of four meat batter systems.

Pertaining to the behavior of color of the raw batters, the following main effects of the two factors were observed. Generally speaking, entrapped air, independent on the formulation, was found to almost consistently cause higher L^* and h^* and lower C^* . The addition of water induced no or minor effect on the behavior of the color attributes. Fat addition, however, caused a large increase in L^* and h^* and a moderate decrease in C^* . Adding of water and fat had a similar effect as that of only back fat addition.

Basically, the effect of air pressure could be explained on the basis of results obtained for PLMBs during previous stages of this project (Palombo and Wijngaards, 1989a,b; Chapter 7). Essentially, this effect was explained by referring to the changes in balance between the absorption and scattering properties of the batters. The observed tremendous effect of formulation was in agreement with results reported in the literature (MacDougall and Allen, 1984). It could mainly be explained by referring to the relative contribution of added water and back fat to the scattering properties of the meat batters.

Different from previous reports in literature (Section 9.1.1), the continuous monitoring of color changes and the experimental design employed in this study, allow a deeper insight into the interesting interaction between the effect of the two factors. Since in this study, for the formulation factor, water addition versus back fat addition had a minor effect on color, we will mainly refer to the effect of back fat addition. The following interacting effects of the two factors namely, entrapped air and addition of back fat were disclosed.

Phase 1. For all three color attributes L^* , h^* , and C^* a clear interaction between the effects of the air pressure and formulation was demonstrated, i.e., the extent of air pressure effect was highly dependent on the addition of back fat. For L^* and C^* this interaction could be explained by referring to scattering induced effects (entrapped air and back fat addition). For h^* , this interactive effect could be explained on the basis of absorption induced changes (the balance between the relative concentrations of MMb and NOMb). Additionally, the behavior of L^* during

chopping and shortly after it, in batters without added back fat and chopped under RAP, could be explained by the behavior of the entrapped air parameters.

Phase 2. For L^* , shortly after the end of chopping, an interaction between the effects of air pressure and formulation was detected. From then the two factors affected L^* in an independent manner. For h^* and C^* no interaction could be detected. A possible explanation for this predominantly non-interacting behavior at this phase could be inferred from the previous finding (Chapter 7) that for L^* , and most likely also for h^* and C^* , the effect of changes in absorption are dominant over the effect of changes in scatter.

For the cooked meat batters, independent of formulation, except for a small effect on h^* , no effect of air pressure could be detected. A detailed quantitative comparison with corresponding results presented in the literature (see Section 9.1.1), could not be made for several reasons: Different de-aeration procedures, different levels of sodium nitrite and, different color measuring systems. However, globally the lower h^* values obtained for chopping under RAP were in agreement with most of the results reported in the literature. The results for L^* and C^* failed to support the latter. The effect of formulation was essentially similar to the one observed in the raw batters, but had markedly lower magnitude than the latter. Both findings could be satisfactorily explained by the masking action of the dramatically high protein denaturation induced scatter.

Measurements of mechanical properties were performed only on the cooked batters. Evidence for their viscoelastic character were provided. In order to interpret the results, obtained during small and large deformations, the cooked batters were considered as composite materials. Water was assumed to affect the mechanical properties through dilution of the protein concentration of the matrix. Fat and entrapped air were considered as interacting fillers. At small deformations addition of water, back fat and air caused a decrease in the modulus of deformability. The magnitude of the effect of entrapped air was approximately predicted by an existing theory for filled gels. The latter could be considered as a model for the cooked batters. The effect of back fat could not be fully explained on the basis of the results obtained.

At large deformations, added back fat caused a decrease in the three fracture parameters (σ_f , ϵ_f and aR) independent on the entrapped air. However, entrapped air in systems with addition of back fat versus systems without back fat addition

induced a smaller decrease in σ_f and aR and no decrease in ϵ_f . These findings could be explained on the basis of the relative contribution of each of the components to the defect size distribution and to the corresponding stress concentrations within the cooked batters.

10. SUMMARY AND CONCLUSIONS

The aim of this study was twofold (Chapter 1):

- (1) To characterize, analyze and predict changes in color of porcine lean meat batters (PLMBs) during processing using graphical analysis, empirical kinetic analysis, and empirical mathematical modeling respectively (part 1).
- (2) To acquire fundamental and systematic knowledge pertaining to the changes in color and related structural properties of porcine batters during processing using a mechanistic approach (part 2).

Based on this division summary and conclusions are presented separately for each part. They are followed by some final comments concerning both parts.

Part 1

In Chapter 2 a theoretical background regarding to color theory, cured meat color, and kinetic analysis and mathematical modeling of food processes was given.

Chapter 3 described the influence of temperature, nitrite, and air pressure during chopping on changes in color of PLMBs during processing. The study employed the psychometric color attributes lightness (L^*), hue angle (h^*), and chroma (C^*).

The main findings from this investigation were:

- (1) L^* and C^* , but not h^* , showed a clear dependence of their course of changes (as a function of time) on temperature. This dependence was demonstrated to be much more complex for C^* than for L^* .
- (2) Nitrite was shown to affect dramatically the course of changes in h^* and C^* , but much less so in L^* .

(3) Air pressure during comminution, had no detectable effect on the course of changes of the three color attributes. Contrary to the mentioned effect of nitrite, however, it caused remarkable differences in the absolute values and magnitude of changes in L^* , and to a smaller extent in h^* and C^* .

The main conclusions from this study were:

- (1) Changes in lightness, and to some degree changes in chroma, could essentially be related to changes in physical characteristics, such as protein denaturation and entrapment of air, of the meat system .
- (2) Changes in hue and chroma were primarily associated with chemical and biochemical reactions related to the state of the pigmentation (mainly myoglobin (Mb)).
- (3) The results obtained could serve as a basis for a possible application of the psychometric color attributes, as useful and indicative working parameters for a quantitative kinetic analysis and mathematical modeling of the effects of processing factors during the production of comminuted-cured-porcine-lean-meats.

In Chapter 4 changes in L^* , h^* , and C^* of PLMBs during processing were kinetically analyzed using the empirical approach of mathematical modeling. Alterations during 24 h storage at 15°C were successfully fitted into a modified first order model and analyzed for the effects of air pressure during chopping, cutter type, and enzyme inhibitors. Such kinetic analysis for changes at 40°C, 50°C, and 60°C was possible for h^* but not for L^* and C^* .

