Functional properties of white maize meal stored under tropical conditions

John Shindano (MSc.)

In memory of my brother
Anthony Shindano
who died on the 24th August 2007

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Thesis submitted in fulfillment of the requirements for the degree of Doctor (PhD) in Applied Biological Sciences: Chemistry

Titel van het doctoraat in het Nederlands:

Functionele eigenschappen van wit maïsmeel bewaard onder tropische omstandigheden

Illustrations on the cover:

http://www.rosslyntemplars.org.uk/maize.htm
http://www.resimao.org/html/en/Togo/product/product_id/1

To refer to this thesis:
Shindano, J. 2007. Functional properties of white maize meal stored under tropical conditions. Thesis submitted in fulfillment of the requirements for the degree of doctor (PhD) in Applied Biological Sciences: Chemistry. Faculty of Bioscience Engineering, Ghent University

ISBN: 978-90-5989-194-4

John Shindano was supported by the Vlaamse Interuniversitaire Raad (Flemish Interuniversity Council) – University of Zambia – Institutional University Cooperation (VLIR-UNZA-IUC) programme.

The research was performed at the:
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Laboratory of Food Chemistry, Department of Food Science and Technology, School of Agricultural Sciences, University of Zambia, Lusaka, Zambia

Acknowledgements

First and foremost, I would like to thank God for the good healthy given to me to reach this far.

I am extremely grateful to Prof. Koen Dewettinck, who whole heartedly accepted me to be my Promoter. From the bottom of my heart, many and many thanks for having extra patience with me. Your guidance and encouragement I received throughout my tough and difficult journey of this Ph.D sandwich program has made me reach this far. I thank Prof. A. Huyghebaert for initially giving me great encouragement to pursue this road. I am grateful to Dr. Kabwit Nguz for being instrumental in initiating me into this PhD sandwich programme and the support given to me during this period. I thank Dr. Rodah Zulu and Mrs. Grace Munthali of NISIR (Zambia) for their assistance on the work on fortified maize meal.

I am grateful to Katleen Anthierens for the administrative work, setting up of the experiments in Gent and for assistance in the translations of the title and summary into Nederlands. Thanks to the staff from the Laboratory of Food Technology and Engineering who assisted me in one way or the other: Dirk Verbeken, Frederic Depypere, Imogen Foubert, Roeland Rombaut, Nathalie De Clercq, Davy van de Walle, Veerle De Graef, Klaas Goddyn, Tine Courtens, Eveline Fredrick, Jeroen Vereecken, Katarzyna Nienaltowska,Benny Lewille, Marleen De Groote, Corine Loijson, Laurent De Smytere, Paul Provijn and Ruth Van der Driessche. I thank Remaut Mie of the Human Nutrition section for the assistance she offered me at the beginning of my sandwich programme and towards the end this programme.Thanks to

I also thank Prof. Bruno De Meulenaer for the time he offered me for some consultation at the beginning of this work, and the staff from his Laboratory for assistance during my laboratory analyses; the Laboratory of Food Microbiology for allowing me to use their facilities. I thank Dr. S. Samapundo for assistance in type settings and proof reading some parts of this work.Thanks to Thien Trung Le for designing the ccover of this work and for the talking momemnts we shared.

I would like to thank the members of the examination committee, who spent their precious time in reading the manuscript and for the constructive criticism of the manuscript.

My special thanks go to the Flemish Interuniveristy Council – University of Zambia – Institutional University Cooperation (VLIR-UNZA-IUC) programme for the financial fellowship given to me. I thank all the staff of VLIR-UNZA-IUC programme in Zambia and Belgium. Annick Verheylezoon for assisting me beyond your duties – my excess baggage of books reached Zambia.

I thank my employer, University of Zambia, School of Agricultural Sciences, Department of Food Science and Technology for identifying me to benefit from the VLIR-UNZA-IUC programme by way of this

sandwich scholarship and granting me study leave when required. Particularly, Mrs. Sichilongo formerly of SDF office, the former Dean (Prof. I. O. Lungu) and the current Dean (Dr. Judith Lungu) of the Sch. Agric Sciences for the parental advices and encouragement. I thank all my colleagues in the Department of Food Science and Technology (Mrs. D. Hikeezi, C. Kasase, N. Lisulo, M. Mwale, T. Haachibamba, B. Himoonga, V. Nyau, Moses Banda, Mr. Sinkala, Mrs. B. Chipeta, Ian Nachibanga and Lister) and the students I worked with, Kenneth Chomba, Audrey Corhill, Mathews Mulenga and Muyenga Wamulume.

My dear wife, Juliet Munguya and my dear kids (Mbayo and Tabita) deserve my deepest and heartfelt gratitude for their bearing with me for the many months I spent away from home. Tabita, you will most likely craw, stand up and walk without the joy of your father seeing you learn these things. To my dear parents, Mr. and Mrs. Shindanos, my brothers and my sisters; mother-in-law, my sister-in-law and brothers-in-law, thanks for the support you have shown to my family in my absence. I thank my cousins Smith Mangalilo and Francis Kandulu, my friends particularly Isaach Simate & family, Evans Mukonka & family and Jacob Yavwa & family, for everything you did.

There are many names to mention individually, should I just say all the people who assisted me in one way or another towards my sandwich PhD programme, many thanks. Lastly, but not the least, I want to thank my fellow members of Lifeway Evangelical Church in Zambia for the moral and spiritual support you rendered to my family when I was away due to this work, may God richly bless you all.

Nasanta bingi mwane bonse,

John Shindano
24th Septmber 2007

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SUMMARY

Summary

Maize meal, particularly white maize meal, the flour from the maize kernel, is the dominant staple food in many parts of Africa. A wide variety of maize meal types, particularly in Eastern and Southern Africa are produced by dry milling. New trends in production methods such as fortification are also coming with added challenges. White Maize meal is stored at various stages of commerce right from production, distribution and as it is being utilized and consumed. The unfavorable climatic conditions of Africa do pose a challenge to the storage of this important staple food during distribution. Being a staple food, white maize meal consumption in Africa is very important as it contributes significantly to caloric and protein intake. The importance of maize meal is also amplified by the home and industrial food applications in Africa.

Despite white maize meal being a staple food for many parts of Africa with high involvement in commerce, literature is either scarce or non-existent on the stability of functional properties of African white maize meal types during storage or distribution. Therefore, this research undertook to contribute to filling-up this gap. The research work undertook to study the influence of storage conditions on functional properties of white maize meal with a particular emphasis to tropical conditions. The experimental work was divided into three parts:

(i) moisture sorption properties
(ii) chemical and sensory properties
(iii) pasting and rheological properties.

In **chapter 2,** experimental work involved moisture sorption of white maize meal. This included determining moisture adsorption isotherms before defatting (non-defatted) and after defatting (defatted) the white maize meal and then, the influence of storage conditions on moisture and water activity (A_w).

The adsorption isotherms were type II. The isotherms and the monolayer moisture contents were temperature dependant. Differential heat of sorption and entropy increased with decreasing moisture content, while the isokinetic theory showed that moisture adsorption in the temperature range studied was enthalpy-driven. Comparing non-defatted and defatted white maize meals, at constant temperature, the non-defatted had lower equilibrium moisture contents than defatted. The sorption models evaluated fitted better for non-defatted than for defatted, with the GAB model being the best.

At constant storage relative humidity, white maize meal absorbed or lost more moisture at high storage temperatures than at low storage temperatures.

The packaging type influenced changes in water activity of white maize meal during storage. Polypropylene interwoven sacks (PP) showed poor protective barrier against changes in water activity while the polyethylene plastic material (PE) showed good properties of retaining the water activity at high storage relative humidity and sunlight exposure conditions.

Chapter 3 involved experimental work on the influence of storage conditions on chemical and sensory properties of the white maize meal during storage. This involved determining the storage influence on acidity, colour, lipolysis, lipid oxidation and sensory properties.

While storage temperature and storage time had significant effects on the evolution of pH, only storage time affected the evolution of titratable acids.

The L-, a- and b-values of color were highly affected by high storage temperatures. At constant relative humidity and storage temperature the evolution of L-, a- and b-values of white maize meal stored in PP were different from that stored in PE, while PP was not significantly different from the control (without packaging). Of the sensory properties evaluated, a consistent trend was established for colour scores, which deteriorated for low storage temperature-high relative humidity and high storage temperature conditions. The colour however, remained essentially constant for low storage temperature-low relative humidity. The observed change in colour was attributed to discoloration of the white maize meal by non-enzymatic browning.

Storage temperature had a higher influence on lipolysis than storage relative humidity, where increasing storage temperature increased the free fatty acid (FFA) contents. However, at constant storage temperature, samples at high storage relative humidity resulted in higher increases in FFA contents than at low storage relative humidity. Fortified white maize meal evolved higher FFA contents than unfortified maize meal during storage. Packaging and sunlight exposure did not seem to play a significant role in lipolysis during storage of white maize meal. However, after 28 days of storage, the FFA contents at high humidity, particularly at high storage temperature, were confounded by appearance of moulds.

Lipid oxidation determined by peroxide value, increased and then decreased to relatively constant values during the storage period. The peak peroxide value in fortified white maize meal was lower and appeared two weeks earlier than the unfortified white maize meal. Lipid oxidation as determined by p-anisidine value initially increased and then decreased to relatively constant values during the storage period, but the influence of storage temperature seemed not to be significant.

In chapter 4, the influence of storage conditions on gelatinization, pasting and rheological behaviour of white maize meal was determined. Gelatinization temperatures were determined for white maize meal and its isolated starches. Pasting behaviour involved cooking cycle of white maize meal suspensions from 30 to 95^{o}C and then cooling to 50^{o}C, whereas rheological behaviour involved determining viscoelastic properties for isolated starch and flow behaviour for white maize meal pastes.

Starch in white maize meal had significantly ($P<0.05$) higher gelatinization onset temperature (T_o) and gelatinization peak temperature (T_p) than the isolated starch. On the contrary, starch in white maize meal had significantly ($P<0.05$) lower gelatinization enthalpy (ΔH) than the isolated starch. Storage temperature had no significant ($P>0.05$) effect on the evolution of T_p and ΔH of the gelatinization properties. The gelatinization properties only significantly ($P<0.1$) changed in the T_o for the isolated starch and gelatinization end temperature (T_E) ($P<0.05$) for white maize meal, with both decreasing during the storage period.

In terms of pasting properties, low storage humidity resulted in increased peak viscosity (PV), initial hot-paste viscosity (V_{95i}) and final hot-paste viscosity (V_{95f}) at both low and high storage temperatures. Increasing storage temperature increased cold-paste viscosity (V_{50}), total setback (SB_t) and cold-paste:hot-paste viscosity ratio (C:H). At constant storage temperature, high storage humidity gave higher SB_t and C:H than low storage humidity and this phenomenon was more pronounced at high storage temperature than at low storage temperature. However, after 28 days of storage, the pasting properties at high storage humidity, particularly at high storage temperature, were confounded by appearance of moulds.

Storing white maize meal at high temperature and for a long period increased the peak elastic modulus (G'_p) while it decreased the peak viscous modulus (G''_p) of the isolated starch during heating.

The white maize meal exhibited shear-thinning behaviour at all storage conditions throughout the storage period. The Herschel-Bulkley and Mizrahi-Berk models best predicted flow behaviour for low temperature storage conditions throughout the study storage period, while only for a limited storage period at high storage temperatures. The stress overshoot at low storage temperature conditions decreased during storage while it increased at high storage temperatures.

The yield stress and flow behaviour indices decreased while the consistency indices increased at all conditions during storage, except at low storage temperature – low humidity conditions.

Thereafter, the conclusions of this research and proposals of some areas requiring further research in this line of study are given.

On the whole, moisture sorption properties are important in the reactivity of other properties like browning of white maize meal during storage. The changes in pH, titratable acids and lipid oxidation could influence the taste and flavor of the white maize meal. The browning colour due to Maillard reactions during storage is undesirable and of nutritional concern as it further lowers the protein quality of the white maize meal. Lipolysis is also of great concern as the abundant linoleic acid in its non-esterified form in maize meal has been associated with esophagus cancer. However, lipolysis has the potential of application to be used as a storage life marker of white maize meal. The changes in gelatinization, pasting and rheological properties due to storage can have consequences for energy consumption during stirring or mixing or pumping white maize meal pastes for the food industry. Manipulation of temperature, humidity and use of appropriate packaging material has the potential to control these phenomena.

SAMENVATTING

Samenvatting

Maismeel, vooral wit maismeel, gewonnen uit gemalen mais, is het belangrijkste basisvoedingsmiddel in grote delen van Afrika. Vooral in Oost- en Zuid-Afrika, worden door middel van droge maling verschillende types maismeel geproduceerd. Nieuwe trends in productie methoden zoals fortificatie bieden ook bijkomende uitdagingen. Wit maismeel wordt opgeslagen na de productie en wordt verder bewaard gedurende distributie en tenslotte bij de consument tot het wordt verwerkt en geconsumeerd. De ongunstige klimaatomstandigheden in Afrika bemoeilijken de opslag van dit basisvoedingsmiddel. Maismeelconsumptie in Afrika is heel belangrijk aangezien het een belangrijke leverancier is van energie en eiwit. Het belang van maismeel wordt nog verhoogd door huiselijke en industriële voedingstoepassingen in Afrika.

Ondanks het grote commerciële belang van maismeel in grote delen van Afrika, is literatuur over stabiliteit en functionele eigenschappen van Afrikaanse maïsmeeltypes gedurende bewaring eerder schaars of onbestaande. Dit onderzoek tracht om deze lacune aan te vullen. In deze doctoraatsthesis wordt het effect van bewaringsomstandigheden op de functionele eigenschappen van wit maismeel onderzocht. Meer in het bijzonder wordt de invloed van tropische omstandigheden bestudeerd. Het experimentele werk kan opgedeeld worden in drie onderdelen:

(iv) watersorptie eigenschappen
(v) chemische en sensorische eigenschappen
(vi) gelerende en reologische eigenschappen

In hoofdstuk 2 werd de vochtsorptie van wit maismeel onderzocht. Dit omhelsde de bepaling van vocht adsorptie isothermen van wit maismeel voor en na het ontvetten. Daarna werd de invloed van bewaringsomstandigheden op vocht en watergehalte (A_w) bepaald.
De adsorptie-isothermen behoorden tot het type II. De isothermen en het monolaag vochtgehalte waren temperatuursafhankelijk. Differentiële sorptiewarmte en entropie namen toe met afnemend vochtgehalte, terwijl de isokinetische theorie aantoonde dat vochtadsorptie in het bestudeerde temperatuursinterval gedreven werd door enthalpie. Bij constante temperatuur had het niet-ontvette maismeel een lager evenwichts vochtgehalte dan ontvet maismeel. De gebruikte sorptiemodellen fitten beter voor niet-ontvet maismeel dan voor ontvet maismeel, waarbij het GAB model het best past.

Bij constante relatieve vochtigheid tijdens de bewaring, adsorbeerde of verloor het witte maismeel meer vocht bij hoge temperaturen dan bij lage.
Het type verpakking had de grootste invloed op de veranderingen in wateractiviteit van het witte maismeel tijdens de bewering. Polypropyleen (PP) zakken boden geen bescherming tegen veranderingen in wateractiviteit terwijl polyethyleen (PE) de wateractiviteit constant hield bij blootstelling aan hoge vochtigheid en zonlicht.

Hoofdstuk 3 behandelde de invloed van bewaringsomstandigheden op chemische en sensorische eigenschappen van wit maismeel. Dit omhelsde de invloed van bewaring op zuurheid, kleur, lipolyse, vetoxidatie en sensorische eigenschappen.
Gedurende bewaring hadden de temperatuur en de bewaarduur een significant effect op de evolutie van de pH terwijl alleen de bewaarduur een effect had op de evolutie van titreerbare zuren.
De L-, a- en b- kleurwaarden werden sterk beïnvloed door hoge bewaartemperaturen. Bij constante relatieve vochtigheid en temperatuur was de evolutie van de L-, a- en b- kleurwaarden van wit maismeel bewaard in PP verschillend dan van maismeel bewaard in PE, terwijl PP niet significant verschilde van de controle zonder verpakking. Wat betreft de sensorische eigenschappen, werd een consistente trend vastgesteld voor kleurwaarden. De kleuren namen af bij lage temperatuur-hoge relatieve vochtigheid en hoge temperatuursomstandigheden. Nochtans bleef de kleur hoofdzakelijk constant bij lage temperatuur-lage relatieve vochtigheid omstandigheden. De waargenomen kleurverandering werd toegeschreven aan verkleuring van maismeel door niet enzymatische bruinkleuring.
De temperatuur had een grotere invloed op de lipolyse dan de relatieve vochtigheid, terwijl een temperatuursstijging de gehaltes aan vrije vetzuren verhoogde. Nochtans, bij een constante bewaartemperatuur vertoonden stalen bewaard bij een hoge relatieve vochtigheid een grotere toename aan vrije vetzuren dan bij lage relatieve vochtigheid. Verrijkt wit maismeel vertoonde hogere gehaltes vrije vetzuren dan niet-verrijkt meel gedurende bewaring. De verpakking en blootstelling aan zonlicht leken de lipolyse niet significant te beïnvloeden. Nochtans, na een bewaarperiode van 28 dagen, werden de gehaltes aan vrije vetzuren bij hoog vochtgehalte en vooral bij hoge bewaartemperatuur, beïnvloed door de aanwezigheid van schimmels.
Vetoxidatie, bepaald door middel van het peroxidegetal, nam eerst toe en daalde daarna tot relatief constante waarden tijdens de bewaarperiode. De piek peroxide waarde in verrijkt maismeel was lager en deed zich twee weken eerder voor dan in het niet-verrijkte maismeel.

Vetoxidatie, bepaald door middel van de p-anisidine waarde, nam eerst toe en daalde dan tot relatief constante waarden tijdens de bewaarperiode. De invloed van de bewaartemperatuur leek echter niet significant te zijn.

In hoofdstuk 4 werd de invloed van bewaaromstandigheden op gelatinisatie, gelerende eigenschappen en reologisch gedrag van wit maïsmeel bepaald. Gelatinisatie temperaturen van wit maismeel en geïsoleerd zetmeel werden bepaald. Het geleergedrag werd bepaald na een verhitting van wit maïsmeelsuspensie van 30 tot 95°C gevolgd door koeling tot 50°C, terwijl het reologisch gedrag het bepalen van de viscoelastische eigenschappen van geisoleerd zetmeel en de gelerende eigenschappen van maismeelpap omhelsde.
Zetmeel uit het wit maïsmeel had een significant ($P<0.05$) hogere gelatinisatie-starttemperatuur (T_o) en –piektemperatuur (T_p) dan geïsoleerd zetmeel. Daartegenover had zetmeel uit wit maïsmeel een significant ($P<0.05$) lagere gelatinisatie enthalpie (ΔH) dan geïsoleerd zetmeel. De bewaartemperatuur had geen significant ($P>0.05$) effect op de evolutie van (T_p) en ΔH. Alleen T_o van het geisoleerd zetmeel ($P<0.1$) en de gelatinisatie-eindtemperatuur (T_E) ($P<0.05$) van wit maïsmeel veranderden significant, waarbij beide gelatinisatietemperaturen afnamen gedurende de bewaarperiode.
Wat betreft de gelerende eigenschappen, een lage vochtigheidsgraad tijdens de bewaring resulteerde in een toenemende piekviscositeit (PV), alsook de initiele warme geleerviscositeit (V_{95i}) en de finale warme geleerviscositeit (V_{95f}), zowel bij lage als hoge bewaartemperaturen. Een toenemende bewaartemperatuur deed de koude geleerviscositeit toenemen, alsook het herstel van viscositeit tijdens koeling (SB_t) en de koude/warme geleerviscositeit ratio (C:H). Bij constante bewaartemperatuur veroorzaakte een hogere vochtigheid hogere SB_t and C:H dan een lage vochtigheid. Dit effect was het meest uitgesproken bij hoge dan bij lage temperaturen. Nochtans, na een bewaarperiode van 28 dagen, werden de gelerende eigenschappen bij een hoge vochtigheidsgraad, vooral bij hoge bewaartemperatuur, beïnvloed door de aanwezigheid van schimmels.
Bewaren van maismeel bij hogere temperaturen gedurende een langere periode deden enerzijds de piek elastische modulus (G'_p) van geisoleerd zetmeel toenemen, terwijl het de piek visceuze modulus (G''_p) tijdens verhitting deed afnemen.
Het witte maismeel vertoonde pseudoplastisch gedrag onder alle omstandigheden bestudeerd tijdens de bewaarperiode. De Herschel-Bulkley en Mizrahi-Berk modellen voorspelden het best het vloeigedrag bij lage temperaturen tijdens de bewaarperiode, terwijl ze dat bij hoge temperaturen alleen konden voor kortere bewaarperiodes. Gedurende de bewaarperiode nam de

spanning overshoot af bij lage bewaartemperaturen terwijl het toenam bij hoge temperaturen. De zwichtspanning en vloeigedragindicatoren namen af terwijl de consistentie-indicatoren toenamen bij alle bewaaromstandigheden, behalve bij lage temperatuur-lage vochtigheid bewaaromstandigheden.

Daarna worden de conclusie van dit onderzoek samengevat en voorstellen gedaan voor verder noodzakelijk onderzoek in het kader van dit doctoraat.

Als algemene conclusie kan gesteld worden dat vochtsorptie eigenschappen belangrijk zijn voor de reactiviteit van andere eigenschappen zoals bruinkleuring van wit maismeel gedurende bewaring. Veranderingen in pH, titreerbare zuren en vetoxidatie kunnen de smaak en geur van wit maïsmeel beïnvloeden. De bruinkleuring tijdens bewaring is ongewenst en ook nutritioneel van belang aangezien het de eiwitkwaliteit van het wit maïsmeel negatief beïnvloedt. Lipolyse is eveneens van groot belang aangezien het overvloedig aanwezige linoleen zuur in zijn niet-veresterde vorm in maismeel geassocieerd wordt met oesofaag kanker. Nochtans heeft lipolyse het potentieel om gebruikt te worden als kwaliteitsindicator voor de bewaring van wit maïsmeel. Veranderingen in gelatinisatie, gelerende en reologische eigenschappen tijdens bewaring kunnen een grote invloed hebben op het energiegebruik tijdens mengen, mixen of pompen van geleerd wit maïsmeel in de voedingsindustrie. De manipulatie van temperatuur, vochtigheid en het gebruik van geschikt verpakkingsmateriaal hebben het potentieel deze effecten onder controle houden.

Chapter 1

White maize meal – Literature review

Chapter 1. White maize meal – Literature review

Abstract

Maize remains an important part of the human diet in many developing countries and, where it is grown, white maize tends to assume much greater importance for human consumption than yellow varieties. White maize production is of paramount importance in Africa and plays a major role in the diet. Maize meal, particularly white maize meal, the flour from the ground maize kernel, is the dominant staple food in many parts of Africa. In Africa, maize meal is produced by dry milling process – non-degerming or degerming process, to produce whole meals (considered as inferior) or varying types of partially degermed maize meals (considered as superior) depending on the extraction rates, respectively. The new trends in maize meal production taking effect in Africa include fortification and fermentation (not entirely new). The nutritional compositions of the maize meals are highly dependent on the extraction rates. The socio-economic favorable importance of maize meal to Africa is enormous and is amplified in its home to industrial food applications. Maize meal is stored at various stages of commerce right from production up to and during consumption. The unfavorable climatic conditions of Africa do pose a challenge to the storage of this important staple food during distribution. However, also of great concern as food technologists is that, despite maize meal being a staple food for Africa with high involvement in commerce, literature is either scarce or non-existent on functional properties of African maize meal types during storage or distribution in commerce.

Key words: Africa, Dry milling, Fortification, Maize meal, Storage

1.1. Introduction

The entire world except Antarctica now produces maize (*Zea mays*) or corn. Maize ranks as the second most, from wheat, widely produced cereal crop world wide (Johnson, 2000). According to the FAO, global production of corn was 721.4 million tons in 2004 (FAOSTAT, 2005). Maize remains an important part of the human diet in many developing countries and, where it is grown, white maize tends to assume much greater importance for human consumption than yellow varieties (FAO/CIMMYT, 1997).

Over 90 percent of the white maize is produced in the developing countries. Among the individual geographical regions of the developing countries, white maize production is of paramount importance in Africa. The main producers include South Africa, Zimbabwe, Kenya, Malawi, Tanzania and Zambia, where white maize represents between two-thirds and 90 percent of total cereals production. Other important producers of the region include Egypt, Ethiopia and Nigeria, where white maize constitutes from 15-35 percent of total cereals production. Two other significant areas of white maize production are, Central America (excluding the Caribbean sub-region) and the northern part of South America (Colombia and Venezuela). In Asia, yellow maize is considerably more important in their total cereal production than white maize. However, the United States is also increasing the white maize production due to more stable outlets and rising profitability in growing white maize (FAO/CIMMYT, 1997).

At least for more than 400 million people world-wide, primarily in sub-Saharan Africa and Central America, white maize plays a major role in the diet. Rough estimates based on production patterns and international trade flows suggest that developing countries consume over 90 percent of the white maize produced globally, with consumption concentrated in Africa and Central America (FAO/CIMMYT, 1997). In Africa, out of the nations maize needs, maize for human consumption takes up most of the requirements. For instance, between 1995 and 1997, Eastern and Southern Africa used an average of 72%, Western and Central Africa used 66% and North Africa used 45% of the total maize national requirements for human consumption (Aquino et al., 2000).

The report by Wiggins (2003), shows that one of the major cereal food items involved in import and export transactions in Southern Africa is maize and maize flour (maize meal). As an example of a particular country in Southern Africa, in Zambia, human consumption accounts for

as much as 90% while livestock feed production and brewing accounts for 8% and 2% only, respectively (RATES, 2003). Maize (mostly in form of maize meal) conjures high nationalistic sentiments in Zambia. This is mainly due to the fact that it is a staple food and affects food security and incomes of about 80% of the population (RATES, 2003). Maize meal, the flour from the ground maize kernel, is the dominant staple food throughout Eastern and Southern Africa (Jayne et al., 1996).

The major parts of the maize kernel are the endosperm and the germ, which contain most of the starch and oil, respectively (Figure 1.1). The distribution of the major components of maize is presented in Table 1.1.

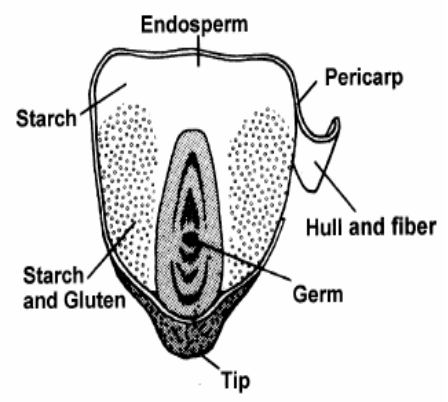

Figure 1.1 Cross-section of corn showing location of major components (Source: Shukla & Cheryan, 2001)

Table 1.1 Distribution of major components corn[$]

Component	Whole kernel (%)	Dry weight of components (%)			
		Endosperm	Germ	Pericarp	Tip carp
Starch	62.0	87	8.3	7.3	5.3
Protein	7.8	8	18.4	3.7	9.1
Oil	3.8	0.8	33.2	1	3.8
Ash	1.2	0.3	10.5	0.8	1.6
Others*	10.2	3.9	29.6	87.2	80.2
Water	15.0	-	-	-	-

*By difference. Includes fiber, non-protein nitrogen, pentosans, phytic acid, soluble sugars, xanthophylls; [$]Source: Shukla & Cheryan (2001)

Maize is processed primarily by four methods: wet milling, the dry grind process for ethanol production, dry milling and alkaline processing. Alkaline processed and dry milled maize goes directly for human consumption (Watson & Ramstad, 1987; Shukla & Cheryan, 2001). All

maize dry mills produce a line of basic products that includes grits, meals, flour, germ (oil) and bran (Peplinski et al., 1984; Johnson, 2000). Maize meal, the flour from the maize kernel and the dominant staple food for most of Africa is processed by dry milling.

The importance of white maize meal to the world - the developing nations and Africa in particular, can not be overemphasized. Therefore, sections 1.2 to 1.4 of this chapter gives an overview of the production, storage and importance of white maize meal in Africa, with a particular emphasis to Eastern and Southern Africa. The later sections of this chapter give a literature review on selected physico-chemical and functional properties of maize and maize products or other cereals with emphasis to effects of storage.

1.2. Production methods and maize meal types

There are significant variations in the type of maize meal consumed in Eastern and Southern Africa. Maize meal may be classified along several continuums: extraction rate, dentiness vs. flintiness, and color (Jayne et al., 1996). Maize meal is produced by a dry-milling process. The objective of dry-milling is to separate the maize kernel into its anatomical parts (endosperm, bran and germ). Two different systems are used to dry-mill the maize grain: Non-degerming and Degerming (Johnson, 2000).

The non-degerming system grinds maize grain into meal with little, if any separation (Johnson, 2000). This process yields whole meal, which contains the bran, germ and endosperm in the proportions found in the whole kernel. Whole meal is produced by three types of mills - stone, plate, and hammer. The former two techniques were used along time ago, but can still be found in use in very remote rural parts of Africa. Hammer mills are by far the most common technique for making whole meal in Eastern and Southern Africa. Hence, the non-degerming system is also referred to as the hammer milling technology. Hammer mill technology does not separate the bran, germ and endosperm, but simply shears and grinds the whole kernel or whatever part of it is fed into the hopper. The broken grain is sheared in the milling chamber until its size is sufficiently reduced to pass through the holes of a screen surrounding the hammers. The most typical whole meal product (96-99 percent extraction rate) is variously called *posho* meal in Kenya, *mgaiwa* in Malawi, and *mugayiwa* in Zimbabwe (Jayne et al., 1996) and Zambia. Hammer milling technology is generally small-scale in nature (Jayne & Argwings-Kodhek, 1997), and is mostly operated as a family business.

The Degerming System is also referred to as the Tempering-Degerming (TD) system (Johnson, 2000) or Roller Milling Technology (Figure 1.2). In this system, water is added to the maize grain to increase the moisture content to about 20%, and the moistened maize grain is allowed to equilibrate (tempering) for 1-3 hours.

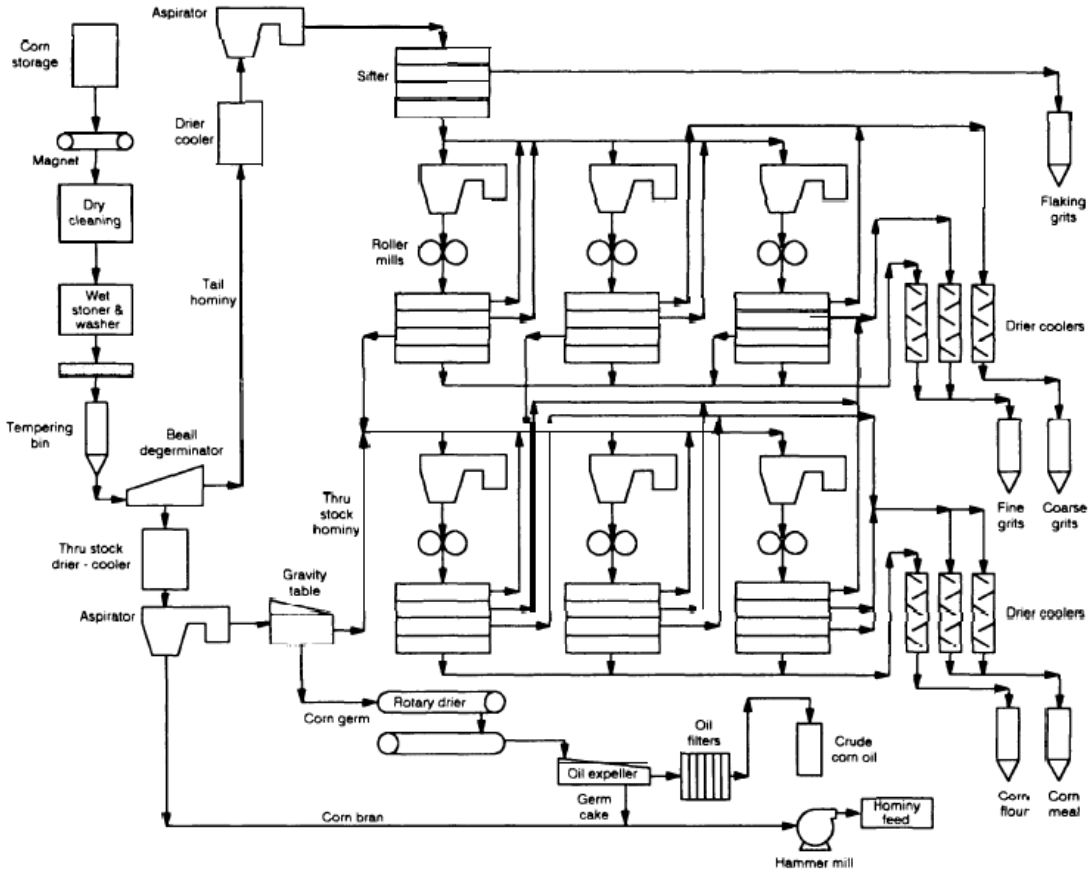

Figure 1.2. Flow sheet for dry corn milling (tempering-degerming system) [Source: Alexander (1987)]

This toughens the germ and the bran so that their particle sizes remain large, making separation easier. Once the germ and hull are removed, the endosperm is reduced in size to grits with roller mills, hence the term roller milling technology. A complex array of additional roller mills and particle-size-separating equipment is used to purify and size the endosperm particles (Johnson, 2000).

Roller milling technology is generally large-scale in nature, and is used by large, urban milling firms in Eastern and Southern Africa. Roller milling process yields a large range of partially or

fully degermed meals. The concentration of milled bran and germ in the milled endosperm is determined by the extraction rate of the maize grain. Extraction rate refers to the proportion by weight of the maize kernel which is processed into meal (Jayne et al., 1996).

In general, the roller milling technology produces two major types of maize meals, *refined* and *super-refined meals.* R*efined meals* refer to the intermediate grade of maize meal. *Refined meals* are produced by removing part of the germ and bran, resulting in a lower extraction rate than whole meals. *Super-refined meal* on the other hand designate highly-refined meals i.e. with much lower extractions rates than *refined meals* (Jayne et al., 1996). Maize meals with very low levels of bran and germ (*super-refined meals*) are variously called *super-refined* in Zimbabwe, *super-sifted* in Kenya, Tanzania and South Africa, and *breakfast meal* in Zambia. Products with slightly higher levels of bran and germ (*refined meals*) are referred to as *sifted meal* in Kenya, Tanzania and South Africa, or *roller meal* in Zimbabwe (Jayne et al., 1996) and Zambia. If all of the bran and germ are re-mixed back with the milled endosperm, this product is often called *straight-run* meal, and is similar to the *mugaiwa or posho* - whole meal produced from hammer mills (Jayne et al., 1996). The major types of maize meal produced in Eastern and Southern Africa are summarized in Table 1.2 (Jayne et al., 1996).

Whole maize is a good source of thiamin, pyridoxine and phosphorus, and a fair source of riboflavin, niacin, folate, biotin, iron and zinc. However, many of these nutrients are lost during milling (MOST/Roche/USAID, 2003). The extraction rate of a meal affects its nutritional content (Table 1.3).

The most common colors of maize grain nowadays are white and yellow. This brings about the type of maize meal based on its color. In the Eastern and Southern African region, white maize has been preferred when priced the same as yellow maize. Yellow maize has been considered as being vastly inferior for human consumption to white maize. As a result, yellow maize has been consumed only in droughts, when insufficient white maize was available (Jayne et. al., 1996). Owing to colour differences in the processed maize meals, white *super-refined* maize meal is preferred to white *refined* maize meals. Equally, white *refined* maize meal is preferred to white *whole meals*. The colour of white maize meal becomes duller or darker from *super-refined* maize meal to *refined* with the darkest being *whole meals*.