The main findings of this investigation were:

- (1) Among the factors studied, "air pressure" had the greatest overall effect on color. The effect of "cutter type" was intermediate and that of "enzyme inhibitors" least.
- (2) For changes in h^* during heating, chopping under reduced air pressure (RAP) versus chopping under atmospheric air pressure (AAP) induced a large and significant ($p < 0.05$) increase in the derived energy of activation (E_a).
- (3) A clear and mostly significant treatment-temperature interaction (A treatment was a level of a factor, e.g., AAP and RAP were levels of the factor "air pressure".) was found for the color values at the end of heating. Higher cooking temperature lowered for L^* and C^* and caused an increase for h^* .

The main conclusions from this investigation were:

- (1) It was speculated that the similarity between the kinetics of chemically determined denatured nitric oxide Mb (DNOMb) formation in frankfurter batters

during storage at 38°C, as reported by Fox et al. (1967), and the successful description of changes in h^* during storage at 40°C by a modified first order model (this study), supplied a theoretical basis for the adequacy of the latter for analysis.

(2) The treatment-temperature interactions found were proposed to be of importance when one considered the effect of the process factors studied on the color of comminuted-cured-cooked-meat-products (CCCMP). Hence, after a thermal treatment, say pasteurization, the effects of processing variables, similar to those checked here, were expected to persist for h^* and much less so for L^* and C^* .

(3) The significant increasing effect of chopping under RAP on the derived E_a values for h^* , could be ascribed to a shift in the balance between the effect of changes in absorption and scatter properties of the meat batters on the measured h^* .

(4) A useful application of this research could be to use the predictive techniques of mathematical modeling to predict intermediate and end-point color values during the processing of comminuted lean meats.

In Chapter 5 a mathematical model for the prediction of L^* values of a PLMB during heating was constructed using kinetic data collected from process temperatures of 50°C, 60°C, 80°C, and 100°C. The heating times were up to 3 h. Intermediate and end point values of lightness could be predicted reasonably well for time-temperature combinations within the range used for the construction of the model. Basically, a similar predictive model could have been built also for h^* , but not for C^* .

Generally, thermal denaturation of proteins had been shown to follow a first order kinetics (Labuza, 1980). Jenkins (1984) showed that an increase in the opacity of cured bacon during cooking was directly related to the denaturation of the muscle proteins. Further, an increase in opacity was found to account for a parallel increase in lightness of the bacon. This information supported the successful description of changes in L^* during heating by a modified first order equation.

Part 2

In Chapter 6 a short introduction presenting the rationale of the mechanistic approach, employed in this part of the study, was given.

Chapter 7 reported a mechanistic study aimed at the elucidation of the

importance of some physical and chemical events in explaining changes in L^* of PLMBs during processing and subsequent storage at 15°C. Two distinguishable phases for the changes in L^* were studied:

Phase (1): An increase during the chopping stage.

Phase (2): A decrease approximating to a plateau, which takes place during the period between "end of chopping" and "24 h".

A working model for the individual effect of several relevant physical and chemical events on the overall changes observed in L^* during the two phases was constructed. This working model was based on theoretical considerations.

Three factors were investigated:

- (1) Absorption traits of the PLMBs;
- (2) Salt and phosphate;
- (3) Entrapped air.

The main findings from this research were:

- (1) Transitions in the absorption traits of the PLMBs were shown to have a large impact on changes in their L^* during phase 2.
- (2) The effect of transitions induced by the presence of salt and phosphate was found to be of low relevance in explaining the behavior of L^* during phase 2.
- (3) The behavior of L^* of PLMBs during phase 1 could, to a large extent, be explained by changes in parameters related to the air entrapped in them. In addition, the results obtained suggested that any effect of a possible irreversible surface coagulation of meat proteins on changes in L^* , during phase 1, was likely to be very small.
- (4) Strong evidence for the occurrence of disproportionation between air bubbles entrapped within PLMBs were provided. However, any effect of this process on the behavior of L^* during phase 2 was restricted to a short period right after the end of chopping.

The main conclusions from this investigation were:

- (1) The entrapment and subsequent size reduction of air bubbles in the PLMB were the main events responsible for the increase in L^* during phase 1.
- (2) The balance between the effects of disproportionation and of the chemical reactions leading to the formation of metmyoglobin (MMb) on L^* could be used to explain its behavior during the period between end of chopping and about 60 min.
- (3) Changes in the absorption traits of the PLMBs were the main events responsible for the subsequent gradual decrease in L^* during phase 2.

(4) In Palombo and Wijngaards (1989a), under the "Temperature effect", it was suggested that the finding that L^* values at 30°C and 40°C were lower than the values obtained at 15°C, during phase 2, could be explained by the increase in translucency of the batter attributable to the action of salt and phosphate. The findings described in this chapter rendered this proposed mechanism invalid.

Based on the findings described in this chapter, it was possible to provide some mechanistic explanation for the marked effect of air pressure during chopping on changes in L^* during phase 2 and the corresponding phases at 30°C and 40°C. The same explanation was applied also to the corresponding changes in the derived E_a values. The markedly higher rate of decrease in L^* in batters chopped under RAP versus batters chopped under AAP, could be explained by the balance between the relative contribution of disproportionation and of the formation of NOMb to the overall changes in L^* . A hypothesis for explaining the higher E_a obtained for batters chopped under RAP versus batters chopped under AAP was proposed. It was based on the assumption that the reaction responsible for the formation of NOMb versus the disproportionation process have a higher E_a and that under RAP condition the reaction with the higher E_a controls.

Finally, it should be stressed that based on this study, the major effect of entrapped air on the behavior of L^* is only valid for PLMBs as used here. In Chapter 9 we checked the existence of such an effect in more commercially oriented formulations.

Chapter 8 reported results of a study on the influence of surface rheological properties of PLMBs on the behavior of entrapped air bubbles during phase 2 and on the behavior of their L^* .

The main findings and conclusions from this investigation were:

- (1) The existence of a finite apparent surface dilational viscosity ($a\eta_s$) was demonstrated by comparing between the calculated (using De Vries Eq.) and the measured (using a stereomicroscope) radius vs. time plots for individual bubbles.
- (2) Evidence for the viscoelastic character of the surface of the PLMB dispersions were provided using a single compression test. Further, the surface behavior could be classified as "shear thinning", i.e., the higher the relative compression rate the lower the value of $a\eta_s$.
- (3) An emulsifier, glycerol lacto palmitate (GLP), caused a considerable increase in the $a\eta_s$ of the PLMB dispersions, that was, their surface became stiffer. It was also

shown to decelerate the rate of shrinkage of individual medium-size (about 50 μm) bubbles. This finding was taken as evidence for supporting our working hypothesis, stating that dynamic surface rheological properties of the PLMBs influence the behavior, during phase 2, of the air bubbles entrapped in them.