Table 1.2 Major types of maize meals produced in Eastern and Southern Africa[$]

Type of maize meal	Description	Extraction rate (%)	Production Technique
Super-sifted (South Africa, Kenya); Super refined (Zimbabwe); Breakfast meal (Zambia); Farinha matabicho (Mozambique)	The bran and germ are completely removed; meal ground from the starch endosperm	60 - 70	Roller milling
Sifted (Kenya, South Africa, Tanzania); Roller meal (Zambia, Zimbabwe); Farinha Sem Farelo (Mozambique)	Much of the bran and germ are removed; meal ground mostly from the endosperm	80 – 85	Roller milling
Hammer milled 'roller meal' (Zimbabwe); Number 1 (Kenya)	Much of the bran and germ are removed; meal ground mostly from the endosperm	75 – 95	Hammer milling using dehulled maize before processing
Straight run meal, mugayiwa (Zimbabwe); Posho (Kenya); Dona (Tanzania); Farinha Corn Farelo (Mozambique)	By hammer milling: the meal is processed from the whole maize kernel, with the bran, germ and endosperm retained	96 – 99%	Hammer milling
	By roller milling: the bran and germ are added back after the milling and sieving process		Roller milling

[$]Jayne et al. (1996)

Table 1.3 Nutrient composition of refined and whole maize meal[$]

Nutrient (%)	Refined meal		Whole meal	Nutrient (Per 100grams)	Refined meal		Whole meal
	Extraction rates				Extraction rates		
	65%	85%	96-99%		65%	85%	96-99%
Protein	7.9	9.3	10.0	Calories (Kcal)	334.0	341.0	343.0
Fat	1.2	2.4	3.8	Calcium (mg)	6.0	7.0	12.0
Carbohydrate	78.4	75.1	73.4	Iron (mg)	1.1	2.0	2.5
Fibre	0.6	1.1	1.9	Thiamin (mg)	0.14	0.30	0.35
Ash	0.5	0.7	1.3	Riboflavin (mg)	0.05	0.08	0.13
				Niacin (mg)	1.0	1.8	2.0

[$]Adopted from Jayne et al., 1996 (Source: West et al., 1987)

The consumption of the more costly sifted maize meal is partially determined by attributes of the product itself. In Kenya, urban sifted maize meal consumption has been explained by a

combination of factors such as inherent taste (Jayne & Argwings-Kodhek, 1997), and cooking attributes of sifted meal compared to whole meal. Mukumbu & Jayne (1995) have noted that the relative importance of these factors has received little research attention. The perception of strong preferences for sifted meal over unrefined maize meal (posho) has been reinforced by substantial advertising by large-scale milling firms portraying refined maize meal as a sign of sophistication and modernity. In a survey in Kenya, more households purchasing *sifted maize meal* chose it because it was convenient to procure compared to *posho* meal. More of those who consumed whole meal chose it because it was cheaper and nutritious. This indicates that many urban households were already aware of whole meal's superior nutritional quality at the time of this survey (Mukumbu & Jayne, 1995).

Maize flour or maize meal has been considered in fortification programs because it is a staple food in many parts of Africa. The growing centralization of maize milling, its world-wide consumption, and the simplicity of the fortification technology makes this vehicle a good choice for nutritional intervention (MOST/Roche/USAID, 2003). In Southern Africa, a number of countries have started maize meal fortification programs: Zambia, South Africa, Zimbabwe and Namibia. The maize meals are being fortified with vitamins A, B_1, B_2, B_6, niacin and folate; iron and zinc (MOST/Roche/USAID, 2003). The South African Government has already made it mandatory legal requirement to have all maize meal milled in South Africa to contain specified amounts of vitamin A palmitate, thiamin mononitrate, riboflavin, nicotinamide/niacinamide, pyridoxine HCl, folic acid, electrolytic iron, and zinc oxide (Duvenage & Schönfeldt, 2007). However, there has been a concern of possible problems of bioavailability, lipid oxidation and sensory quality due to fortification (Hurrell et al., 1991; Nestel, 1993; Bovell-Benjamin et al., 1999). Factors that influence the stability of added vitamins and minerals during storage and preparation of maize flour or maize meal must also be considered: temperature, moisture content, type of preparation, presence/absence of light, length of cooking, pH, presence of oxygen, length of storage, packaging (MOST/Roche/USAID, 2003).

In many African countries, maize is also used for preparations of fermented sour doughs or meals. There have been a number of studies in fermentation of maize meals for the purpose of innovation of the quality of maize meal (Adeniji & Potter, 1978; Hamad & Fields, 1979; Plahar et al., 1983; Addo et al., 1996).

1.3. Storage of maize meal in Africa

The climate for storage of food products in Africa is quiet hostile, particularly in terms of temperature and relative humidity. Table 1.4 shows the maximum temperatures and relative humidity recorded in selected parts of Africa. It is evident that high temperatures above 45^{o}C are not uncommon and relative humidity above 70% are equally not uncommon, although the humidity drops during the day. This environment gives concern for the storage of maize meal.

Table 1.4 Maximum temperatures (Max Temp), relative humidity (RH) and average sunshine hours during the year in selected parts of Africa[$]

Month	Southern Africa		East Africa		Central Africa		West Africa		North Africa		Southern Africa
	Mozambique (Zumbo)		Kenya (Mombasa)		Central African Republic (Bangui)		Cameroun (Yaounde)		Algeria (In Salah)		Zambia (Lusaka)
	Max Temp (^{o}C)	Max RH (%) am*	Max Temp (^{o}C)	Max RH (%) am*	Max Temp (^{o}C)	Max RH (%) am*	Max Temp (^{o}C)	Max RH (%) am*	Max Temp (^{o}C)	Max RH (%) am*	Average Sunshine (Hours/ day)
Jan	42	79	35	76	37	92	33	97	31	63	5
Feb	40	78	35	75	38	90	33	97	35	64	5
Mar	40	76	36	77	38	91	33	97	39	51	7
Apr	41	69	36	81	37	92	36	97	42	40	9
May	38	65	33	85	36	94	34	98	46	37	9
Jun	36	65	32	82	35	95	32	97	50	36	9
Jul	35	64	33	82	34	96	31	97	50	29	9
Aug	39	60	31	76	34	96	34	97	50	31	10
Sep	43	53	32	81	34	95	31	98	49	38	9
Oct	44	48	32	79	34	94	33	98	44	44	9
Nov	49	57	34	78	34	94	32	98	36	61	7
Dec	43	71	36	78	36	92	32	98	31	65	6

[$]Source: BBC weather (2005); *am – morning relative humidity

In Zambia, maximum daily temperatures of 30°C to 40°C are not uncommon particularly for low-lying valley areas such as the Zambezi, Gwembe and Luangwa valleys (AQUASTAT, 2005). Table 1.4 also gives an overview of the average sunlight period per day for the capital of Zambia, Lusaka. It is evident that Zambia or most African countries have long hours of day sunlight coupled with high temperatures and relative humidity. These observations are of significance because white maize meals in Africa are also sold in open markets with exposure to sunlight.

Food processing companies have a trend to overlook the intrinsic dimension of quality that includes safety, health and shelf-life to focus more on extrinsic factors that promote sales and boost the image of the company (Nguz, 2007). In the trade of maize meal and maize meal

products, Africa has not been spared from this syndrome. Quality and safety of food products have to be assured at each stage of the maize meal value chain – processing, storage and distribution.

Packaging is necessary for preserving the organoleptic, nutritional and hygienic characteristics of food during storage and commercialization (Ou et al., 2005). The success of most preservation methods depends on how well the processed food is protected from adverse environmental conditions, which is mostly accomplished by packaging. Characteristics of the packaging materials such as mechanical and barrier properties are very important to decide on what type of material will be used in the packaging of different types of foods. Exposure to different processing conditions may alter the physical and/or chemical properties of the packaging materials and the modifications in the properties of the packages may have an effect on the quality of the packaged food products (Ozen & Floros, 2001). Different types of packaging materials are in use for the packaging of maize meal in different African countries. Packaging materials ranging from polypropylene interwoven sacks, polyethylene plastics (thin, thick, opaque, translucent and transparent), paper etc can be found in use for packaging maize meal in Africa. No research has been found as a scientific basis for the choice of the type of packaging in use. Most probable, the choice is dependent on historical use and marketing reasons (package appearance).

Raw material quality, the degree to which raw materials (i.e. whole grain, grits, meal, flour) possess good physicochemical, nutritional and processing properties, can vary considerably from fresh to aged material even though they meet the same physico-chemical specifications (McDonough et al., 2004). There has been a number of publications on mycotoxin contaminations of maize meals (Gelderblom et al., 1988; Sydenham et al., 1990; Sydenham et al., 1991; Rheeder et al., 1992; Thiel et al., 1992; Okoth & Ohingo, 2004; Soriano & Dragacci, 2004; Williams et al., 2004); however, publications on the stability of physico-chemical and functional properties of maize meal, particularly white maize meal, during storage are either scarce or non-existent.

In one survey research on the occurrence of aflatoxins in different types of weaning flours for young children (maize, cassava, green grams, sorghum, beans, millet, rice, groundnuts and dried fish) in Kenya by Okoth & Ohingo (2004) it was found that the duration of storage of the flours for the households ranged from 1 day (32.8%) through 1 week (35.0%) to 2-5 weeks (32.2%).

However only 20% of the mothers appreciated that their flour would deteriorate with time and therefore had spoilage signs (strongly sour or sharp flavour taste, offensive smell, color change, shiny surface and formation of lumps). The rest of the mothers used the flour for as long as it lasted. Their description of spoilage was close to mould growth and insect infestation.

Some analysts have contended that households may be averse to *posho* meal (wholemeal) because of its shorter shelf life (*posho meal* contains oil from the maize germ) (Mukumbu & Jayne, 1995). In a survey by Mukumbu & Jayne (1995), according to the Nairobi respondents that consumed it, *posho meal* was said to have an average shelf life of 3.7 weeks. This is assumed to be at room storage conditions, as the conditions of storage for these estimates of shelf life were not stated. Mukumbu & Jayne (1995) have further stated that, the shelf life problem is probably more relevant to potential commercial manufacturers of whole meal, who would have to be concerned about timely distribution to retail outlets after milling to avoid spoilage.

1.4. Importance of maize meal in Africa

Maize in its different processed forms, but particularly in the form of maize meal, is an important food for large numbers of people in Africa, providing significant amounts of nutrients, in particular calories and protein. FAO (1992) publications showed that 22 of 145 developing countries had a maize consumption of more than 100 g per person per day. In a dietary intake survey in South Africa, MacIntyre et al. (2002) found that maize meal was consumed by almost, all of the respondents, both males and females, in the rural, farm, informal settlement and middle class urban strata.

Mukumbu & Jayne (1995) reported that the average quantity of maize meal consumed per adult equivalent (AE) was 1.68 kilograms per week (7.22 kgs per month). In Zambia, it has been reported that over 90% of the population consume maize meal with a daily per capita consumption of 250-300g (Laleye & Wesley, 2001). In Zambia, over two-thirds of the daily energy intake comes from maize and in a number of other countries between 10 and 30 percent of daily energy intake is from maize flour or maize meal (MOST/Roche/USAID, 2003).

This data confirms the importance of maize meal as a staple food in a number of African countries. It follows that if the maize meal intake is high, maize meal contributes significant amounts of calories and protein to the daily intake of people in Africa. Maize meal is further

processed into other foods as a sole ingredient or is used as one of the ingredients in processing other food products.

Home consumer food applications of maize meal constitute human consumption of maize meal as a dough or thick porridges, common in Southern Africa (Van der Merwe et al., 2001); in Zambia (Laleye & Wesley, 2001), in Zimbabwe, South Africa, East Africa including Kenya, Tanzania, Uganda, Burundi, Rwanda, and Democratic Republic of the Congo, West Africa particularly in Nigeria (Tembo, 2007) and light porridges at breakfast (Sammon, 1999). Ogi or Pap a traditional fermented cake (Onyekwere et al., 1989) is consumed in Nigeria (Banigo et al., 1974; Steinkraus, 1996), in the republic of Togo, Benin, and Ghana (Onyekwere et al., 1989). Maize meal porridge is used as complementary food for infants in many African countries (Lartey et al., 1999; Huffman et al., 2000; Mamabolo et al., 2004; Faber et al., 2005). In Eastern and Southern Africa, fermented starch-based porridges are particularly popular; uji, togwa, kenkey, mahewu, ogi and enjera (spongy bread) (Steinkraus, 1996).

In many African countries, maize, in form of maize meal, is also used to prepare non-alcoholic fermented products - mostly as beverages: Munkoyo beverage in Zambia and Zaire (Lovelace, 1977; Lovelace, et al., 1978; Simwamba & Elahi, 1986; Steinkraus, 1996; Zulu et al., 1997), mageu or mahewu typical of Southern Africa (Holzapfel, 1989; Steinkraus, 1996), akamu or uji in East Africa, mawe in Benin and Togo, togwa in East Africa, especially in Tanzania and a variety of sour maize doughs in Ghana (Steinkraus, 1996).

For centuries maize beers have occupied an important place in the diets of many African peoples (Haggblade & Holzapfel, 1989). There are various types of African opaque beers: Kenyan urwaga, Kenyan bussa, Nigerian and Ghanian pito (Steinkraus, 1996), Zambian opaque maize beer (Lovelace, 1977; Steinkraus, 1996) and *doro*, *hwahwa*, *mhamba*, or *utshwala* in Zimbabwe (Gadaga et al., 1999). The essential steps in brewing are malting, mashing, souring, boiling, conversion, straining and alcoholic fermentation (Steinkraus, 1996). In contrast with old-fashioned brewers, many today add maize meal rather than malted or unmalted sorghum or millet as a starchy adjunct (Haggblade & Holzapfel, 1989).

Industrial food applications of maize meal include its use in production of non-alcoholic fermented products such as commercial production of mageu (Holzapfel, 1989). Maize meal is also used in the commercial production of African alcoholic products at industrial level. Africa's

brewers confection a wide variety of indigenous beers using two principal inputs: malt and starchy adjunct. Factory brewers almost invariably use maize grits (or maize meal) as starchy adjuncts (Haggblade & Holzapfel, 1989). Extrusion products are beginning to have a huge market in Africa, especially for children's ready-to-eat snacks. Maize meal (flour) is one of the major ingredients in extruded products (Wen et al., 1990; Martinez-Bustos et al., 1998; Zhang & Hoseney, 1998; Onwulata et al., 2001a, 2001b). Maize meal is also used extensively in animal feeds as an energy source in Africa. In livestock feeding, yellow maize is preferred because it gives poultry meat, animal fat and egg yolk the yellow colour appreciated by consumers in many countries (FAO/CIMMYT, 1997).

1.5. Physico-chemical properties

1.5.1. Moisture sorption

Moisture sorption isotherms show in graphical form the variation in water activity (Aw) with change in moisture content of a sample at a specified temperature (Rahman, 1995). Labuza et al. (1985) determined sorption isotherms in yellow corn meal at 25, 30, 45 and 65^{o}C. Table 1.5 below gives the equilibrium moisture content (EMC) at constant water activities and temperatures of corn meal/flour as obtained by Labuza et al. (1985), Abdullah et al. (2000) and Wicklow et al. (1998) determined adsorption isotherms in a hybrid maize grain. Samapundo et al. (2007) determined the adsorption and desorption isotherms of yellow dent corn at 25, 30 and 37^{o}C. The moisture isotherms for yellow dent corn have been found to exhibit Type II behaviour and to be temperature dependent as the equilibrium moisture content decreases with increase in temperature (Samapundo et al., 2007).

A number of models, mostly semi-empirical and empirical, have been attempted to be fitted to maize and maize products moisture isotherms. The GAB model has been considered the best-fit model for many food materials in general over a wide range of water activity (Van den Berg, 1984; Rahman, 1995; McMinn & Magee, 1999; Timmermann et al., 2001; Al-Muhtaseb et al., 2004a), and yellow dent corn (Samapundo et al., 2007) in particular. The GAB and BET models have been used to estimate the monolayer moisture contents. However, different researchers have found differing monolayer moisture contents. Samapundo et al. (2007) from the adsorption isotherms using the GAB equation found 7.44, 6.57 and 6.03 kg/100 kg db at 25, 30 and 37^{o}C, respectively, whereas Labuza et al. (1985) obtained 8.23, 6.50 and 5.68 g/100g db at 25, 30 and

45°C, respectively. This shows that while there is agreement on the moisture isotherm trends, there is no agreement on the exact positions of the isotherms in maize and maize products.

Table 1.5 Adsorption isotherms of corn meal/flour*,# and a hybrid maize grain$

Aw-25°C *	EMC-25°C*	Aw-25°#	EMC-25°C#	Aw-25°C$	EMC-25°C$
0.115	4.69	0.10	3.85	-	-
0.234	7.44	0.20	5.43	-	-
0.329	9.12	0.35	6.75	-	-
0.443	11.04	0.50	8.80	0.43	10.7
0.536	11.91	0.65	10.52	0.57	12.6
0.654	13.14	0.75	12.70	-	-
0.765	15.47	0.85	15.60	0.75	14.9
0.846	19.58	0.95	19.43	0.85	15.9
-	-	0.98	20.69	-	-

Aw-30°C *	EMC-30°C*	Aw-30°C$	EMC-30°C$	Aw-45°C*	EMC-45°C*
0.110	4.46	-	-	0.103	3.39
0.231	6.35	-	-	0.197	5.34
0.325	8.12	-	-	0.309	7.07
0.437	9.90	0.43	10.4	0.429	8.39
0.521	10.43	0.575	12.1	0.496	8.75
0.648	12.90	-	-	0.599	10.80
0.727	13.69	0.755	14.6	0.727	13.69
0.841	19.51	0.845	15.5	0.786	17.04

* Labuza et al. (1985); #Abdullah et al. (2000); $Wicklow et al. (1998)
Equilibrium moisture content (EMC): gH_2O/100g solids

Thermodynamic parameters such as differential enthalpy and entropy, and integral enthalpy and entropy determine the end-point to which food must be dehydrated in order to achieve a stable product with optimal moisture content, and yield the theoretical minimum amount of energy required to remove a given amount of water from the food. These parameters also provide an insight into the food microstructure, water sorption kinetics, and an interpretation of physical–chemical phenomena occurring at the food–water interface (Rizvi & Benado, 1984; Al-Mahasneh et al., 2007; Toğrul & Arslan, 2007). Differential heat of sorption can be related to the extent of binding between solid food particles and liquid solvent (McMinn & Magee, 2003; Al-Mahasneh et al., 2007). The net isosteric heat is the amount of energy by which the heat of vaporization of moisture in a product exceeds the latent heat of pure water (Toğrul & Arslan, 2007). It is a measure of the interaction between an absorbate and absorbent (Toğrul & Arslan, 2007). Differential entropy is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996). The isokinetic, or enthalpy–entropy compensation, theory has been used to evaluate sorption processes. Madamba et al. (1996) and Beristain et al. (1996)

successfully applied the enthalpy–entropy compensation to water adsorption in garlic and starchy materials, respectively.

The sorption of water vapour by foods has also received much attention because of its importance in dehydration processes and in changing of quality during storage. The changes in chemical, physical and biological properties of foods, which do not appear to be related directly to either moisture content or A_w, often can be explained in terms of the interrelationship between the two parameters expressed as a moisture sorption isotherm. Changes in isotherm characteristics, related to temperature, provide insight into the physical and chemical changes that influence food quality and stability (Sing et al., 2006b).

1.5.2. Maize Lipids

The major classes of lipids includes: free fatty acids, triacylglycerols (triglycerides) consisting of fatty acids esterified to glycerol, and phosphoglycerides consisting of fatty acids esterified to glycerol and containing phosphoric acid and organic bases (Frankel, 2005). Free lipids are portions easily extractable with nonpolar solvents such as petroleum ether, hexane and diethylether by a Soxhlet extractor or by shaking. Bound lipids are extracted from the free lipid residues at room temperature with more polar solvents-generally alcohol alone or mixed with small portion of another solvent, most commonly water. Water-saturated n-butanol is considered to be the most efficient solvent system for bound lipid extraction. A mixture of chloroform and methanol (2:1, 1:1, 1:2 by volume) also is commonly used. In cereals, the sum of free lipid and bound lipid is termed the non-starch total lipids. Non-starch total lipids can also be obtained by polar solvent extraction at room temperature without the free lipid extraction step. Measured lipid content and composition depend largely on extraction and purification procedures. Therefore, it is extremely difficult to compare lipid content or composition data reported by various researchers. There are wide ranges in FA compositions of corn oils. A range of 14-64% oleic acid and 19-71% linoleic acid for the world collection of 788 varieties of corn was reported. They found palmitic acid ranges of 6.3 – 7.6% and 16.7 – 18.2% for low and high saturated corn genotypes, respectively. They also reported a range of 43.9 – 46.1% of oleic acids for high oleic acid lines (Chung & Ohm, 2000).

Deterioration in the quality of maize meal during storage could be attributed to lipolysis and lipid oxidation. Sammon (1999) reported that freeing of fatty acids takes place from the time of

milling, presumably due to mixing of natural lipases with esterified fatty acids. Castello et al. (1998) reported that wheat and fungal lipases have been implicated in the increase of free fatty acids during long term storage of flour. Several food studies have reported increases in free fatty acids during storage, for instance, in wheat flour (Castello et al., 1998) and in pistachio nut paste (Gamli & Hayoglu, 2007).

Lipid oxidation is a major cause of quality deterioration in dehydrated foods (Pershem et al., 1995; Maskan & Karatas, 1998). To produce oxidatively stable products, both process and storage conditions must be considered (Rutgersson et al., 2000). Although other degradation mechanisms are also possible, the oil degradation process has been generally established as being a free radical mechanism yielding hydroperoxides, also called primary oxidation products, which in turn degrade into aldehydes, ketones, lactones, alcohols, acids, etc., or secondary oxidation products (Guillen & Cabo, 2002). The free radical chain mechanism proceeds by three major steps: initiation, propagation and termination. These can be complex series of sequential and overlapping reactions (Frankel, 2005).

Initiation

Lipid free radicals (L^{o}) are from unsaturated lipids (LH) which loses a hydrogen radical in the presence of initiators (I) (reaction 1.1)

$$LH \xrightarrow{I} IH + L^{o} \qquad (1.1)$$

For oxygen to initiate lipid oxidation, conversion of triplet $^{3}O_2$ to singlet $^{1}O_2$ must occur. This conversion occurs in the presence of initiators that can produce radicals by different mechanisms:

(a) Hydroperoxides (LOOH) present as impurities produce radicals by thermal dissociation (reaction 1.2):

$$LOOH \longrightarrow LO^{o} + {}^{o}OH \qquad (1.2)$$

(b) Redox metals (M) of variable valency catalyse the decomposition of hydroperoxides into radicals (reaction 1.3 and 1.4):

$$LOOH + M^{2+} \longrightarrow LO^{\circ} + {}^{\circ}OH^{-} + M^{3+} \quad (1.3)$$

$$LOOH + M^{3+} \longrightarrow LOO^{\circ} + H^{+} + M^{2+} \quad (1.4)$$

(c) Sensitizer moleculecules such as a ketone (RCOR) decompose into radicals when exposed to light as shown in reaction 1.5:

$$RCOR + h\nu \longrightarrow RCO^{\circ} + {}^{\circ}R \quad (1.5)$$

Sensitizers exist in two excited states. When the singlet (^{1}Sens) absorbs light it can be converted to the triplet state (^{3}Sens). The triplet state initiates photosensitized oxidation especially that it has a longer life-time than the singlet state. In foods, pigment molecules such as chlorophyll, hemeproteins and riboflavin are known to initiate photosensitized oxidation. Initiation of oxidation by sensitizers can proceed by two pathways. A Type I sensitizer serves as a photochemically activated free radical initiator. By means of hydrogen atom or electron transfer the lipids can react with a triplet state sensitizer to form radicals, which can react with O_2 (reaction 1.6).

$$^3\text{Sens} + LH \xrightarrow{h\nu} [\text{intermediate}] + O_2 \longrightarrow \text{hydroperoxide} + \text{Sens} \quad (1.6)$$

The hydroperoxides produced in (Equation 1.6) are the same as those from free radical autoxidation. However, this photosensitized reaction is not inhibited by *chain-breaking* antioxidants. Riboflavin reacts with unsaturated fatty acid esters by type I photosensitized oxidation to give the same isomeric hydroperoxides as free radical autoxidation.

The type II sensitizer in the triplet state reacts with O_2 by energy transfer to give nonradical singlet oxygen. The singlet oxygen reacts with unsaturated lipids to produce hydroperoxides (reaction 1.7). The *chain breaking antioxidants* do not also inhibit this type of photosensitized oxidation.

$$^3\text{Sens} + O_2 \xrightarrow{h\nu} [\text{intermediate}] + {}^1\text{Sens} \longrightarrow {}^1O_2 \xrightarrow{LH} \text{hydroperoxides} \quad (1.7)$$

Chlorophyll, methylene blue, protoporphyrins and erythrosine react with unsaturated fatty esters by type II photosensitized oxidation.

Propagation

Peroxyl radicals are formed by a rapid reaction between molecualar oxygen and an alkyl of unsaturated lipid (L^o) containing a labile hydrogen (reaction 1.8). Hydroperoxides are also formed by the hydrogen transfer reaction between peroxyl radicals and unsaturated lipids (reaction 1.9).

$$L^o + O_2 \longrightarrow LOO^o \quad (1.8)$$

$$LOO^o + LH \longrightarrow LOOH + L^o \quad (1.9)$$

Termination

Towards the end of autoxidation the peroxyl radicals accumulate. At relatively high levels the peroxyl radicals interact with each other to form non-radical products by the termination reaction. Condensation of peroxyl, alkoxyl or alkyl radicals can constitute termination reactions. Peroxyl radicals can combine to produce peroxyl-linked dimmers (LOOL) with formation of oxygen at low temperatures (reaction 1.10).

$$LOO^o + LOO^o \longrightarrow LOOL + O_2 \quad (1.10)$$

At low oxygen pressures and elevated temperatures, alkoxyl and alkyl radicals can combine to produce ether-containing dimmers (reaction 1.11), and carbon-carbon linked dimmers (reaction 1.12).

$$LO^o + L^o \longrightarrow LOL \quad (1.11)$$

$$L^o + L^o \longrightarrow L\text{-}L \quad (1.12)$$

Antioxidants inhibit or retard lipid oxidation, therefore may be considered under the termination stage. Antioxidants may be classified under various categories depending on their mechanism of inhibition or retardation of lipid oxidation. The *chain-breaking* antioxidants inhibit or retard lipid oxidation by interfering with either chain propagation or initiation by hydrogen-atom transfer and readily donating hydrogen atoms to lipid alkyl, alkoxyl and peroxyl radicals (reactions 1.13 to 1.16).

$LOO^{o} + AH \rightleftharpoons LOOH + A^{o}$ (1.13)

$L^{o} + AH \longrightarrow LH + A^{o}$ (1.14)

$A^{o} + LOO^{o} \longrightarrow LOOA$ (1.15)

$LOO^{o} + AH \longrightarrow LOOH + A^{o}$ (1.16)

Where AH is a chain breaking antioxidant.

To be effective, *chain-breaking* antioxidants produce a relatively stable radical A^{o}. The antioxidant radical A^{o} will either react again with peroxyl radicals to form stable peroxides LOOA by reaction (reaction 1.15) or dimerize with another antioxidant radical to produce A-A by reaction (reaction 1.17).

$A^{o} + A^{o} \longrightarrow A\text{-}A$ (1.17)

Phenolic compounds with bulky alkyl substituents near the hydroxyl group, such as BHA, BHT, TBHQ are effective *chain-breaking* antioxidants. To effectively break the free radical chain, the structure of an active antioxidant is designed to produce phenoxyl radicals in which the unpaired electron is delocalized around the aromatic structure and is stabilized by high resonance energy.

Several types of compounds can inhibit lipid oxidation by mechanisms that do not involve deactivation of free radical chains. One class of antioxidants in this category is known as *initiator inhibitors or preventive antioxidants*. Metal inactivators are the most important compounds of this type; they deactivate metal ions, which promote the initiation and decomposition of hydroperoxides, and thus retard the formation of aldehydes. They function either by coordinating the metals and changing their potential by suppressing the redox reactions producing peroxyl and alkoxyl radicals (reactions 1.3 and 1.4), or by blocking complex formation with hydroperoxides and preventing their decomposition. Common inactivating chelating compounds include citric acid, phosphoric acid, ethylenediamine tetraacetic acid (EDTA), polyphosphates, phytate, and 8-hydroxy-quinoline.

In multi-component systems antioxidants may also be used in combination and reinforce each other by cooperative effects through *synergistic mechanisms*. Many antioxidants are known to

impart more protection against lipid oxidation than sum of the activities of the components when used separately. Effective synergistic inhibition can be achieved if both initiation and propagation are suppressed. Combinations of a preventive metal inactivator such as citric acid or EDTA and a *chain breaking* antioxidant, such as BHA, BHT, TBHQ, or tocopherols are commonly used in foods (Frankel, 2005).

It is evident from the above mechanism that lipid oxidation in food can be influenced by several factors such as temperature, oxygen availability, water activity, exposure to light, the concentration of antioxidants and prooxidants, fat content and distribution, etc (Rutgersson et al., 2000) and metal catalysts (Frankel, 2005). Oxidation of lipids during processing or storage of cereals is a complicated phenomena where the state of the substrate and the balance between antioxidative and prooxidative factors of the matrix play an important role (Kaukovirta-Norja et al., 1998).

Regardless of the actual mechanism of the oxidation and the reasons for it, oxidation of lipids reduces the nutritional value of cereal products, affects the color, and the appearance of the products, and causes the formation of off-odors and off-flavors. Thus, the overall quality of cereal products is affected (Kaukovirta-Norja et al., 1998). Such oxidative processes ultimately leads to the condition of rancidity, resulting in the food becoming unacceptable for consumers.

The methods used to determine the rate at which the oxidation process advances are related to the measure of the concentration of primary or of secondary oxidation products or of both, or to the amount of oxygen consumed during the process. Among those based on the evolution of the concentration of primary oxidation products, peroxide value, which measures hydroperoxide concentration, is one of the most widely used. Some other methods are based on the concentration of secondary oxidation products including aldehydes, ketones, acids, alcohols, lactones, ethers, hydrocarbons and furan derivatives (Gray, 1978; Guillen & Cabo, 2002). Determination of α and β-alkenals content is the basis of the anisidine value method (Guillen & Cabo, 2002

1.5.3. Colour during storage

Color is one of the most important appearance attributes of food materials, since it influences consumer acceptability (Maskan, 2001; Kahyaoglu & Kaya, 2006). Several researchers have

studied the color of food instrumentally (Ahmed et al., 2000; Ahmed et al., 2002). Tristimulus colorimetry has been accepted as a rapid and simple instrumental method of specifying visual perception of the food products (Rocha et al., 1993). The color of any product may be represented in terms of tristimulus L-, a-, and b-values, or combination thereof, depending upon the nature of pigment present in the food material (Shin & Bhowmik, 1994; Avila & Silva, 1999; Ahmed et al., 2000; Ahmed et al., 2002; Zhu et al., 2004; Corzo et al., 2006).

The L a b color space (also referred to as CIELAB) is presently one of the most popular color space for measuring object color and is widely used in virtually all fields. It is one of the color spaces defined by CIE in 1976. In this color space, L indicates lightness and a and b are the chromaticity coordinates. In the a, b chromaticity diagram, the a and b indicate color directions: +a is the red direction, -a is the green direction, +b is the yellow direction, and –b is the blue direction (Minolta, 2002). L-values can range from 0 to 100, while a- and b-values vary between -60 and +60 (Carrefio & Martinez, 1995). ΔE shows the difference in the space between two colors. The sensitivity of the human eye is capable approximately to notice small differences between the colors of the order of 0.2 ΔE (Esteller et al., 2006).

Common browning of foods during storage is usually caused by a chemical reaction between reducing sugars and a free amino group that could part of a protein chain. This reaction is called the Maillard reaction (MR). It is also called non-enzymatic browning to differentiate it from the often rapid enzyme-catalyzed browning (BeMiller & Whistler, 1996). The chemistry underlying the Maillard reaction is very complex. It encompasses a whole network of pathways (Martins et al., 2001) as outlined in Fig. 1.3. In the first step of the MR, the carbonyl group of the reducing carbohydrate and the free amino group of the amino acid or protein form a condensation product with the loss of a molecule of water to form a Schiff base. The N-substituted glucosylamine derived from the cyclisation of the Schiff base is converted to the 1-amino-1-deoxy-2-ketose by the Amadori rearrangement (Dexter et al., 1984; Sensidoni et al., 1999). The subsequent degradation of the Amadori product is dependent on the pH of the system. At pH 7 or below, it undergoes mainly 1,2-enolisation with the formation of furfural (when pentoses are involved) or hydroxymethylfurfural (HMF) (when hexoses are involved). At pH >7 the degradation of the Amadori compound is thought to involve mainly 2,3 enolisation, where reductones, such as 4-hydroxy-5-methyl-2,3-dihydrofuran-3-one (HMFone), and a variety of fission products, including acetol, pyruvaldehyde and diacetyl are formed (Martins et al., 2001).

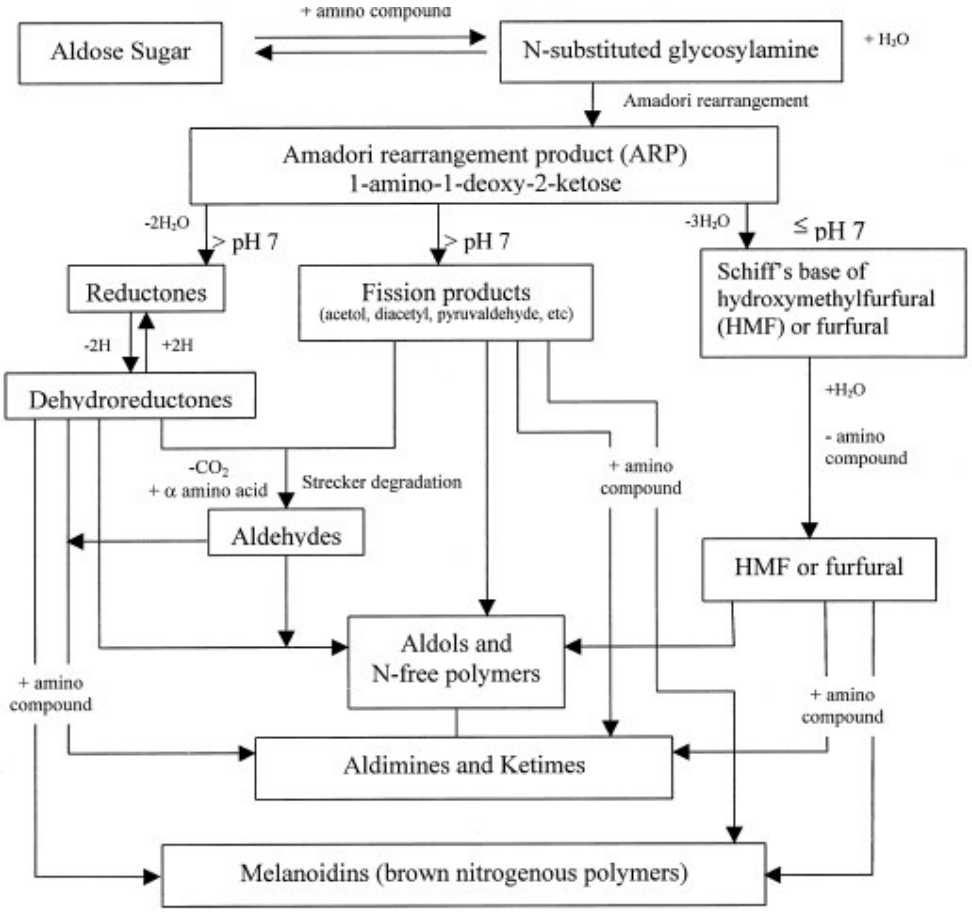

Figure 1.3. Maillard reaction scheme adapted from Hodge (Source: Martins et al., 2001)

The extent of browning reactions is influenced by many other factors such as temperature, time, water activity and state of food system (Resnik & Chirife, 1979; Petriella et al., 1985; O'Briene, 1986; Lerici et al., 1990; Sensidoni et al., 1991; Sensidoni et al., 1999; Kumar et al., 2006), and the concentrations of components (Oh et al., 2006).

Of the many factors which influence the Maillard reaction rate, water activity appears to be particularly important; the initial reaction which produces glycosylamine plus water can be slowed by high water activity values (inhibition by reaction product). In addition, water may enhance deamination reactions for the production of furfural or hydroxyl-methylfurfural (HMF). Another important factor which could decrease reaction rates is the dilution of the reactive components when the water content increases (Sensidoni et al., 1999).

The early stages of Maillard reaction can reduce nutrition value, because they induce a decrease in amino acid availability. For example, the ε-amino group of lysine forms a stable Amadori compound (ε-fructosyl-lysine) which blocks the amino acid; ε-fructosyl-lysine is converted by acid hydrolysis into furosine, an index of the early stages of MR (Dexter et al., 1984; Sensidoni et al., 1999). It has also been speculated that Maillard reaction products inhibit proteolytic and glycolytic enzymes (Friedman, 1996; Rombo et al., 2001).

1.5.4. Microbiological quality of maize meal

Cereals meals ordinarily are not processed to greatly reduce their natural micro flora. Consequently, these products are likely to contain molds, yeasts, and bacteria, which will grow if enough moisture is added. A little moistening will permit growth of molds only, whereas more moisture will allow yeasts and bacteria to grow. Usually, the natural microflora of maize meal does not constitute a spoilage problem in themselves because moisture content is too low to support even the growth of molds. However, storage temperature and moisture may be critical factors affecting quality**.** In a storage study of maize meal, the predominant microorganism molds identified in maize meal were *Aspergillus glaucus* and *Aspergillus candidus*. A few species of *pencillium* and *Fusarium* were also observed. A very small number of *Actinomycetes* were detected in a few samples, but no particular pattern to their occurrence was found (Bothast et al., 1981).