(4) PLMB containing GLP (+GLP system) versus PLMB not containing GLP (-GLP system) had, at the end of chopping, markedly higher values for the "number of bubbles per field of view" (NB), higher proportion of bubbles in the size class $< 50 \mu\text{m}$ and higher L^* value. Conversely, during phase 2, similar behavior could be observed in both systems for the three parameters.

(5) An apparent discrepancy between the definite effect of GLP on the behavior of individual air bubbles, and its minor effect on the behavior of the bubble parameters, NB and "bubbles size distribution" (BSD) was established. An explanation for it was provided based on the wide range of bubble sizes at the end of chopping in combination with the "shear-thinning" character of the surface of the PLMB dispersions.

(6) The behavior of NB and BSD, but not of percent entrapped air, during the first stage of phase 2 (until about 40 min) could be used to explain the corresponding dramatically higher L^* value for the +GLP system. This result was in accordance with results found in Chapter 7. Conversely, de-aeration experiments indicated that the continuously higher L^* for the +GLP system during phase 2, could not be attributed to the behavior of the entrapped air fraction. Further research is needed in order to explore the cause for this observation. One may speculate, however, that GLP stabilized entrapped microbubbles (D'Arrigo, 1986) which were not affected by the applied de-aeration treatment.

(7) The established "shear-thinning" nature of the surface of the PLMB dispersions, may be used to provide some explanation for the consistent principal pattern of changes in NB and BSD during phase 2. Due to high Laplace pressure within very small bubbles and the "shear thinning" character of the surface of the PLMBs they disproportionate relatively fast in spite of the high rate of surface compression. Conversely, bigger bubbles persisted relatively longer. Indeed, shortly after the end of chopping sharp decrease in NB values and a large increase in the values of the median of the BSD histograms was always observed. Thereafter, the NB and the median of BSD remained almost constant until 24 h.

Chapter 9 presented the results of a study on the effect of two factors on the

color, rheology and fracture of some meat batter systems. One factor was "air pressure during chopping" and the other one "formulation". The former had two levels: (1) AAP, and (2) RAP, and the latter had four levels: (1) 100% porcine lean meat (PLM), (2) 85% PLM and 15% water, (3) 70% PLM and 30% porcine back fat (PBF), and (4) 60% PLM, 30% PBF, and 10% water. Changes in color were examined in both raw and cooked batters. Changes in mechanical properties were examined only in cooked batters. Contrary to previous research in this field, here the aim was to gain fundamental and systematic knowledge pertinent to the abovementioned effects. Accordingly, the study included a time dependent monitoring of color changes, and the use of a fundamental rheological test.

The findings and conclusions from this investigation were:

Color:

(1) Large effects of the two studied factors on changes in color during processing and subsequent storage at 15°C were observed. Generally speaking, entrapped air was found to almost consistently cause higher L^* and h^* , and lower C^* values. The addition of water induced no or a minor effect on the behavior of the color attributes. PBF addition, however, caused a large increase in L^* and h^* and a moderate decrease in C^* . Addition of water and fat had a similar effect as that of only PBF addition. Essentially, the effect of air pressure was explained by referring to the changes in the dynamic balance between the absorption and scattering properties of the batters. The effect of formulation could be explained by referring to the relative contribution of added water and PBF to the scattering properties of the meat batters.

(2) The experimental procedure in combination with the experimental design used in this investigation allowed a deeper insight into the interactive effects of the two factors on the color of the raw batters.

During phase 1 (i.e., chopping stage) a clear interaction between the effect of added PBF and the effect of entrapped air was observed. For L^* and h^* the effect of added PBF was larger in batters chopped under RAP. Conversely, for C^* its effect was larger in batters chopped under AAP. The findings for L^* and C^* could be explained by referring to scattering induced changes. For h^* absorption induced changes could be used to explain the results during phase 2 (i.e., storage at 15°C from "end of chopping" until "24 h"), a mostly non-interacting behavior was found for all three color attributes. This could be explained on the basis of previous findings (Chapter 7) indicating that along this phase the effect of transitions in absorption

traits of the PLMBs was dominant over the effect of transitions in scatter.

(3) The behavior of L^* , in raw batters without added PBF and chopped under AAP, during phase 1 and shortly afterward could be explained by the corresponding behavior of the entrapped air parameters NB and BSD. Owing to the immense scattering properties of the added PBF such an explanation could not be provided for batters containing it. Hence, the big effects of entrapped air in batters without added fat (shown also in Chapter 7) were largely outweighed by the scatter of added PBF.

(4) The color of the cooked batters versus that of raw batters was far less affected by the two factors. The reason for this smaller magnitude was the high opacity of the cooked batters.

Except for small effects on h^* , the color of the cooked batters was not affected by the air pressure during chopping. Conflicting reports in the literature, as to the magnitude of the effect of RAP during comminution on the color of frankfurters, had been mentioned in Section 9.1. The present results supported studies reporting small positive effect on the color of the final product. Further detailed comparison between the different studies was not possible owing to the large variation in the experimental procedure and the color measurement technique.

Essentially, the effect of formulation on the color of the cooked batters was similar to that reported for the raw batters.

Rheological and fracture properties:

In the first stage of this investigation some evidence for the viscoelastic behavior of the cooked batters were presented. A qualitative explanation for the effects of the two studied factors on the measured rheological and fracture parameters was based on the "composite material" theory.

The main findings and conclusions from this investigation were:

- (1) Effects at small deformations: Entrapped air caused a decrease in the modulus of deformability (E_d) of the batters independent on their formulation. The magnitude of this effect was in agreement with that predicted by an existing theory for filled gels which could be considered as models for the cooked batters. Water addition caused a decrease in E_d . This finding could be explained by a dilutive effect of water on the proteinaceous matrix. PBF addition also caused a decrease in E_d . However, this effect could not be fully explained on the basis of the experimental evidence obtained in this study.
- (2) Effects at large deformations: The effect of entrapped air was dependent on the

addition of PBF. In batters without added PBF it caused a decrease in all fracture parameters, i.e., stress at fracture (σ_f), strain at fracture (ϵ_f), and apparent toughness (aR). In batters with added PBF it caused a decrease only in σ_f and aR. Further, this decrease was much smaller compared with the corresponding one in batters without PBF addition. Added PBF caused a decrease in all three parameters independent on the level of entrapped air. These findings could be explained on the basis of the relative contribution of each of the components (entrapped air and PBF) to the defect size distribution and to the corresponding stress concentrations within the cooked batters.