1.6. Pasting and rheological properties

Starch is the major plant storage carbohydrate consumed by mankind. It is an important component of our diet present in starch-rich and processed foods (Ridout et al., 2002). Starch is a major form of carbohydrate in maize meal as well. Starch often contributes to the characteristic properties of foods, and is also added as a functional ingredient in many products. The demand for functionality may vary for different products (Fredriksson et al., 1998). In evaluating the functional properties of starch and starchy-foods, gelatinization, pasting and flow behaviour properties are some of the properties usually studied (Abdelrahim et al., 1995; Bhattacharya & Bhattacharya, 1996; Chen & Ramaswamy, 1999; Jane et al., 1999; Song & Jane, 2000; Yoshimoto et al., 2000; Yoshimoto et al., 2002; Tang et al., 2004; Hagenimana et al., 2007)

1.6.1. Overview of starch granule structure

Despite the advances in the understanding of starch biochemistry and genetics, there is still incomplete understanding of the bio-assembly of granule structure, and insufficient information on the ultra-structure of granules. However, there is a growing interest in this field (Buleon et al., 1998a; Ridout et al., 2002). Native starch granules present three levels of organization: macromolecular structure, crystal structure and ultrastructure. The macromolecular structure of many plant starches have been investigated in detail (Tang et al., 2004).

Based on scattering data and TEM, various models of the crystalline architecture of starch granules have been proposed (Oostergetel & van Bruggem, 1993; Gallant et al., 1997; Ridout et al., 2002). By combining research results provided over the years by a range of microscopic techniques, scientists have been able to gather together some of the pieces of the puzzle concerning starch granule internal structure and organization. This gathering of information is illustratively summarized in Figure 1.4.

Starch granules (2–100 μm) are composed of alternating semi-crystalline (120–500 nm) and amorphous (120–500 nm) growth rings (Vandeputte & Delcour, 2004). Inside the granule the starch polysaccharides are arranged into concentric rings radiating out from the central hilum to the surface of the granule. The number and size of the rings depends on the botanical origin of the starch (Ridout et al., 2002). Experimental studies suggest that the rings are semi-crystalline and composed chiefly of amylopectin (Buleon et al., 1998b; Ridout et al., 2002). It has been suggested that rings can be further subdivided into blocklets (Gallant et al., 1997; Ridout et al., 2002). It is now widely accepted that the amylopectin polymer (which comprises around 75% of the granule composition in non-mutant starches) is predominantly responsible for granule crystallinity (Gallant et al., 1997).

Collaborating evidence for the presence of channels within starch granules comes from the observations of Fannon et al. (1992; 1993) who, using TEM and SEM, have observed surface pores and interior channels in corn, sorghum and millet starches and have observed surface pores along the equatorial groove of wheat, rye and barley starch granules. The surface pores and interior channels are believed to be naturally occurring features of the starch granule structure, with the pores being the external openings of the interior channels (Gallant et al., 1997).

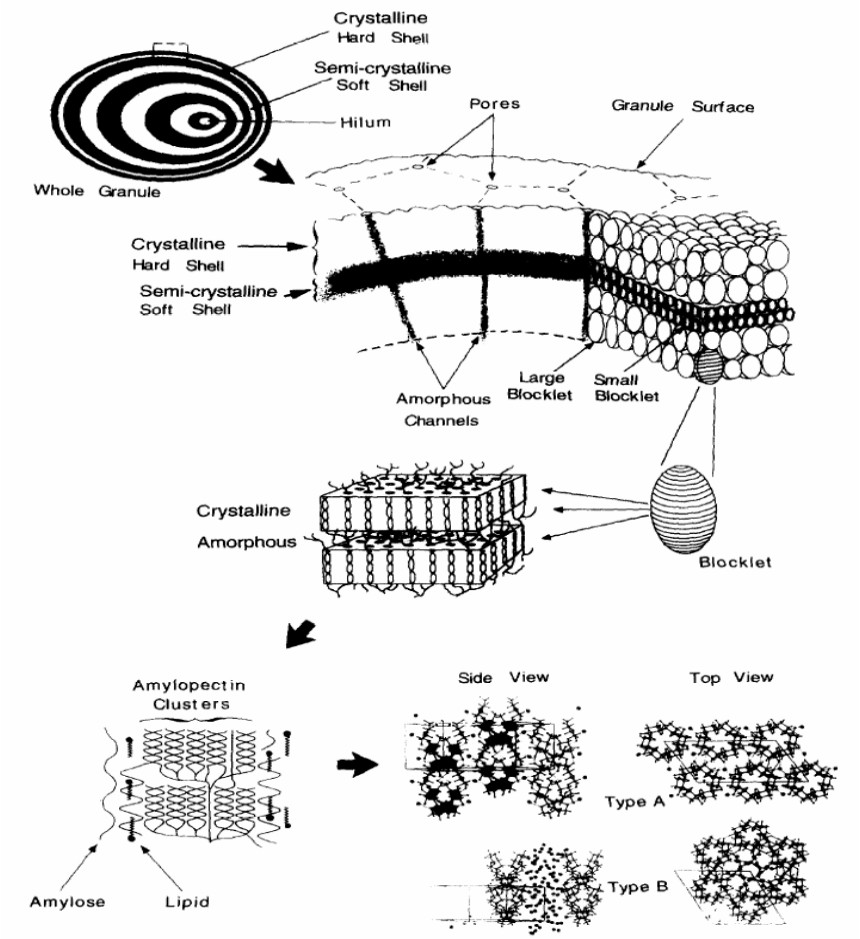

Figure 1.4 Starch granule internal structure and organization (Source: Gallant et al., 1997)

The most probable location of amylose is as randomly interspersed radial chains (Jane et al., 1992; Kasemsuwan & Jane, 1994) with an increasing concentration of amylose (in non-mutant starches) towards the granule exterior (Morrison & Gadan, 1987; Gallant et al., 1997). Furthermore, it is has been hypothesized that amylose may be predominantly located in the amorphous zones of the granule and that increased interaction between amylose and amylopectin in these regions causes their decreased crystallinity (Zobel, 1988; Morrison et al., 1994; Jenkins & Donald, 1995; Gallant et al., 1997).

1.6.2. Starch granule and gelatinization

Many different definitions have been proposed for gelatinization: a phase transition of starch granules from an ordered to a disordered state during heating with excess water (Chaiwanichsiri et al., 2001); the collapse (disruption) of molecular orders within the starch granule manifested in

irreversible changes in properties such as granular swelling, native crystallite melting, loss of birefringence, and starch solubilization (White et al., 1990); ability of starch granules to progress from semi-crystalline to amorphous material when heated in excess water (Tester & Sommerville, 2003); and the break up and partial dissolution of the starch granule upon heating in the presence of water (Tananuwong & Reid 2004).

Research on the structural changes in starch granules induced by heating in the presence of moisture has been achieved using techniques such as differential scanning calorimetry (DSC), infra-red spectroscopy (IR), dynamic mechanical thermal analysis (DMTA), nuclear magnetic resonance (NMR), microscopy and small- and wide-angle X-ray scattering (SAXS, WAXS) (Thiewes & Steeneken, 1997).

The knowledge regarding starch granule structure may be related to the structural changes which occur at the beginning of starch granule swelling. This is the phase when structural changes within the granule are just starting to occur, and relates to the region of the DSC curve when the endothermic peak is just beginning to form. This phase can, therefore, also be considered as the stage where the amorphous regions have been swollen due to water absorption and crystallite melting is just starting to occur (i.e. the beginning of the irreversible swelling process) (Miller et al., 1973; Gallant et al., 1997).

By combining simultaneous SAXS/WAXS data with the results from DSC and SANS experiments, Jenkins & Donald (1998) studied the nature of the gelatinisation process in more detail for a variety of starches. It was found that all starches studied by SAXS/WAXS behaved in broadly the same way. Most of the crystallinity loss occurred during the DSC gelatinization endotherm, but this occurred only after a significant amount of water had already entered the amorphous background region, which has been tentatively identified with the amorphous growth ring seen in etched SEM micrographs. The amorphous background is where all the initial swelling is concentrated, and the repeat distance of the semicrystalline stack remains unchanged at all times during gelatinisation. The driving force for water uptake appears to be so strong in the amorphous background region that SANS on waxy maize shows it appears to pull water out of the amorphous lamellae. Jenkins & Donald (1998) suggested that this is because the rate of transport of water from outside the granule is not sufficiently fast on its own to accommodate the potential swelling process. It appears that only once a large amount of swelling has occurred in the amorphous background is there sufficient stress imposed, by virtue of the connectivity of

molecules from the growth ring into the semicrystalline lamellae, to start disrupting the crystals themselves. Thus the final loss of crystallinity and ultimate breakdown of the granule only occurs quite late in the gelatinisation process.

It has been reported that upon enzymatic attack, the semi-crystalline (soft) layers of the granule are more easily and rapidly hydrolyzed than the crystalline (hard) layers (Gallant et al., 1997). Several researchers have shown that α-amylases can simultaneously solubilize both amorphous and crystalline regions of starch granules (Colonna et al., 1988; Lauro et al., 1999). Crystallinity and gelatinization enthalpy have been shown to decrease during the later stages of α-amylolysis (Lauro et al., 1999). This has been suggested to mean that extensive hydrolysis effectively destroys and solubilizes the crystalline areas of the granule. Gallant et al. (1997) hypothesized that the hydrolysis rate of starch granules depends to a great extent on the distribution of the semi-crystalline and crystalline layers and on the size, identity and interaction of their constituents.

1.6.3. Hydrothermal treatments of starch

Annealing and heat–moisture treatments are related processes, where the starch to moisture ratio, temperature and heating time affects the starch functionality. Annealing represents 'physical modification of starch slurries in water at temperatures below gelatinisation' whereas heat–moisture treatment 'refers to the exposure of starch to higher temperatures at very restricted moisture content (18–27%). Annealing leads to physical reorganisation of starch granules (or appropriate polysaccharide matrices like amylose–lipid complexes) when heated in water (or appropriate plasticiser) at a temperature between glass transition temperature and the onset gelatinisation temperature of the native starch (or polymeric system). Fig 1.5(a) shows the structure of the starch granule of a dry starch, while Fig 1.5(b) shows the hydrated annealed starch (Tester & Debon, 2000).

The effect of annealing at the molecular level of the starch granule has been explained in various ways. Some researchers have discussed the molecular event in terms of increasing granule stability, reorganising granule structure or lowering free energy (Tester & Debon, 2000). Other researchers have discussed annealing with more emphasis on the crystalline and amorphous domains. Crystallinity and crystalline 'perfection' (optimisation of crystalline order) have been proposed (Jacobs et al., 1998; Tester & Debon, 2000).

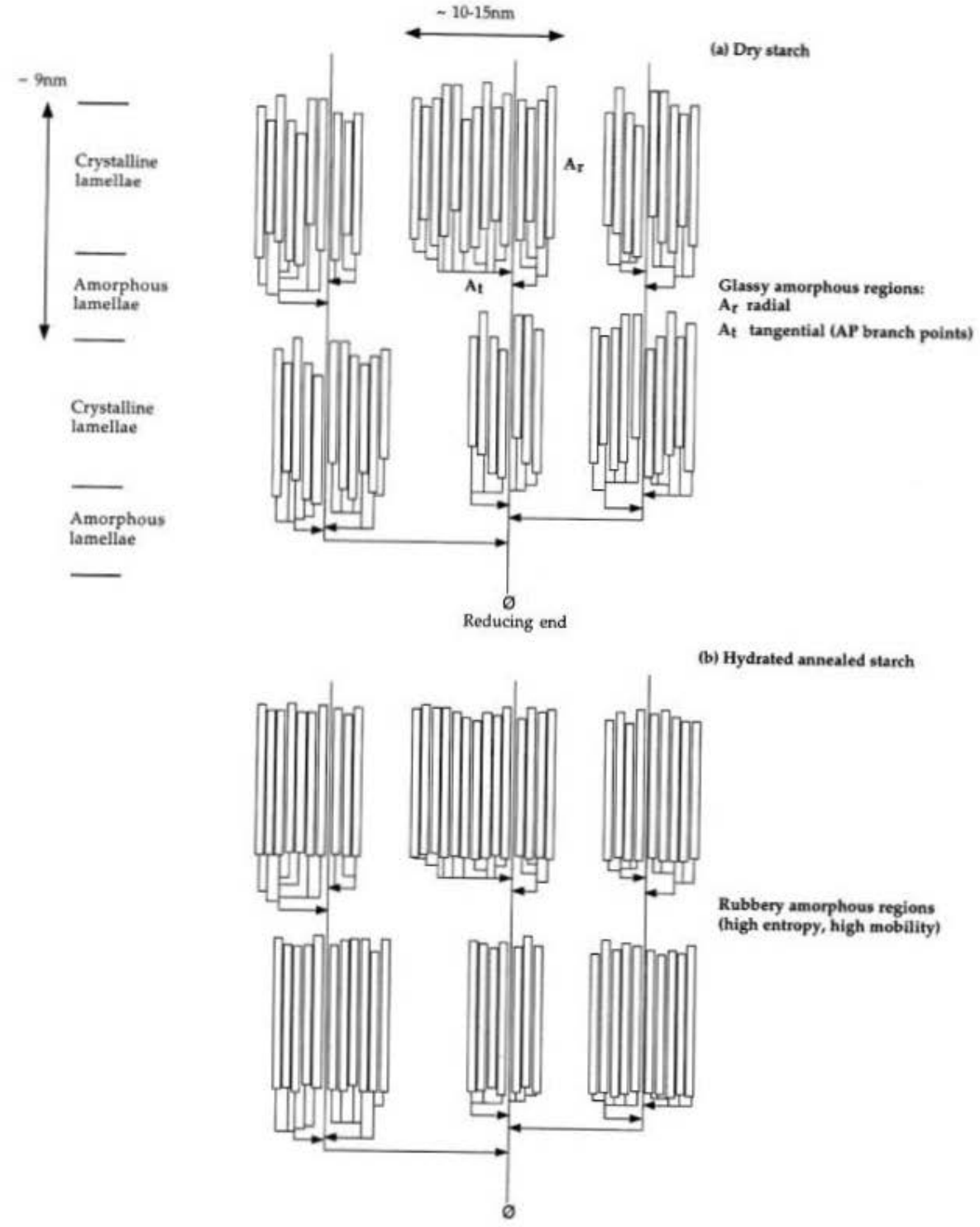

Fig. 1.5. Pictorial representation of the effect of hydration and subsequent annealing on the semi-crystalline lamellae (amylopectin double helices are represented as rectangles): (a) dry starch with glassy amorphous regions; (b) hydrated annealed starch with rubbery amorphous regions (Adopted from Tester & Debon, 2000).

The annealing process improves the crystalline register of existing helices, thereby 'perfecting' starch crystallites (Tester & Debon, 2000). The perfection of the crystallites has been attributed to incipient swelling and the resulting mobility of amorphous α-glucans, which facilitates ordering of double helices and, probably greater ordering of the amorphous regions (Lawal, 2005). Others recognise the importance of interactions between, and mobility of, amorphous and crystalline regions, and the constituent amylose and amylopectin molecules. Further more, granular reorganizations have been discussed in terms of rigidity and realignments and partial melting (Tester & Debon, 2000).

Annealing causes structural rearrangement within starch granules, leading to increase in starch crystallinity. Structural rearrangement enables realignment of bonding forces in starch granules, promoting formation of ordered double helical amylopectin side chain clusters, thereby limiting starch swelling (Lawal, 2005). Enhancement of crystallinity after hydrothermal treatments limits starch swelling which contribute significantly to starch viscosity (Lawal, 2005). The decreased swelling power has been attributed to restriction in percolation of water within starch matrices as a result of increased starch crystallinity after starch modifications (Adebowale et. al., 2005). Reduction in viscosity values following heat moisture treatment has been reported a number of starch types (Hoover & Manuel, 1996a, Hoover & Manuel, 1996b; Adebowale et. al., 2005).

1.6.4. Dynamic rheology

Oscillation tests are known as dynamic tests. In such tests, the stress and strain are temporary oscillatory functions. These functions can be in phase ($\delta = 0^oC$), out of phase ($\delta = 90^oC$) or between 0 and 90^oC. In the first case, a maximum deformation occurs for a maximum stress imposed and it distinguishes an elastic solids. In the second case, a maximum stress is imposed and a minimum deformation is obtained, corresponding to a viscous fluid. In the third case, it is a viscoelastic fluid. Oscillation tests give important results such as the Complex modulus (G*).The complex modulus can be represented as a function of the elastic modulus or storage modulus (G′), and as a function of the viscous modulus or loss modulus (G″):

$$G^* = G' + i\,G'' \qquad (1.18)$$

(Da Costa & Pereira, 2002). In eq. (2.2), G′ measures the elastic response or energy stored per deformation cycle of the material or represents the temporary energy of storage during the test,

and can be recovered afterwards. In the same equation, G″ measures the viscous response or the energy dissipated per deformation cycle of the material or the energy necessary for the fluid flow, being converted into heat. Thus a fluid can be considered viscous (G′ = 0 and G″ = G*), elastic (G′ = G* and G″ = 0) or viscoelastic (G′ ≠ 0 and G″ ≠ 0). The two moduli characterize the solid-like or elastic behavior of the tested material (G′) and liquid-like or fluid-like or viscous (G″) behavior of the material (Tadros, 1996; Da Costa & Pereira, 2002; Chiou et al., 2005; Line, et al., 2005)**.** Rheological measurements, either by transient rotational viscometry or dynamic oscillatory methods, are useful in determining the stability of starch-based products submitted to different processing conditions or in testing different formulation performances (Navarro et al., 1997).

1.6.5. Pasting properties

Pasting is the phenomenon following gelatinisation in the dissolution of starch. A starch paste is a viscous mass consisting of a continuous phase (a molecular dispersion) of solubilised amylose and/or amylopectin and a discontinuous phase of granule remnants (granule ghosts and fragments) (Nelles et al., 2000). It involves granular swelling, exudation of molecular components from the granule, and eventually total disruption of the granules. To some degree, the terms gelatinisation and pasting are interchangeable. Gelatinisation, however, refers specifically to the disruption of molecular order of the starch polymers and occurs first; whilst pasting refers more to the evidence of disruption of molecular order such as viscosity development (i.e. increase in the viscosity of the starch paste). A combination of granule swelling and solubilisation results in a very high increase in viscosity (Ziegler et al., 1993). If shear is applied at this stage, granules are disrupted and a paste is formed (Nelles et al., 2000). Without shear, the granule is not completely solubilised until a temperature in excess of 120 °C is reached (Hoseney, 1998; Nelles et al., 2000).

Typically the pasting curve for maize starch shows a rapid increase in viscosity due to granule swelling and amylose leaching, with a peak in viscosity above the starch gelatinization temperature (Figure 1.6). This is typically followed by a decline in viscosity (viscosity breakdown) due to soluble starch molecules orienting themselves in the direction that the system is being stirred and the break up of starch granules (Nelles et al., 2000). Finally, viscosity increases due to a decrease of energy in the system and subsequent hydrogen bond formation

between starch chains (setback) when the starch product is cooled (Hoseney, 1998; Nelles et al., 2000).

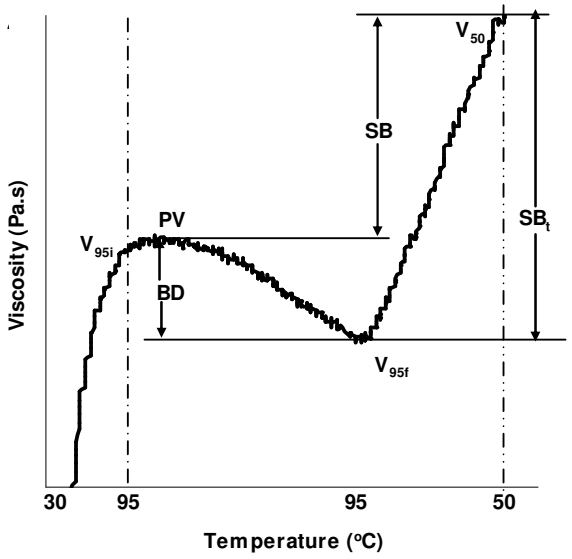

Figure 1.6 Illustration of a pasting curve (Source of definition of parameters: Sowbhagya & Bhattacharya, 2001)

Some of the properties obtained directly from pasting curve include:

(i) Peak viscosity (PV) – maximum value of viscosity reached during 'heating' and 'cooking'
(ii) Initial Hot-paste viscosity (V_{95i}) – initial viscosity as the temperature first reached 95°C
(iii) Final Hot-paste viscosity (V_{95f}) – final viscosity reached at the end of cooking at 95°C
(iv) Cold-paste viscosity (V_{50}) – viscosity value attained as the paste was cooled to 50°C.
(v) Swelling rate (SR) – slope of the pasting curve (McDonough et. al., 2004)

Other properties are derived by calculation from the above properties. These include:

(i) Breakdown index (BD) = PV - V_{95f} (1.19)

(ii) Setback (SB) = V_{50} – PV (1.20)

(iii) Total setback (SB_t) = V_{50} - V_{95f} = BD + SB (1.21)

(iv) Cold-paste: Hot-paste viscosity ratio $C:H = \frac{V_{50}}{V_{95f}}$ (1.22)

Cold-paste viscosity indicates the extent of starch retrogradation that occurs during the cooling process. When hot pastes are cooled, the extent of increase in viscosity is governed by the

re-association tendency of the starch (Hagenimana et al., 2006). Setback value is the recovery of the viscosity during cooling of the heated starch suspension (Singh et al., 2006a). During cooling, re-association between starch molecules, especially amylose, will result in the formation of a gel structure and, therefore, viscosity will increase to a final viscosity. This phase is commonly described as the setback region and is related to retrogradation and reordering of starch molecules (Ragaee & Abdel-Aal, 2006). Sowbhagya & Bhattacharya (2001) have defined C:H ratio as the true reflection of retrogradation during cooling. Sowbhagya & Bhattacharya (2001) found that the C:H ratio is relatively unaffected by the paste concentration but is species specific. They interpreted this as showing that C:H ratio might be a fundamental property and a characteristic index of various starches.

The pasting viscosity properties may be classified into two major groups: primary viscosity values and derived viscosity indexes. Primary viscosity values are properties obtained straight from the viscosity profile graphs during the heating and cooling of the sample suspensions. These properties include PV, V_{95i}, V_{95f} and V_{50}. On the other hand, derived viscosity indexes are calculated values using primary viscosity values and they include BD, SB, SB_t and C:H ratio (Sowbhagya & Bhattacharya, 2001). Sowbhagya & Bhattacharya (2001) has also reported that viscograms of starch flour or flour are on the whole of three types (Figure 1.7).

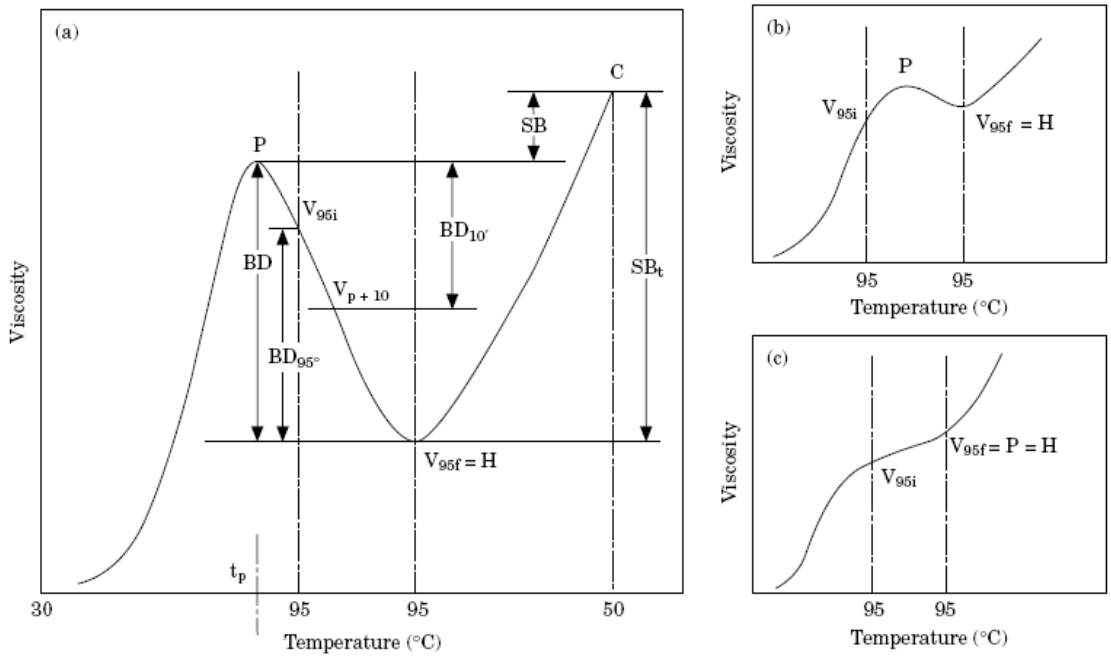

Figure 1.7 Viscograms (Source: Sowbhagya & Bhattacharya, 2001)

The first type is characterized by the PV appearing before the V_{95i}, (Figure 1.7a) whereas the second type by PV appearing between the cooking period i.e. between V_{95i} and V_{95f} (Figure 1.7b) and the third by the absence of a well defined PV (Figure 1.7c). In the third type, the viscosity continues to rise until V_{95f}, where the V_{95f} is taken as PV.

A number of studies have reported significant changes in the Rapid Visco-Analyzer (RVA) in cereals during storage such as in maize (McDonough et al., 2004), in rice (Zhou et al., 2002) and rough rice (Sowbhagya & Bhattacharya, 2001; Zhou et al., 2003). The pasting of starch granules have been mostly studied (Noomhorm et al., 1997; Wang et al., 2000; Zhou et al., 2003; Oluwamukomi et al., 2005; Anderson & Guraya, 2006; Lim & Narsimhan, 2006; Ragaee & Abdel-Aal, 2006;).

1.6.6. Flow behavior properties

Rheological properties of food products have been found to be strongly influenced by temperature, concentration and physical state of dispersion (Ahmed et al., 2007). A number of models are used to describe flow behaviour. The most commonly evaluated models include Power law, Herschel-Bulkley, Casson, and Bingham, for instance, in starch solution (Abdeh-ahim et al., 1995), cooked maize flour suspensions (Bhattacharya and Bhattacharya, 1996), rice flour (Hagenimana et al., 2007) and tapioca starch (Chen & Ramaswamy, 1999). Food industries often use cooked maize flour and starch suspensions (Bhattacharya & Bhattacharya, 1996). In maize meal related products, Bhattacharya & Bhattacharya (1996) found the Herschel-Bulkley and Mizrahi-Berk models to best fit cooked maize flour suspensions at concentrations between 2 and 10%. The flow behaviour index (*n)* less than unity means that the substance exhibits a shear-thinning behavior, while a greater than unity value means that the substance exhibits a shear-thickening behaviour (Al-Malah et al., 2000).

Rheological measurements have been considered as an analytical tool to provide fundamental insights on the structural organization of food and play an important role in heat transfer to fluid foods (Ahmed et al., 2007). Rheological data, such as shear rate and shear stress, can provide information that is useful for the design of flow systems, heat exchangers, mixing and pumping, evaporators, sterilizers and filters (Rao, 1987; Bhattacharya & Bhattacharya, 1996), as well as for the sensory assessment of viscosity (Bhattacharya & Bhattacharya, 1996). Yield stress is an important quality control parameter to process industries. A true value of the yield stress could

be beneficial for the optimal design of food-processing systems such as those required during thermal processing (Steffe, 1992; Ahmed et al., 2007), and is important in preventing flow (Bhattacharya & Bhattacharya, 1996).

1.7. Conclusions

Maize, particularly white maize, is a staple food in many parts of Africa, of which maize meal is the major form of maize utilization in Africa. Maize meal is produced by dry milling process – degerming and non-degerming processes. The degerming processes are used by large commercial milling firms and produces varying types of superior (refined) maize meals depending on the extraction rates. The nutritional compositions of the maize meals are highly dependent upon the extraction rates. Consumer preference of the maize meal types is much more dependent on the color and level of refining the product. The new trends in maize meal production underway in Africa include fortification. The socio-economic importance of maize meal to Africa lies in its home to industrial food applications; hence a major contributor to the nutrition of the African population. Despite maize meal being a staple food for Africa with high involvement in commerce, literature is either scarce or non-existent on the stability of functional properties of the African maize meal types during storage or distribution in commerce. Moisture sorption isotherms in literature for maize related products seem to have concentrated on yellow maize grain and maize meal. Research done on maize grain and other cereals has shown that storage can have influence on the functional properties.

1.8. Problem statement

It has been established from the literature review that white maize meal is of economic importance in many of the African countries as a staple food. Many small to large international enterprises are involved in processing and distribution of white maize meal. The distribution chains of the white maize meal may vary from one country to another. However, in Zambia, the distribution of white maize meal from the commercial millers to the final consumer involves many forms of product treatment some of which affect its quality.

When white maize meal is produced at the mills, it might be in the warehouse for days or weeks before being dispatched to wholesalers or directly to retailers. At the wholesalers or retailers the white maize meal might further stay for days or weeks before the consumer buys it. The

consumer as well will keep it for days or weeks while consuming it, depending on the packaging volume and other factors such as the consumption rate. Some data about how long consumers keep the maize meal has been provided by Okoth & Ohingo (2004) who found that weaning flours (including maize meal) for young children was kept up to five weeks while it was being consumed.

Most millers in Zambia use polypropylene sacks for packaging white maize meal. Often, it is also packed in polyethylene plastics of varying properties. At the retail level, white maize meal is often repackaged from the manufacturer's package into smaller and thin transparent polyethylene plastics to make the price of white maize meal affordable. In addition, the re-packaged white maize meal is usually sold by placing it on shelves exposed to the direct sunlight during the day in open markets. These practices may affect the quality of white maize meal during storage and distribution. This ultimately affects its shelf life. Like any food, if the quality of white maize meal is to be retained, the optimal conditions must be provided during processing, marketing, distribution and storage. However, to obtain the optimum conditions for the storage and distribution of white maize meal, there is need to have adequate data on the chemical, microbiological and physical stability of the white maize meal under such varying conditions.

The chemical, microbiological and physical properties of the white maize meal will depend on the climatic storage conditions where the white maize meal is stored and distributed. It has been shown from the literature review (section 1.3) and is well known fact that Africa's climatic conditions such as temperature, humidity and sunlight are on the extreme high, where for example, temperatures of above 45^{o}C are not uncommon. If the white maize meal is affected in the storage and distribution chain, being a staple food and a major ingredient in preparations of many African foods as shown from literature review, it will have far reaching consequences on the food quality and safety for the populations consuming such foods. In addition, the new trends of maize meal production, such as fortification, will probably make white maize meal even more susceptible to deterioration under the already difficult storage and distribution chain.

The literature review has also shown that data on the stability of physico-chemical and functional properties of the white maize meal types being consumed in Africa is either scarce or non-existent. This data might be important in determining the possible quality and safety effects that maize meal will impart on the food products made from it. Without such data, it also becomes difficult to recommend storage conditions during distribution, types of suitable packaging and

the accurate determination of the shelf life of the maize meal. Studies into such aspects may generate data required by policy makers and implementers of regulations regarding food quality and safety. Therefore, the research objectives of this study were:

1.9. Research objectives

1.9.1. Overall objective

The main objective of this research was:

- To investigate changes in functional properties of white maize meal during storage under tropical conditions

1.9.2. Specific objectives

The specific objectives of the research were:

- To determine the moisture sorption behaviour of Zambian white maize meal during storage
- To determine changes in chemical and sensory properties of Zambian white maize meal during storage at tropical conditions
- To determine pasting and rheological behaviour of Zambian white maize meal during storage at tropical conditions

1.10. Storage conditions to be studied

Storage conditions to be evaluated in this study were chosen on the basis of approximating the average normal to worst case climatic scenarios in Africa in general. Four conditions were selected as given below:

(a) Normal average seasonal temperature taken as 25^{o}C with low humidity taken as 43%

(b) Normal average seasonal temperature taken as 25^{o}C with high humidity taken as 90%

(c) Hot season temperature for worst case taken as 45^{o}C with low humidity taken as 43%

(d) Hot season temperature for worst case taken as 45^{o}C with high humidity taken as 90%

Further more, three packaging case scenarios were to be evaluated for storage under these climatic conditions as described below:

(a) *Open bulk storage*: This scenario was experimentally simulated by storing the maize meal directly exposed to the four climatic case scenarios above
(b) *Maize meal storage in commonly used packaging materials in Zambia*: This scenario was simulated by storing maize meal covered in the packaging materials under investigation, then exposed to the four climatic case scenarios above
(c) *Maize meal in closed bottles*: This scenario was simulated by storing maize meal in glass bottles with cover caps and the bottles with their contents were stored at the normal average seasonal temperature (25^{o}C) and hot seasonal temperature (43^{o}C).

The experiments involving fortified maize meal were performed as a special case in which the interest was to establish the influence of fortification and sunlight exposure on the quality properties dealing with rancidity of maize meal.

Chapter 2

Moisture sorption of white maize meal

Chapter 2. Moisture sorption of white maize meal

Abstract

This chapter outlines moisture sorption properties of white maize meal. This included determining moisture adsorption isotherms before defatting (non-defatted) and after defatting (defatted) the white maize meal. The influence of storage conditions on moisture and water activity was also evaluated. Adsorption moisture isotherms of the non-defatted and the defatted white maize were experimentally determined at 25, 30 and 45^{o}C. The adsorption isotherms for non-defatted and defatted white maize meal, exhibited a sigmoidal shape, representing Type II isotherms. The equilibrium moisture content increased with decrease in temperature at the same water activity. The isotherm data was better fitted to GAB, Oswin and Smith models for both non-defatted and defatted white maize meals, with the GAB model being the best. The models fitted much better for non-defatted than for defatted white maize meals. The differential heat of sorption and entropy increased with decreasing moisture content and the moisture adsorption was found to be enthalpy-driven. The monolayer moisture content decreased with increase in temperature of sorption. Monolayer moisture content increased upon defatting at a lower temperature (30^{o}C) but not significantly at higher temperature (45^{o}C).

The changes in moisture content of maize meal stored at temperature-humidity of 25^{o}C-43%RH, 25^{o}C-90%RH, 45^{o}C-43%RH and 45^{o}C-90%RH showed that at constant storage relative humidity, white maize meal absorbed or lost more moisture at high storage temperatures than at low storage temperatures.

The water activity of maize meal stored in polypropylene at low storage relative humidity decreased whereas at high storage relative humidity increased during the storage period. On the other hand, the water activity of the maize meal stored in polyethylene at high storage relative humidity was essentially constant while at low storage relative humidity decreased. Changes in water activity in fortified and unfortified maize meal during storage was influenced by the packaging type.

Key words: *Adsorption isotherms, Differential heat of sorption, Differential entropy of sorption, Fortification, Maize meal, Moisture, Packaging, Storage, Relative humidity, Water activity*

2.1. Introduction

Moisture sorption isotherms show in graphical form the variation in water activity (A_w) with change in moisture content of sample at a specified temperature (Rahman, 1995). Moisture sorption is an extremely valuable tool for the food scientist because it can be used in, prediction of potential changes in food stability, packaging selection, ingredient selection (Bell & Labuza, 2000), process design, process control, thermodynamic properties prediction and structure investigation (Rahman, 1995). On the basis of this insight, more rational bases are established for improving processing, packaging and storage conditions for both raw and processed foods (Sing et al., 2006b).

In terms of thermodynamic properties, the net isosteric heat of sorption, or differential enthalpy, is an indicator of the state of water adsorbed by the solid particles, which in turn is a measure of the physical, chemical and microbial stability of biological materials under storage (Fasina et al., 1997; McMinn et al., 2007; Toğrul & Arslan, 2007); differential entropy is proportional to the number of available sorption sites at a specific energy level (Madamba et al., 1996). Enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as sorption reactions. The theory states that in order to minimize free energy changes due to these phenomena, compensation (by changing ΔH_d or ΔS_d) arises from the nature of the interaction between the solute and solvent causing the reaction and that the relationship between the enthalpy and entropy for a specific reaction is linear (Madamba et al., 1996; Fasina, 2006). Beristain et al. (1996) successfully applied the enthalpy–entropy compensation to water adsorption in starchy materials.

White maize meal is stored at various stages of commerce and Africa's climatic conditions are on the extreme high in temperature, humidity, and sunlight, where temperatures of above 45^{o}C are not uncommon (BBC Weather, 2005). This may alter the moisture sorption properties of maize meal; hence affect the water activity of the maize meal during distribution. One of the major differences in the composition of the commercial maize meal brands in Africa is the oil content due to different levels of germ extraction. It is envisaged that oil in maize meal influences the moisture adsorption properties.

Literature found shows that most moisture sorption studies have been concentrated on yellow maize and maize meal (Labuza et al., 1985; Wicklow et al., 1998; Abdullah et al., 2000;

Samapundo et al., 2007). Despite white maize meal being a staple food and hence of commercial significance to many parts of Africa, data on sorption isotherms of white maize meals under commerce in this region is scarce.

Therefore, the purpose of this part of the study was to determine the:
(a) adsorption isotherms of white maize meal at 25, 30 and 45^{o}C, assess several sorption models for their ability to describe the experimental adsorption data, use the best fitting model to estimate thermodynamic properties and, compare the adsorption isotherms of non-defatted and defatted white maize meal
(b) influence of storage conditions on moisture content and water activity of maize meal

2.2. Adsorption isotherms of white maize meal before and after defatting

2.2.1. Materials

Freshly produced 25kg of white roller meal was obtained from National Milling Corporation (Lusaka, Zambia). Roller maize meal is a partially degermed commercial brand on the Zambian market (Table 1.2). It is produced by dry milling at extraction rates between 80-85% (Jayne et al., 1996). Chemicals were purchased from (Merck, South Africa). The glass jars were purchased from Game Stores (Zambia).