Part 1 and part 2 - final comments

Intentionally, the study is named "a model study". Most of the research has been performed on a model system comprising 100% PLM processed under a well defined and highly standardized experimental procedure. Only in Chapter 9 has the formulation been extended to include added PBF and added water. However, even then, the variation in the formulation was restricted to the levels of only PLM, PBF, and water. It is well established that other ingredients, commonly used in industrial formulations of CCCMP, like raw meats rich in connective tissue, starch, and blood have considerable influence on the quality marks studied. Hence, in comparison to commercial CCCMP, the batters used in Chapter 9 should still be referred to as model systems. In spite of these facts the present study contributes unique fundamental knowledge for systemizing and structuring the complex theme of CCCMP processing.

In the first part of the study kinetic analysis and modeling have been applied to color changes during the processing of PLMBs. Kinetic analysis has been shown to be a powerful tool of research for a reliable time dependent examination of the effects of various processing factors. Additionally, it has been shown to be useful in the detection and quantification of interactions between various process variables. Predictive models can save labor, time and energy during process control and production. To this end, this study contributes important knowledge for a better steering of CCCMP manufacturing. Failure in a final product's color can be avoided if the processor would have a predictive model for changes in a single color attribute during heating. This could be achieved by color measurement of the raw batter (zero time of heating) and adequate correction before the irreversible

transition to a cooked final product. The first step in approaching these possible applications in industrial manufacturing should include additional modeling work. To this end, models including the effect of the composition factor and other processing variables, beside time and temperature should be developed. The work pertaining to color reported in chapter 9 supplies basic knowledge for this purpose (i.e., incorporating of the composition factor into predictive models). An interesting future application of such modeling techniques, for achieving the goal of high color uniformity and quality, may be "in-line"-color-monitoring-sensors which are connected to computerized control systems possessing the data of predictive models for a meat product color.

In the second part of the study, the fundamental information regarding the air fraction of porcine meat batters has provided a better insight into the manner in which it influences the behavior of color, rheology, and fracture of the porcine meat batters. Distinct effects of entrapped air and formulation on rheological and fracture properties of the porcine batters have been revealed. The successful application of the "composite material" theory for the analysis of these effects offers a unique possibility of predicting the rheological and fracture behavior of CCCMP having untested formulation and produced under variable processing conditions.

It should be remembered, however, that such tests describe only part of the physical properties perceived during mastication of CCCMP. Sensory tests are necessary to make the link between the present findings and subjective appreciation.

In the light of this summary and conclusions the present study contributes to the trend in which the art of meat processing is increasingly becoming the science of meat processing.

SAMENVATTING EN CONCLUSIES

Hoofdstuk 1 beschrijft dat het doel van dit onderzoek bestaat uit twee onderdelen:

Deel 1: het karakteriseren, analyseren en voorspellen van kleurveranderingen van magere varkensvleesdegen (PLMBs) gedurende het bereidingsproces. Hierbij is respectievelijk gebruik gemaakt van grafische en empirisch kinetische analysemethoden en van empirische mathematische modellen.

Deel 2: het verkrijgen van fundamentele en systematische kennis omtrent kleurveranderingen en daarmee verbonden structuureigenschappen van varkensvleesdegen gedurende het bereidingsproces, waarbij van een mechanistische benaderingswijze wordt uitgegaan.

Deze samenvatting en de conclusies zijn, gebaseerd op deze tweedeling, voor elk onderdeel apart beschreven en wordt gevolgd door enkele algemene opmerkingen, die op beide onderdelen betrekking hebben.

Deel 1

Hoofdstuk 2 is gewijd aan de theoretische achtergrond met betrekking tot het meten en waarnemen van kleur in het algemeen, de kleur van vleeswaren in het bijzonder en daarnaast aan de achtergrond van de kinetische analyse en van het mathematisch modelleren van het bereidingsproces.

In hoofdstuk 3 wordt een beschrijving gegeven van experimenten die zijn uitgevoerd om de invloed die de temperatuur, de aanwezigheid van natriumnitriet en de luchtdruk tijdens het cutterproces hebben op de kleurveranderingen van PLMBs

tijdens de deegbereiding. De kleurveranderingen van het deeg gedurende de tijd werden vastgesteld met behulp van de psychometrische kleurparameters helderheid (lightness L^*), kleur (hue angle h^*) en kleurverzadiging (chroma C^*).

De belangrijkste resultaten van het onderzoek zijn:

- (1) L^* en C^* , in tegenstelling tot h^* , vertoonden een duidelijke temperatuurafhankelijkheid voor hun verloop met de tijd. Deze afhankelijkheid was voor C^* veel complexer dan voor L^* .
- (2) De toevoeging van natriumnitriet blijkt een zeer grote invloed te hebben op het verloop met de tijd van h^* en C^* en aanzienlijk minder op L^* .
- (3) De luchtdruk tijdens het cutterproces had geen meetbaar effect op het verloop van de curves van L^* , h^* en C^* tegen de cuttertijd. In tegenstelling tot het onder (2) genoemde effect van nitriet bleek de absolute waarde van de veranderingen in L^* echter groot te zijn, terwijl de waarden van de veranderingen voor h^* en C^* veel kleiner waren.

De belangrijkste conclusies van het vermelde onderzoek zijn:

- (1) De veranderingen in helderheid, en in geringere mate die in chroma, konden in essentie worden gerelateerd aan veranderingen van de fysische eigenschappen van het vleessysteem, zoals eiwitdenaturatie en het insluiten van lucht.
- (2) De gevonden veranderingen in kleur en kleurverzadiging moeten in eerste instantie worden verklaard met chemische en biochemische reacties die aan de toestand van het vleespigment (hoofdzakelijk myoglobine (Mb)) zijn gerelateerd.
- (3) De verkregen resultaten zouden kunnen dienen als een basis voor de mogelijkheid psychometrische kleurwaarden toe te passen als bruikbare en indicatieve parameters voor de kwantitatieve kinetische analyse en voor het mathematisch modelleren van de effecten van procesfactoren tijdens de productie van magere varkensvleesdegen.

In hoofdstuk 4 worden de veranderingen van L^* , h^* en C^* van de magere varkensvleesdegen kinetisch geanalyseerd, waarbij van de empirische benadering van het mathematisch modelleren gebruik is gemaakt. De veranderingen die gedurende een opslagperiode van 24 h bij 15°C optraden bleken goed te voldoen aan een gewijzigd eerste orde reactiemodel. Het model werd geanalyseerd voor de effecten van luchtdruk tijdens het cutteren, type cutter en de aanwezigheid van enzymremstoffen. Een dergelijke kinetische analyse voor veranderingen bij 40°C, 50°C en 60°C kon worden toegepast op h^* , doch niet op L^* en C^* .

De belangrijkste resultaten van dit onderzoek kunnen als volgt worden samengevat:

- (1) De factor "luchtdruk" vertoonde het grootste effect op de kleur. Het effect van "cuttertype" was intermediair en dat van "enzymremstoffen" het kleinst.
- (2) In het geval van veranderingen in h^* tijdens het verhitten bleek, dat cutteren onder verlaagde luchtdruk (RAP) ten opzichte van cutteren onder normale luchtdruk (AAP) een grote en significante ($P < 0,05$) toename veroorzaakt van de berekende activeringsenergie (E_a).
- (3) Een duidelijke en meestal significante wisselwerking tussen behandeling (onder behandeling wordt het niveau van een factor verstaan; zo zijn AAP en RAP niveaus van de factor "luchtdruk tijdens cutteren") en temperatuur werd voor de kleurwaarden aan het eind van het verhittingsproces vastgesteld. Een hogere verhittingstemperatuur veroorzaakte een lagere L^* en C^* en een hogere waarde van h^* .

De belangrijkste conclusies van het onderzoek zijn:

- (1) De gelijkenis tussen de door Fox e.a. (1967) beschreven kinetiek van de, langs chemische weg bepaalde, vorming van gedenatureerd nitrosomyoglobine (DNOMb) in frankfurter worstdeeg tijdens opslag bij 38°C en het in dit hoofdstuk beschreven eerste orde model voor veranderingen van h^* gedurende opslag van het deeg bij 40°C kan als bewijs dienen voor de juistheid van de toegepaste kinetische analysemethode.
- (2) De gevonden wisselwerking tussen behandeling en temperatuur wordt geacht belangrijk te zijn in het kader van het effect van de bestudeerde procesfactoren op de kleur van verhitte verkleinde vleeswaren (CCCMP). Dus wordt verwacht dat, na verhitten (bijvoorbeeld pasteurisatie), de effecten van procesvariabelen, die vergelijkbaar zijn met de onderzochte variabelen, voor h^* zullen bestaan en in mindere mate voor L^* en C^* .
- (3) Het effect van de "luchtdruk tijdens cutteren" op de voor de gemeten h^* waarden berekende E_a -waarden kon worden toegewezen aan een verschuiving in de balans tussen de invloed van absorptieveranderingen en verstrooiende eigenschappen van de vleesdegen op h^* .
- (4) Een bruikbare toepassing van het vermelde onderzoek zou kunnen worden gevonden in het voorspellen van tussenliggende waarden en eindwaarden voor de kleur tijdens het bereidingsproces van degen met verkleind, mager vlees, waarbij gebruik wordt gemaakt van de techniek van mathematisch modelleren.

Hoofdstuk 5 is gewijd aan een mathematisch model voor het voorspellen van de L^* -waarden van PLMB gedurende verhittingsprocessen. Het model is opgebouwd met behulp van kinetische gegevens, die werden verzameld voor de procestemperaturen 50°C, 60°C, 80°C en 100°C en verhittingstijden oplopend tot 3 h. Tussenvallende waarden en eindwaarden van de helderheid kunnen redelijk goed voorspeld worden binnen het tijd-temperatuurgebied, dat voor de opbouw van het model werd gebruikt. In principe zou een dergelijk model voor h^* , doch niet voor C^* , gemaakt kunnen worden.

De thermische denaturatie van eiwitten blijkt in het algemeen een proces met eerste orde kinetiek te volgen (Labuza, 1980). Jenkins (1984) toonde aan dat het in toenemende mate opgaak worden van gepekeld bacon tijdens verhitten rechtstreeks gerelateerd is aan denaturatie van vleeseiwitten. Tevens werd geconstateerd dat het toenemen van het opgaak zijn van de bacon parallel verliep met een stijging van de helderheid van de bacon. Deze informatie ondersteunt het, in dit hoofdstuk, met succes beschrijven van veranderingen in L^* als gevolg van verhitten door een gewijzigde eerste orde reactievergelijking.

Deel 2

Hoofdstuk 6 bevat de introductie die de mechanistische benadering van het onderzoek in dit deel behandelt.

In hoofdstuk 7 wordt het onderzoek besproken, dat het belang aangeeft van een aantal fysische en chemische gebeurtenissen die de veranderingen in L^* van de PLMBs tijdens de bereiding en opslag (bij 15°C) verklaren. Twee duidelijk te onderscheiden fasen in de veranderingen van L^* werden onderzocht:

Fase (1): een stijging van L^* gedurende het cutterproces en

Fase (2): een fase met afnemende L^* , die tot een plateauwaarde van L^* nadert. Deze tweede fase werd bestudeerd tussen "einde van het cutterproces" en "24 h" opslag.

Een werkmodel, dat betrekking heeft op de individuele effecten van verschillende relevante fysische en chemische gebeurtenissen op het totale patroon van veranderingen van L^* gedurende de beide fasen, werd opgezet. Voor het opstellen van dat werkmodel is gebruik gemaakt van theoretische overwegingen. De volgende drie factoren zijn onderzocht:

- (1) lichtabsorptie-eigenschappen van de PLMBs
- (2) zout en fosfaat
- (3) ingesloten lucht.

De belangrijkste resultaten van het onderzoek zijn:

- (1) Wijzigingen in absorptie-eigenschappen van de PLMBs bleken een grote invloed te hebben op veranderingen in L^* gedurende de tweede fase.
- (2) Het effect van zout en fosfaat bleek van weinig belang voor het verklaren van het gedrag van L^* in fase 2.
- (3) Het gedrag van L^* van de PLMBs gedurende fase 1 kon in hoge mate worden verklaard door wijzigingen in parameters die verband houden met in het deeg ingesloten lucht. De resultaten wijzen, daarenboven, in de richting dat de mogelijke invloed van onomkeerbare eiwitcoagulatie aan het faseoppervlak op veranderingen in L^* tijdens fase 1 zeer klein is.
- (4) Sterke aanwijzingen worden verkregen voor het optreden van het disproportioneren van in het deeg ingesloten luchtbelletjes. Het effect van dit proces op het gedrag van L^* tijdens de tweede fase bleek zich te beperken tot een korte periode, direct aansluitend op het beëindigen van het cutterproces.