2.2.2. Proximate analysis of white maize meal

Proximate analysis of the white maize meal was carried out in triplicates according to AOAC methods (1998): moisture content, crude protein content, ash content, and crude fiber content. Oil content of the maize meal was determined in triplicates by shaking 5g of maize meal in 100ml chloroform-methanol (2:1 v/v) mixture for 8 hours at room temperature according to Folch et al. (1957). The mixture was passed through filter paper to remove the insoluble material. The extract was evaporated to dryness in a rotary evaporator at 40°C under reduced pressure. Total carbohydrate was calculated by difference. The determinations were calculated as % on wet basis.

2.2.3. Defatting the white maize meal for adsorption isotherms

Samples of 100g were extracted using redistilled technical n-hexane, by continuous extraction in a Soxhlet equipment for 8 h. Residual solvent was removed by evaporation in a forced air circulation oven at 40°C for 1 hour.

2.2.4. Sample preparation for adsorption isotherms

About 200g of the maize meal sample was dehydrated in a forced air circulation oven at 70°C for 24 h.

2.2.5. Determination of adsorption isotherms

The equilibrium moisture content (EMC) of the dehydrated non-defatted and defatted white maize meal was determined by a gravimetric technique, in which the weight was monitored discontinuously. A 2 ± 0.001 g sample of the white maize meal was weighed in a glass petri-dish and the petri-dishes were placed inside a glass jar in triplicate. Sulphuric acid solutions were used to maintain the specified relative humidity inside the glass jars. The effect of temperature and acid concentration on the equilibrium relative humidity values of sulphuric acid solutions are presented in Table 2.1 (Ruegg, 1980). Sulphuric acid has been used in sorption isotherm studies by other researchers (Peng et al., 2007).

Table 2.1. Water activity of sulphuric acid solutions at selected concentrations and temperature[$]

H_2SO_4 solutions %(v/v)	Water activity (A_w)		
	25°C	30°C	45°C
20	0.8805	0.8814	0.8839
30	0.7521	0.7549	0.7629
40	0.5656	0.5711	0.5866
50	0.3509	0.3574	0.3765
60	0.1625	0.1677	0.1834
70	0.0445	0.0470	0.0548

[$]Source: Ruegg (1980)

The prepared glass jars were capped and placed in temperature controlled incubators maintained at 25, 30 and 45 ± 1°C. The samples were allowed to equilibrate until there was no discernible weight change (±0.001 g). After equilibration, the moisture content was determined by drying in a forced air circulation oven at 130°C for 1 h (AOAC, 1998). The moisture content was calculated on dry basis.

2.2.6. Modelling of adsorption isotherms

Six sorption isotherm models, shown in Table 2.2, were fitted to the experimental data of adsorption isotherms for non-defatted and defatted white maize meal.

Table 2.2. Isotherm models for experimental data fitting

Isotherm	**Model***	**Source**
Smith (1947)	$M_w = A + BLn(1-a_w)$	Rahman (1995)
Oswin (1946)	$M_w = A\left[\frac{a_w}{1-a_w}\right]^B$	Rahman (1995)
Henderson (1952)	$M_w = \left[\frac{Ln(1-a_w)}{-A}\right]^{1/B}$	Rahman (1995)
Chung and Pfost (1967)	$M_w = -\frac{1}{B}Ln\left[\frac{-Lna_w}{A}\right]$	Rahman (1995)
Iglesias and Chirife (1981)	$M_w = A + B\left[\frac{a_w}{(1-a_w)}\right]$	Shivhare et al. (2004)
GAB$ (1985)	$M_w = \frac{M_{gm}YKa_w}{(1-Ka_w)(1-Ka_w+YKa_w)}$	Rahman (1995)

*A and B are constant, M_w the moisture content (g/g dry basis), a_w the water activity, M_{gm} the GAB monolayer moisture content (gH_2O/g db), Y the GAB model parameter and K the GAB model parameter.

$Guggenheim-Andersen-de Boer

These sorption models are amongst those most widely used to describe sorption isotherms for various food materials. The parameters of the sorption models were estimated using nonlinear regression function of SPSS® Version 11.0 (SPSS Inc., Chicago). The goodness of fit of the

models was evaluated by means of determination coefficient (r^2) and the mean relative error (MRE) as a percentage, defined as:

$$MRE(\%) = \frac{100}{N}\sum_{i=1}^{N}\frac{\left|E_{ei} - E_{ci}\right|}{E_{ei}} \tag{2.1}$$

where E_{ei} and E_{ci} are the experimental and predicted EMC values, respectively, and N is the number of experimental data. A model is considered acceptable if it has a MRE value less than 10% (Kaymak-Ertekin & Gedik, 2005).

2.2.7. Thermodynamic functions

2.2.7.1. Isosteric heat of sorption

The net isosteric heat of sorption, or differential enthalpy (Δh_d) was determined from the experimental data using the Clausius–Clapeyron equation (Tsami et al., 1990):

$$-\Delta h_d = R\left[\frac{d(LnA_w)}{d(1/T)}\right]_x \tag{2.2}$$

Re-plotting the experimental sorption isotherm in the form $Ln(A_w)$ versus $1/T$, for a specific moisture content x, the slope of the regression line $-\Delta h_d / R$ provided a measure of the net isosteric heat of sorption.

This procedure is based on the assumption that (Δh_d) is invariant with temperature, with measurement of the sorption isotherms at more than two temperatures being required for application of the method (Tsami et al., 1990; McMinn et al., 2007).

2.2.7.2. Enthalpy–entropy compensation

The differential entropy (ΔS_d) was obtained by fitting the equation:

$$(-InA_w)_x = \Delta h_d / RT - \Delta S_d / R \tag{2.3}$$

to the equilibrium data $Ln(A_w)$ versus $1/T$. The differential entropy of sorption (ΔS_d) at a specific moisture content, was determined from the intercept $\Delta S_d / R$. The differential entropy (ΔS_d) was determined at different moisture contents allowing the variation in (Δh_d) and (ΔS_d) with moisture content to be determined (Aguerre et al., 1986).

The enthalpy–entropy compensation theory proposes a linear relationship between (Δh_d) and (ΔS_d) (Leffer & Grunwald, 1963):

$$\Delta h_d = T_\beta \Delta S_d + \Delta G \tag{2.4}$$

From a plot of (Δh_d) versus (ΔS_d), the isokinetic temperature T_β and free energy at T_β (ΔG) were calculated using linear regression. To corroborate the existence of true compensation a statistical analysis test, proposed by Krug et al. (1976a, 1976b) was applied to the data. This involved comparison of the isokinetic temperature with the harmonic mean temperature (T_{hm}):

$$T_{hm} = \left(\frac{n}{\sum_{i=1}^{n} \frac{1}{T}} \right) \tag{2.5}$$

Where n is the total number of isotherms used and T is the temperature in kelvins.

An approximate $(1-\alpha)100$ percent confidence interval for T_β may be calculated from:

$$T_\beta = \hat{T}_\beta \pm t_{m-2,\alpha/2} \sqrt{Var(T_\beta)} \tag{2.6}$$

Where

$$\hat{T}_\beta = \frac{\sum (\Delta h_d - \overline{\Delta h}_d)(\Delta S_d - \overline{\Delta S}_d)}{\sum (\Delta S_d - \overline{\Delta S}_d)^2} \tag{2.7}$$

$$Var(T_\beta) = \frac{\sum (\Delta h_d - \Delta G - \hat{T}_\beta \Delta S_d)^2}{(m-2)\sum (\Delta S_d - \overline{\Delta S}_d)^2} \tag{2.8}$$

In Eq. 2.7 and 2.8, m is the number of $(\Delta h_d, \Delta S_d)$ data pairs, $(\overline{\Delta h_d})$ is the average enthalpy, and $(\overline{\Delta S_d})$ the average entropy (Gabas et al., 2000; McMinn et al., 2007). The compensation theory only applies if $T_\beta \neq T_{hm}$. If T_{hm} is within the T_β interval, the observed distribution of data in the $(\Delta h_d, -\Delta S_d)$ plane solely reflects experimental error, and not chemical factors (Beristain et al., 1996). In this work a 95% confidence interval for T_β was calculated for the data.

2.2.7.3. Monolayer moisture content

The monolayer moisture content (M_{gm}) was determined from the GAB model (Table 2.2).

2.2.8. Results and Discussion

2.2.8.1. Proximate composition

The non-defatted white maize meal used in this study was analysed for proximate composition and was found to have moisture 10.37 ± 0.05%, crude protein (Nx6.25) 9.17 ± 0.15%, crude oil 3.66 ± 0.04 %, crude fibre 1.96 ± 0.42 %, ash 1.92 ± 0.12 % and carbohydrates (by difference) 72.92% wb.

2.2.8.2. Adsorption isotherms of non-defatted white maize meal

The sorption isotherm is defined as the relationship between the water activity (or the equilibrium relative humidity – ERH of the surrounding air) and the equilibrium moisture content (EMC) of the material at constant temperature. Desorption isotherms are obtained when the equilibrium process departs from wet samples and allows them to equilibrate with the surrounding air by loosing moisture, and adsorption isotherms are the equilibrium process that departs from dry samples. The adsorption isotherms of the non-defatted white maize meal at 25, 30 and 45^{o}C are shown in Figure 2.1. The adsorption isotherms have a sigmoidal shape showing an increase in the EMC with A_w. Adsorption of water can be ascribed to the basic components of foods such as polymeric materials, proteins, starch and soluble solids e.g. sugars at high moisture contents (Kumar et al., 2005b). The sigmoidal-shaped curve of the isotherms obtained in this study represents Type II isotherms, according to the classification introduced by Brunauer as

reported by Bell & Labuza (2000). This has also been reported for yellow dent corn by Samapundo et al. (2007).

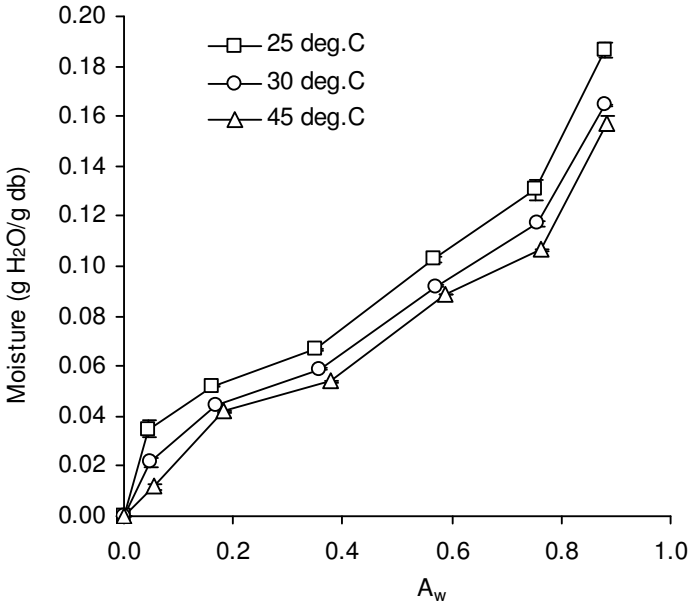

Figure 2.1. Adsorption isotherms of non-defatted white maize meal at 25, 30 and 45^{o}C (Bars represent standard deviations for n=3)

The EMC values of white maize meal obtained are very comparable to the ones by Abdullah et al. (2000) in their determination in corn flour (cornmeal) and Wicklow et al. (1998) in a hybrid maize grain, particularly at 25^{o}C (corn flour, cf. Section 1.5.1). However, comparing EMC values obtained for white maize meal to those obtained by Labuza et al. (1985) and Samapundo et al. (2007) at 25, 30 or 45^{o}C, they appear to be lower. This is probably due to the different working conditions such as dehydration methods and variety differences in the products.

Figure 2.1 also illustrates the temperature dependence of the adsorption isotherms of the white maize meal. The EMC is seen to increase with decrease in temperature at the same A_w, or A_w is seen to increase with temperature at the same EMC. This indicates that the white maize meal becomes less hygroscopic when temperature is increased. This is because with increase in temperature, water molecules get activated due to their energy level, causing them to become less stable and to break away from the water binding site of the food materials (Hossain et al., 2001; Fasina, 2006). Further, Mazza & Lemaguer (1980) and Samapundo et al. (2007) have

suggested that an increase in temperature induces physical and/or chemical changes in the product that can reduce the number of active sites for water binding. The temperature shifts observed have an important practical effect on the chemical and microbiological reactions which cause quality deterioration (Al-Muhtaseb et al., 2004a). An increase in temperature causes an increase in the A_w, at the same moisture content, which in turn causes an increase in the reaction rates leading to quality deterioration (Van den Berg & Bruin, 1981; Al-Muhtaseb et al., 2004a). Hence, this phenomenon can be a major determinant of shelf life of food products.

2.2.8.3. Modelling of adsorption isotherms for non-defatted white maize meal

Tables 2.3 shows the coefficients of the models fitted to the experimental adsorption isotherm data by non-linear regression for non-defatted and defatted white maize meal. The table also gives the MRE (%) and the determination coefficients (r^2) which are used to assess the fitness of the model to the experimental data. The GAB, Oswin, Smith and Chung-Pfost models had an average MRE (%) less than 10 for non-defatted maize meal. The GAB model gave the smallest average MRE followed by the Oswin, Smith and Chung-Pfost models. The Henderson and Iglesias-Chirife models had an average MRE (%) greater than 10. The determination coefficients (r^2) for all six models were greater than 0.939. The GAB and Oswin models had the same and highest determination coefficients ($r^2 = 0.9967$), followed by the Smith, Chung-Pfost, Henderson and Iglesias-Chirife models which had the least.

The experimental adsorption data and the fitted models for the best-fit (GAB model) is shown in Figures 2.2. The usefulness of models may also be assessed considering the number of parameters involved. The Oswin and Smith models use two against three parameters on the GAB model. A small number of parameters for modeling not only simplifies the calculation procedure, but also contributes to obtain more reliable values, since it decreases the degrees of freedom on the identification procedure (García-Pérez et al., 2007). While the model-selection-statistics show that the GAB, Oswin and Smith models could be used acceptably for the white maize meal, it seems that the GAB model would be the best option. The GAB model would additionally provide parameters with physical meaning. Its only drawback, however, is the high number of parameters to be identified.

Table 2.3 Parameter estimates of the models fitted to adsorption isotherms of non-defatted and defatted white maize meal at 25, 30 and 45°C

Model	Non-defatted roller meal			Defatted roller meal	
	Temperature (°C)			Temperature (°C)	
	25	30	45	30	45
Smith (1974)					
A	0.03686	0.02837	0.02420	0.04270	0.03678
B	-0.07035	-0.06492	-0.06133	-0.08432	-0.07450
r^2	0.9966	0.9924	0.9891	0.9980	0.9654
MRE (%)	5.0920	9.8135	11.7868	4.9674	10.1991
Oswin (1946)					
A	0.09049	0.0777	0.07014	0.10622	0.09075
B	0.3561	0.3759	0.3959	0.36512	0.38677
r^2	0.9972	0.9978	0.9945	0.9977	0.9684
MRE (%)	5.6711	5.2470	8.4206	5.2115	12.5752
Henderson (1952)					
A	51.6837	50.3207	47.4015	34.2815	37.1383
B	1.8402	1.7168	1.6254	1.7870	1.7053
r^2	0.9849	0.9940	0.9910	0.9821	0.9383
MRE (%)	16.6100	9.6229	9.3735	17.6659	23.3736
Chung & Pfost (1967)					
A	5.3952	4.5880	4.1704	5.2332	5.0530
B	21.2987	22.7280	23.7301	17.7540	20.0076
r^2	0.9885	0.9949	0.9916	0.9860	0.9451
MRE (%)	10.7738	7.8792	8.9988	11.5340	15.2144
Iglesias & Chirife (1981)					
A	0.05571	0.04652	0.04202	0.06525	0.05571
B	0.019158	0.01735	0.01617	0.02302	0.02089
r^2	0.9549	0.9388	0.9394	0.9646	0.9749
MRE (%)	16.4788	21.0749	21.0780	15.8517	14.0219
GAB (1984)					
M_{gm} (gH_2O/g solids)	0.05304	0.05065	0.04642	0.06047	0.0461
Y	43.6805	18.6116	14.9885	49.3066	123.4292
K	0.8138	0.7907	0.7982	0.8299	0.8790
r^2	0.9974	0.9979	0.9944	0.9996	0.9735
MRE (%)	3.3173	3.3029	6.7148	1.3283	11.5532

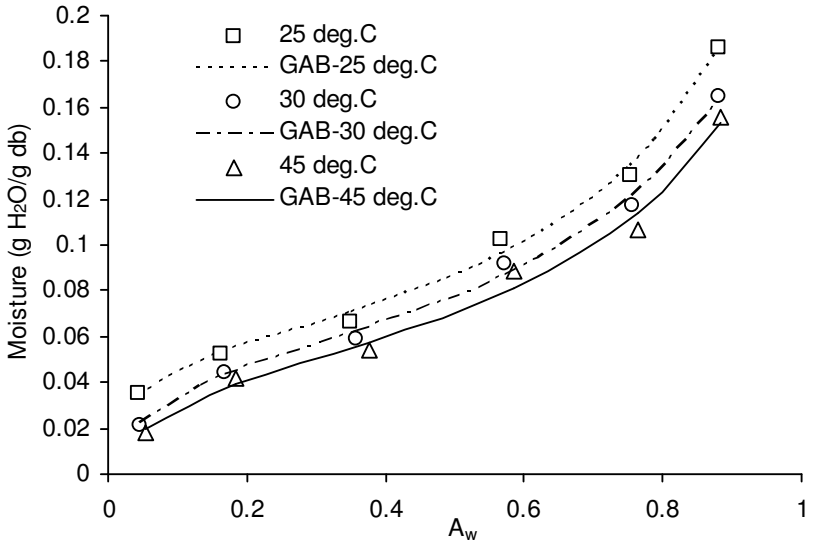

Figure 2.2. Experimental vs predicted values of the GAB model for non-defatted white maize meal

The GAB model has also been previously considered the best-fit model for many food materials in general over a wide range of water activity (Van den Berg, 1984; Rahman, 1995; McMinn & Magee, 1999; Timmermann et al., 2001; Al-Muhtaseb et al., 2004a), and yellow dent corn (Samapundo et al., 2007) in particular. However, it must be mentioned that the goodness of fit of a sorption model to experimental data does not describe the nature of the sorption process, it only reflects on the mathematical quality of the model. Also as water is associated with the food matrix by different mechanisms in different A_w regions, no single model can be considered accurate over the entire A_w range (Labuza, 1975; Samapundo et al., 2007).