De belangrijkste conclusies, die uit het onderzoek kunnen worden getrokken, zijn:

- (1) Het insluiten van luchtbelletjes in de PLMBs en de daaropvolgende afname van de grootte van deze belletjes zijn de belangrijkste gebeurtenissen, die verantwoordelijk zijn voor de toename van L^* tijdens fase 1.
- (2) Het evenwicht tussen de effecten op L^* van het disproportioneren enerzijds en de chemische reacties die tot de vorming van metmyoglobine (MMB) leiden anderzijds kan gebruikt worden om het gedrag van L^* te verklaren in de periode van "eind van het cutterproces" tot 60 min later.
- (3) Veranderingen van de absorptie-eigenschappen van de PLMBs zijn de belangrijkste gebeurtenissen die verantwoordelijk zijn voor de op (2) volgende geleidelijke daling van L^* in fase 2.
- (4) In de publicatie van Palombo en Wijngaards (1989a) werd onder het onderdeel temperatuureffect verondersteld dat het meer doorschijnend (translucent) worden van het deeg, als gevolg van de werking van zout en fosfaat, een verklaring is voor het feit dat tijdens fase 2 de L^* -waarden bij deegtemperaturen van 30°C en 40°C lager zijn dan bij 15°C. Het in hoofdstuk 7 uitgevoerde onderzoek toont aan dat het in de publicatie veronderstelde mechanisme niet werkzaam is.

Uitgaande van de in dit hoofdstuk beschreven resultaten is het mogelijk een mechanistische verklaring te geven voor het sterke effect van de luchtdruk tijdens cutteren op veranderingen van L^* gedurende fase 2 en de overeenkomstige fasen bij 30°C en 40°C. Dezelfde verklaring kan worden gebruikt voor de overeenkomstige veranderingen in de berekende E_a -waarden. De duidelijk hogere snelheid van afname van L^* in degen, die onder RAP i.p.v. onder AAP waren gecutterd, kan worden verklaard door de balans tussen de relatieve bijdragen van het disproportioneerende enerzijds en van de vorming van nitrosomyoglobine (NOMB) anderzijds op de totale veranderingen van L^* . Verder wordt een hypothese opgesteld ter verklaring van de hogere E_a , die werd bereikt voor de onder RAP i.p.v. onder AAP gecutterde degen. Deze hypothese is gebaseerd op de aanname dat de reactie die de vorming van NOMB veroorzaakt vergeleken met het disproportioneerende een hogere E_a heeft en dat onder de RAP omstandigheid de reactie met de hogere E_a het proces beheerst.

Tenslotte dient te worden vermeld dat gebaseerd op het in dit hoofdstuk gerapporteerde onderzoek een groot effect van ingesloten lucht op het gedrag van L^* wordt gevonden. Dit resultaat is echter slechts geldig voor PLMB, zoals het in dit onderzoek gebruikt is. In hoofdstuk 9 wordt het bestaan van een dergelijk effect onderzocht aan de hand van meer commerciële deegsamensellingen.

In hoofdstuk 8 zijn de resultaten gerapporteerd van een onderzoek naar de invloed van oppervlakte-reologische eigenschappen van PLMBs op het gedrag van ingesloten luchtbelletjes gedurende fase 2 en op het gedrag van de L^* van de degen.

De belangrijkste resultaten en conclusies van dit onderzoek zijn:

- (1) Het bestaan van een eindige schijnbare oppervlakte dilatatie viscositeit (η_s) werd gedemonstreerd door het vergelijken van de berekende straal (uitgaande van de De Vries vergelijking) en de door stereomicroscopie gemeten straal van individuele belletjes in afhankelijkheid van de tijd.
- (2) Een enkelvoudige compressietest werd gebruikt voor het verkrijgen van gegevens over het visco-elastisch karakter van het PLMB-oppervlak. Het gedrag van dit oppervlak bleek "shear thinning" te zijn, d.w.z. hoe hoger de relatieve compressiesnelheid is, des te lager de waarde van η_s wordt.
- (3) Het toevoegen van de emulgator glycerol-lacto-palmitaat (GLP) veroorzaakte een aanzienlijke verhoging van de η_s -waarde van de PLMB-dispersie. Anders gezegd: het oppervlak wordt stijver. GLP bleek de krimpsnelheid van individuele luchtbelletjes

met afmetingen in het middengebied (circa $50\ \mu\text{m}$) te verlagen. Dit resultaat is ondersteunt de werkhypothese dat dynamische oppervlakte-reologische eigenschappen het gedrag van ingesloten luchtbellen tijdens fase 2 beïnvloeden.

(4) De PLMB die GLP bevatte (+GLP systeem) had op het tijdstip "end of chopping", ten opzichte van PLMB zonder GLP (-GLP systeem), een aanmerkelijk hogere NB-waarde (aantal bellen per gezichtsveld), een groter deel van de bellen lag in de klasse met afmetingen $< 50\ \mu\text{m}$ en het +GLP systeem had een hogere L^* -waarde. In tegenstelling hiermee wordt in fase 2 waargenomen dat beide systemen zich gelijk gedragen.

(5) De schijnbare discrepantie tussen het vastgestelde grote effect van GLP op het gedrag van individuele luchtbellen in fase 2 en het kleine effect op het gedrag van de parameters NB en BSD (grootte verdeling) van de bellen in dezelfde fase wordt verklaard met behulp van de grote variatie in afmetingen van de bellen op het moment "end of chopping", in combinatie met het "shear thinning" karakter van het PLMB-oppervlak.

(6) Het gedrag van NB en BSD, maar niet van het percentage ingesloten lucht, gedurende het eerste stadium van fase 2 (gedurende ongeveer 40 min) kan als verklaring worden gebruikt voor de aanzienlijk hogere L^* -waarde in het +GLP systeem. Dit resultaat is in overeenstemming met de bevindingen die in hoofdstuk 7 werden gerapporteerd. Uit ontluchtingsexperimenten bleek dat de tijdens de gehele fase 2 gevonden hogere L^* -waarde voor het +GLP systeem niet kan worden toegeschreven aan het gedrag van de ingesloten luchtfractie. Aanvullend onderzoek is nodig om de oorzaak van dit verschijnsel te doorgronden. Het zou mogelijk kunnen zijn dat GLP microbellen (D'Arrigo, 1986), die niet door het ontluchtingsproces worden beïnvloed, stabiliseert.

(7) Het vastgestelde "shear thinning" karakter van het PLMB-oppervlak kan worden gebruikt ter verklaring van het consistente principiële patroon van veranderingen in NB en BSD tijdens fase 2. Als gevolg van de hoge Laplace druk in de zeer kleine bellen, en het "shear thinning" karakter van het oppervlak, zullen zij relatief snel disproportionaliseren, ondanks de hoge compressiesnelheid van het oppervlak. Omgekeerd blijven de grotere bellen langer bestaan. Inderdaad worden altijd kort na het "end of chopping" zowel een sterke afname van de NB waarden als een grote toename van de waarde van de mediaan van de histogrammen van BSD waargenomen. Daarna blijven de waarden van NB en de mediaan van BSD vrijwel constant tot het eind van fase 2.

In hoofdstuk 9 worden de resultaten van het onderzoek naar de invloed van twee factoren gepresenteerd op de kleur en de reologie en het breukgedrag van enkele vleesdeegsystemen. Een der factoren is "luchtdruk gedurende het cutteren", de andere "samenstelling van de degen". De eerste factor heeft twee niveaus: (1) AAP en (2) RAP; de laatste vier niveaus: (1) 100% mager varkensvlees (PLM), (2) 85% PLM in combinatie met 15% water, (3) 70% PLM gecombineerd met 30% spek (PBF) en (4) 60% PLM met 30% spek en 10% water. Kleurveranderingen werden gemeten aan zowel rauwe als verhitte degen. In tegenstelling tot voorafgaand onderzoek op dit terrein, was nu het verkrijgen van fundamentele en systematische kennis betreffende de bovengenoemde effecten het doel. Als gevolg daarvan omvatte het onderzoek een tijdafhankelijk vervolgen van kleurveranderingen en het gebruik van fundamentele reologische tests.

De resultaten en conclusies van het onderzoek zijn:

Kleur:

(1) Grote effecten van de beide factoren op kleurveranderingen tijdens het bereidingsproces en tijdens daaropvolgende opslag bij 15°C werden waargenomen. In het algemeen werd gevonden dat ingesloten lucht over het gehele verloop van de tijd een sterke verhoging van L^* en h^* en een matige daling van C^* veroorzaakte. Het toevoegen van water leidde tot geen enkel of een gering effect op het gedrag van de kleurparameters. Echter, toevoegen van vet veroorzaakte een grote toename van zowel L^* als h^* en een matige afname van C^* . Het toevoegen van de combinatie van water en spek gaf een gelijk effect als dat van het toevoegen van spek alleen. Het effect van de luchtdruk werd in essentie verklaard door te verwijzen naar de veranderingen in de dynamische balans tussen absorptie- en lichtverstrooiende eigenschappen van de degen. Het effect van de samenstelling kon worden verklaard door te verwijzen naar de relatieve bijdrage van toegevoegd water en spek tot de lichtverstrooiende eigenschappen van de vleesdegen.

(2) De experimentele werkwijze, gecombineerd met de experimentele opzet van het onderzoek, maakte het mogelijk een dieper inzicht in de wisselwerkingen van beide factoren op de kleur van de rauwe degen te verkrijgen.

Tijdens fase 1 (d.w.z. de cutterfase) werd een duidelijke interactie tussen het effect van toegevoegd spek en het effect van ingesloten lucht gevonden. Het effect van toegevoegd spek op L^* en h^* was groter in degen die onder RAP werden gecutterd. Omgekeerd was dit effect op C^* groter voor degen die onder AAP werden gecutterd. De voor L^* en C^* verkregen resultaten konden met behulp van

door lichtverstrooiing aan vetdeeltjes en luchtbellens veroorzaakte veranderingen worden verklaard. De door absorptie veroorzaakte veranderingen konden worden gebruikt voor het verklaren van de resultaten met h^* .

Tijdens fase 2 (d.w.z. tijdens opslag bij 15°C tussen "end of chopping" en "24 h") werden voor het gedrag van de drie kleurparameters vrijwel geen wisselwerkingen gevonden. De verklaring is gebaseerd op eerder gevonden resultaten (hoofdstuk 7), waaruit blijkt dat tijdens deze fase het effect van gewijzigde absorptie-eigenschappen van de PLMBs domineert over het effect van veranderingen van lichtverstrooiing.

(3) Het gedrag van L^* in rauwe degen, zonder toegevoegd spek en onder AAP gecutterd, tijdens fase 1 en kort daarna kan worden verklaard uit het overeenkomstige gedrag van de parameters NB en BSD van de ingesloten lucht. Als gevolg van de zeer sterk lichtverstrooiende eigenschappen van het toegevoegde spek kan een dergelijke verklaring niet voor spek bevattende degen worden gebruikt. Dus: de grote effecten van ingesloten lucht in vetarme degen (zie ook hoofdstuk 7) worden sterk overtroffen door de lichtverstrooiing van toegevoegd spek.

(4) De kleur van de verhitte degen werd, vergeleken met die van onverhitte degen, slechts in geringe mate door de beide factoren beïnvloed. De reden van dit verschijnsel is het sterk opgaak zijn van de verhitte degen.

De kleur van de verhitte degen werd, met uitzondering van kleine effecten op h^* , nauwelijks beïnvloed door de luchtdruk tijdens cutteren. Tegenstrijdige publicaties met betrekking tot de grootte van het effect van RAP tijdens het verkleiningsproces op de kleur van knakworst worden in sectie 9.1 vermeld. Het resultaat van dit onderzoek ondersteunt de studies waarbij een klein positief effect op de kleur van het eindproduct werd waargenomen. Een meer gedetailleerde vergelijking bleek onmogelijk als gevolg van de grote variatie in de experimentele werkwijze en in de gebruikte kleurmeettechniek.

Het effect van de deegsamenvestelling op de kleur van de verhitte degen was in belangrijke mate vergelijkbaar met het effect op de kleur van rauwe degen.

Reologische en breuk eigenschappen:

In het reologische deel van dit onderzoek werden enige gegevens over het viscoelastisch gedrag van verhitte degen verkregen. Een kwalitatieve verklaring voor de effecten van de twee bestudeerde factoren (luchtdruk en samenstelling) op de gemeten reologische en breuk parameters wordt verkregen door de "composite material" theorie toe te passen.

De belangrijkste resultaten en conclusies van het onderzoek zijn:

(1) Effecten van kleine vervormingen: ingesloten lucht veroorzaakt, onafhankelijk van de deegsamenvorming, een afname van de vervormingsmodulus (E_d) van de degen. De grootte van dit effect komt overeen met de grootte die kan worden voorspeld met de bestaande theorie van de gevulde gelen. Deze gelen kunnen model staan voor de verhitte vleesdegen. Het toevoegen van water veroorzaakte een afname van E_d . Dit resultaat kan worden verklaard door het verdunnend effect van water op de eiwitbevattende matrix. Het toevoegen van spek veroorzaakte eveneens een verlaging van E_d . Dit laatste effect kan echter niet geheel worden verklaard op basis van de bij het onderzoek verkregen gegevens.

(2) Effecten van grote vervormingen: het effect van ingesloten lucht was afhankelijk van de toevoeging van spek. In degen zonder toegevoegd spek veroorzaakte de lucht een afname van alle breukparameters, d.w.z. breukspanning (σ_f), vervorming bij breuk (ϵ_f) en schijnbare breukenergie (aR). In degen met toegevoegd spek veroorzaakte de lucht slechts een afname van σ_f en aR . Deze afname was, vergeleken met die in degen zonder spek, veel kleiner. Spektoevoeging veroorzaakte een daling van alle drie parameters, onafhankelijk van de hoeveelheid van de ingesloten lucht. Deze resultaten kunnen worden verklaard met behulp van de relatieve bijdrage van elk der componenten (ingesloten lucht en spek) op verdeling van de defectafmetingen en de daarmee overeenkomende stressconcentraties in de verhitte degen.

Deel 1 en deel 2 - laatste commentaar

Deze studie is met een vooropgezet doel "een modelstudie" genoemd. Het grootste deel van het onderzoek is uitgevoerd met een modelsysteem dat uit 100% PLM bestond en dat met een goed gedefinieerde en sterk gestandaardiseerde experimentele werkwijze werd be- en verwerkt. Slechts in hoofdstuk 9 werd de samenstelling uitgebreid met toegevoegd spek en water. De variatie in samenstelling was echter ook toen slechts beperkt tot de niveaus van mager vlees, spek en water. Het is bekend dat andere ingrediënten dan vers vlees, zoals vlees met een hoog bindweefselgehalte, zetmeel en bloed een aanzienlijke invloed hebben op de bestudeerde kwaliteitscriteria. Daarom moeten, in vergelijking met commerciële CCCMP, de in hoofdstuk 9 gebruikte degen toch als modelsystemen worden beschouwd. Niettegenstaande deze feiten hoopt deze studie bij te dragen tot de fundamentele kennis omtrent het systematiseren en structureren van het complexe

thema der bereiding van CCCMP.

In het eerste deel van deze studie werden kinetische analyse en modelleren van kleurveranderingen tijdens de bereiding van PLMBs toegepast. Kinetische analyse blijkt een sterk onderzoeksinstrument te zijn voor een betrouwbaar en tijdsafhankelijk onderzoek naar de effecten van diverse procesvariabelen. In aansluiting daarop blijkt de analyse zeer bruikbaar te zijn voor het ontdekken en kwantificeren van wisselwerkingen tussen verschillende procesvariabelen. Voorspellende modellen kunnen werk, tijd en energie besparen tijdens procescontrole en productie. Wat dit aspect betreft draagt deze studie kennis bij voor het beter beheersen van de bereiding van CCCMP. Kleurfouten van het eindproduct kunnen worden vermeden indien de fabrikant de beschikking zou hebben over een voorspellend model voor veranderingen van een enkele kleurparameter tijdens het verhittingsproces. Dit zou kunnen worden bereikt door kleurmeting van het rauwe deeg (tijdstip vlak voor verhitting) en afdoende correctie voordat de onomkeerbare veranderingen naar een verhit eindproduct plaatsvinden. Voor dit doel moeten modellen worden ontwikkeld, die behalve de effecten van tijd en temperatuur, ook de effecten van de samenstellingsfactor en andere procesvariabelen bevatten. Het werk met betrekking tot kleur, dat in hoofdstuk 9 werd gerapporteerd, verstrekt basiskennis voor het invoeren van de samenstellingsfactor in voorspellende modellen. Een interessante, toekomstige toepassing van dergelijke modelleringstechnieken, met als doel een grote uniformiteit van de kleur en van de kwaliteit, zou kunnen worden gevonden in het toepassen van "in-line" kleurmetende sensoren, die zijn verbonden met een gecomputeriseerd controlesysteem dat de gegevens voor het voorspellend modelleren van de kleur van vleesprodukten bevat.

In het tweede deel van de studie werd, door fundamentele informatie over de luchtfractie in vleesdegen, een beter inzicht verworven in de wijze waarop deze fractie het gedrag van de kleur, de reologie en het breukgedrag beïnvloedt. Bepaalde effecten van ingesloten lucht en van de deegsamenstelling op de reologische en breuk eigenschappen van de varkensvleesdegen werden ontrafeld. Het met succes toepassen van de theorie der "composite material" op de analyse van deze effecten biedt een unieke mogelijkheid voor het voorspellen van het reologische en het breuk gedrag van CCCMP met een ononderzochte samenstelling en dat het CCCMP onder variabele procescondities wordt gemaakt.

Men dient echter te bedenken dat zulke reologische tests slechts een deel van alle fysische gebeurtenissen beschrijven, die tijdens het kauwen van CCCMP worden

ervaren. Sensorische tests zijn noodzakelijk om een verband te leggen tussen de hier gevonden resultaten en de subjectieve waardering.

Uitgaande van deze samenvatting en conclusies kan worden gesteld, dat deze studie bijdraagt tot de tendens waarbij de kunst van vleeswarenbereiding in toenemende mate de kunde van de vleeswarenbereiding wordt.

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LIST OF SYMBOLS

A	surface area
A_0	initial stress bearing area
A_t	stress bearing area at time t
C	rate constant
C^*	psychometric chroma
C_0	constant (in Arrhenius equation)
D	diffusion coefficient
E_a	activation energy
E_d	modulus of deformability
F	force
h^*	psychometric hue or hue angle
H_0	initial sample height
H_t	sample height at time t
K	absorption coefficient
L^*	psychometric lightness
n	number of replicates
n'	reaction order
P_0	atmospheric pressure
Q	quality parameter
aR	apparent toughness
R	radius
R_0	initial radius
R_t	radius at time t
R'	gas constant

R_o	reflectivity
S	scatter coefficient
S	gas solubility
t	time
T	temperature
V	compression rate
γ	surface tension
ΔP	Laplace pressure
ϵ_h	Hencky strain
$\dot{\epsilon}_h$	Hencky strain rate
ϵ_f	fracture strain
$a\eta_s$	apparent surface dilational viscosity
Θ	film thickness
σ	stress
σ_f	fracture stress

LIST OF ABBREVIATIONS

AAP	atmosphric air pressure
BSD	bubbles size distribution
COMb	carboxymyoglobin
CCCMP	comminuted cured cooked meat product
DNOMb	denatured nitric oxide myoglobin
E.I .	enzyme inhibitors
E.I.S.	enzyme inhibitor solvents
E.O.C.	end of chopping
GLP	glycerol lacto palmitate
Mb	myoglobin
MMb	metmyoglobin
NOMb	nitric oxide myoglobin
NB	number of bubbles in a microscopical field of view
OxyMb	oxymyoglobin
Phase 1	chopping stage
Phase 2	storage at 15°C from "end of chopping" until "24 h"
PLM	porcine lean meat
PLMB	porcine lean meat batter
PBF	porcine back fat
RAP	reduced air pressure (0.15 bar)
RCR	relative compression rate

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