2.2.8.4. Thermodynamic functions of non-defatted white maize meal

2.2.8.4.1. Differential enthalpy and entropy

The differential enthalpy and entropy at different moisture contents were respectively obtained from the slope and intercept of $Ln(A_w)$ versus $1/T$. The A_w at different constant EMCs were obtained by the best fitting model, the GAB model. Figure 2.3 shows the plots of differential enthalpy and entropy as a function of moisture content. The graphs clearly show an exponential decrease in differential enthalpy and entropy with increasing moisture content.

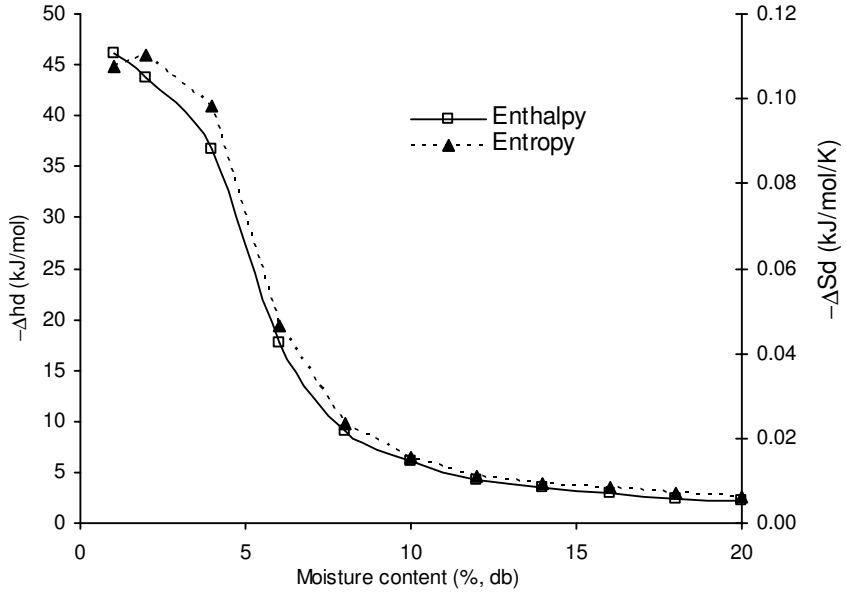

Figure 2.3. Differential Enthalpy and Entropy of adsorption as a function of moisture content for white maize meal

This trend has also been reported in yellow dent corn for isosetric heat of sorption (Samapundo et al., 2007); and for isostetric heat of sorption and entropy in cookies and corn snacks (Palou et al., 1997), potatoes (Beristain et al., 1996; McLaughlin & Magee, 1998), sweet potatoes (Fasina, 2006) and potato starches (Al-Muhtaseb et al., 2004b). This marked decrease has been attributed to the fact that sorption initially occurs on the most active primary sites giving rise to higher exothermic interaction energies than those released when these sites become occupied (Iglesias & Chirife, 1976; Samapundo et al., 2007). Other researchers have also interpreted this as reflecting the water binding strength; initial occupation of highly active polar sites to form a surface monolayer, followed by the progressive filling of the less available sites (with lower bonding activation energies) (Tsami et al., 1990; McMinn et al., 2007).

The existence of enthalpy–entropy compensation was checked by plotting differential enthalpy against differential entropy (Figure 2.4). A linear relationship was obtained as follows:

$$\Delta h_d = 404.6\Delta S_d - 0.4227, \quad r^2 = 0.9947 \tag{2.9}$$

where Δh_d is the differential enthalpy (kJ/mol) and ΔS_d is the differential entropy (kJ/mol/K). The slope of equation (2.9) is called the isokinetic temperature (T_β) which is the temperature at which all reactions in the series proceed at the same rate (Al-Mahasneh et al., 2007).

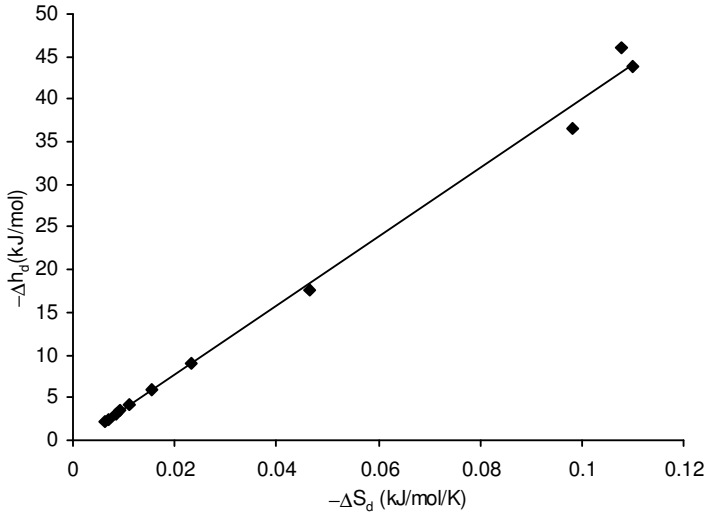

Figure 2.4. Diferential Enthalpy against Differential Entropy of adsorption for white maize meal

As a linear relation between Δh_d and ΔS_d was exhibited for the white maize meal the compensation theory was assumed to exist. The isokinetic temperature (T_β) and free energy at (T_β) (ΔG) were determined by linear regression (Eq. 2.4) within a 95% confidence interval, and the T_β value was found to be 404.6 ± 6.2 K. The isokinetic temperature for white maize meal found in our work is within the results reported by other researchers in starchy materials; 466.8 and 423 K for high amylose and amylopectin corn starch powders, respectively for adsorption (McMinn et al., 2005), 407.6 K in sweet potatoes (Fasina, 2006), 376.6, 377.8 and 366.8 K for potato, potato gel and potato starch powder, respectively, for adsorption (McMinn et al., 2005) and 382.5, 327 and 380.5K for starchy food products (Ferro-Fontan et al.,1982; Aguerre et al., 1986; Beristain et al.,1996), respectively.

The compensation theory can be proved to exist if the calculated harmonic mean temperature T_{hm} (Equation 2.5) was significantly different from T_β (Krug et al., 1976a). For our white maize meal, T_{hm} was found to be 306.2 K. This temperature was significantly lower than T_β of 404.6 K obtained from Δh_d vs ΔS_d linear relationship (Equation 2.9). If $T_\beta > T_{hm}$ the process is enthalpy driven, while if $T_\beta < T_{hm}$, the process is entropy controlled (McMinn et al., 2007). In the white maize meal, the former condition was observed; this suggested that the sorption mechanism was enthalpy-driven or controlled. This is in agreement with other researchers who

have reported similar findings in starchy materials (Aguerre et al., 1986; Beristain et al., 1996; McMinn et al., 2005; Fasina, 2006).

From a thermodynamic point of view, the free energy change (ΔG) can be considered as indicative of the affinity of the sorbent for water, and further provide a criterion as to whether the moisture sorption behaviour is spontaneous $(-\Delta G)$, or non-spontaneous $(+\Delta G)$ (Apostolopoulos & Gilbert, 1990). The negative value of (ΔG) found (cf. Equation 2.9 and 2.4) in the white maize meal suggest that adsorption in white maize meal was spontaneous. The spontaneous sorption process for starchy materials has been reported (Aguerre et al., 1986; Beristain et al., 1996; McMinn et al, 2005; Fasina, 2006).

2.2.8.4.2. Monolayer moisture content

The monolayer moisture contents of the non-defatted white maize meal at each of the temperatures studied were calculated using the GAB model (Table 2.2). The estimated monolayer moisture contents, M_{gm}, from the adsorption isotherms were 5.30, 5.06 and 4.64 g/100 g db at 25, 30 and 45°C, respectively (Table 2.3). The estimated values in our study are somewhat lower than the values reported for yellow cornmeal by Labuza et al. (1985) who obtained 8.23, 6.50 and 5.68 g/100g db at 25, 30 and 45°C, respectively and yellow dent corn by Samapundo et al. (2007) who obtained 7.44 and 6.57 g/100g db at 25 and 30°C, respectively. However, Abdullah et al. (2000) in their determination in corn flour (maize meal) and Wicklow et al. (1998) in a hybrid maize grain did not determine the monolayer moisture contents for us to compare with. M_{gm} was plotted against temperature in °C as shown in Fig. 2.5. The results show that monolayer moisture content decreased with increase in temperature of sorption. A decreasing linear relationship was obtained as follows:

$$M_{gm} = -0.0003T + 0.0607, \quad r^2 = 0.9852 \tag{2.10}$$

The decrease in the monolayer moisture content with increase in temperature has also been reported by Labuza et al. (1985) in yellow cornmeal, Samapundo et al. (2007) in yellow dent corn, and in other foods (Westgate et al., 1992; McLaughlin & Magee, 1998; Al-Muhtaseb et al., 2004a).

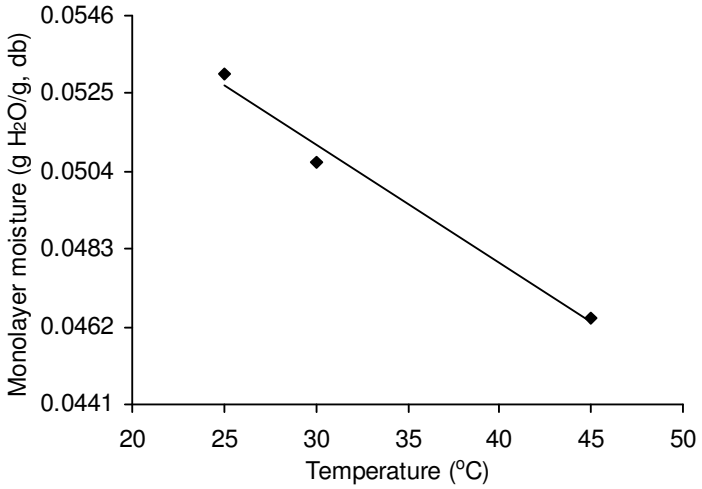

Figure 2.5. Changes in monolayer moisture content of adsorption for white maize meal as a function of temperature in ^{o}C

The reason is probably that, with an increase in temperature the water molecules get activated due to an increase in their energy level, causing them to become less stable and to break away from the water binding site of the food material, thus decreasing the monolayer moisture content (Palipane & Driscoll, 1992; Chowdhury et al., 2006).The reason for the decrease has also been attributed to reduction in the number of sites available for water binding as a result of physiochemical changes caused by temperature increase (Mazza & LeMaguer, 1978).

It was imperative to study the moisture sorption behaviour of maize meal as it is a major determinant in the reactivity or behaviour of the other properties studied. A number of research works are in agreement with the observation made here that, maize and maize products moisture isotherms exhibit Type II behaviour, are temperature dependent as the equilibrium moisture content decreases with increase in temperature and the GAB model best describes the experimental data (Labuza et al., 1985; Wicklow et al., 1998; Abdullah et al., 2000; Samapundo et al., 2007). However, variations in data still exists on the actual positions of the isotherms and the estimated monolayer moisture contents (Labuza et al., 1985; Wicklow et al., 1998; Abdullah et al., 2000; Samapundo et al., 2007). These differences could be attributed to the different working conditions such as dehydration methods, variety differences in the products and the extraction rates, in case of maize meal. For maize meals, the particle size could also have an influence on the position of the isotherms.

2.2.8.5. Non-defatted Vs defatted white maize meal adsorption isotherms

One of the major differences in the composition of the commercial brands or types of maize meal in Africa is in the oil content due to different levels of germ extractions. The oil content in the maize grain is concentrated in the germ, although the endosperm also contains oil. During dry milling most of the oil removed by the degerminator is oil contained in the germ. It is a well known fact that the lower the oil contents of the maize meal the longer the shelf life. The comparison of the defatted and non-defatted was carried out in order to determine the role of oil in affecting the A_w value of the maize meal. A_w is related to shelf life of maize meal. Figure 2.6 (a) and (b) gives adsorption isotherms at 30 and 45°C, respectively, for non-defatted and defatted white maize meals. In comparison to non-defatted, the defatted white maize meal maintained a sigmoidal shape, typical of Type II isotherms at both temperatures.

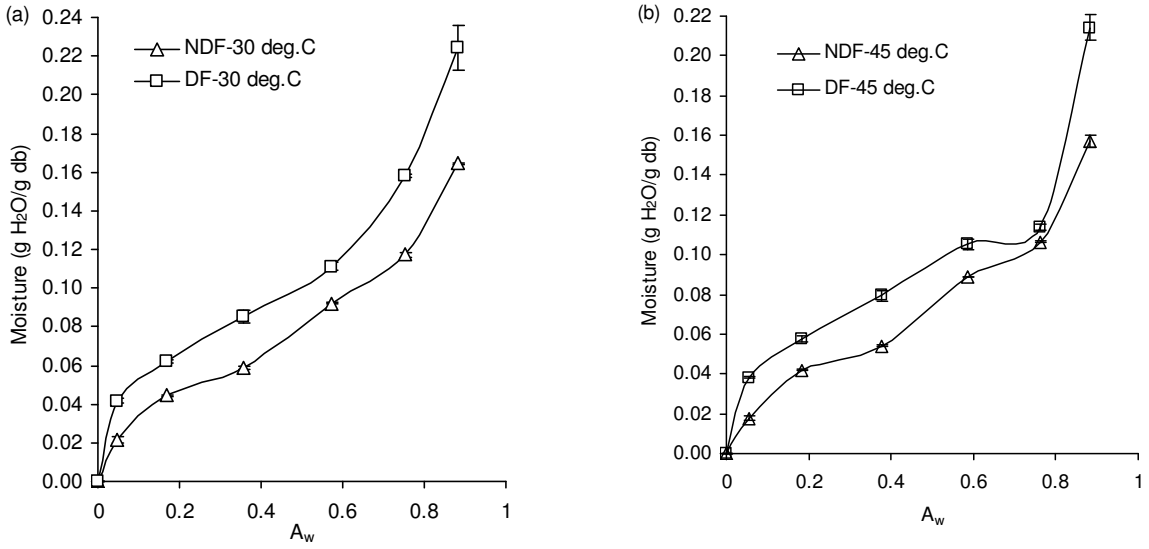

Figure 2.6 Adsorption isotherms of non-defatted and defatted white maize meal at 30 and 45°C. DF: Defatted maize meal and NDF: Non-defatted maize meal (Bars are standard deviations for n=3)

Figure 2.6 also illustrates the dependence of the adsorption isotherms of the white maize meal on the oil content. At constant temperature, the EMC is seen to increase upon defatting at the same A_w. Other researchers (Pollio et al., 1984; Pollio et al., 1987; Bianco et al., 2001) also reported that soybeans and sunflower samples with higher oil content have a lower EMC. This indicates that the white maize meal becomes more hygroscopic when defatted. It seems that the oil hinders access of water molecules to hydrophilic sorption sites. Other researchers have interpreted the

the presence of fat as having a lowering effect of the binding energy of sorbed water (Aviara et al., 2002; McMinn et al., 2007). This phenomenon of the EMC dependence on oil content may have an important practical bearing on chemical and microbiological reactions associated with spoilage, hence, may affect the shelf life of food products as well. At the same EMC, higher oil content entails a higher A_w which is associated with faster rates of deterioration. Therefore, at the same water content, the faster deterioration of foods higher in oil contents may also be explained based on its effect on A_w. However, some of the differences could be attributed to the change in microstructure due to the hexane extraction process. There is also a possibility that the particle size of the maize meal changed after the fat extraction. All these factors may contribute to the moisture isotherm positional differences observed between the defatted and undefatted white maize meal.

Table 2.3 also shows the coefficients of the models fitted to the experimental adsorption data by non-linear regression for defatted white maize meal. The GAB, Oswin, Smith and Chung-Pfost models had an average MRE (%) less than 10 for non-defatted whereas it was only for the GAB, Smith and Oswin models for defatted white maize meal. Generally, the MRE (%) and the determination coefficients for non-defatted white maize meal were lower and higher than those for the defatted white maize meal, respectively. This means that the models fitted much better for non-defatted than for defatted white maize meal. The experimental adsorption isotherm data and the best-fitted model (GAB) for the defatted white maize meal is shown in Figure 2.7.

The estimated monolayer moisture contents M_{gm} by the GAB model from the adsorption isotherms for non-defatted white maize meal were 5.06 and 4.64 g/100 g db whereas for defatted white maize meal were 6.05 and 4.61 g/100 g db at 30 and 45^{o}C, respectively. The results show that monolayer moisture content increased upon defatting at 30^{o}C, but no significant change was observed at 45^{o}C. The increase in monolayer moisture content upon defatting could be due to increased access of water molecules to hydrophilic sorption sites. Studies on the rates of chemical reactions in foods have shown that for most dry foods a moisture content exists below which the rates of quality loss are negligible.

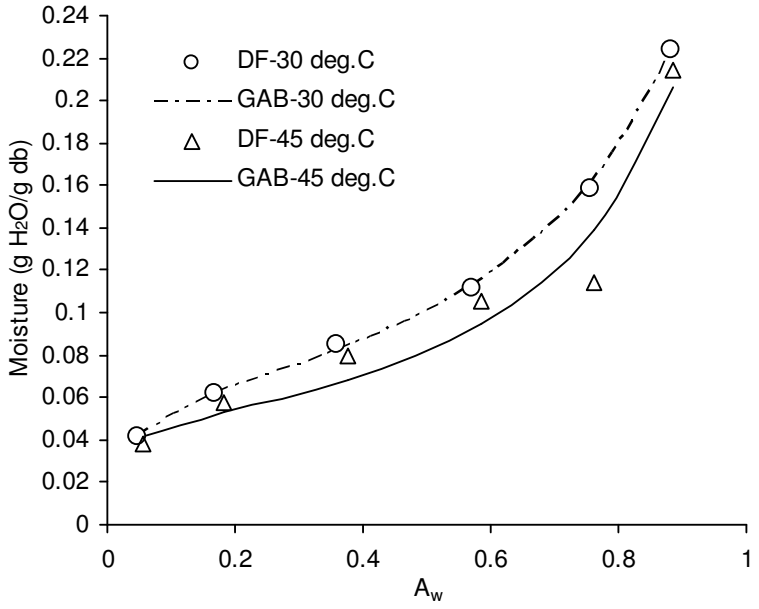

Figure 2.7. Experimental vs predicted values of the GAB model for defatted white maize meal

This moisture content corresponds fairly well with the monolayer value, as determined from the BET isotherm equation or GAB isotherm equation. This monolayer value can be viewed as a critical moisture content which is associated with a critical A_w value (Bell & Labuza, 2000). In our case, this entails that defatting increased this critical moisture content or critical A_w. The meaning of this is that, for a defatted food dried to below its critical moisture content or A_w, it must adsorb more moisture to exceed its critical moisture content or A_w than if it was not defatted.

2.3. Influence of storage conditions on moisture content

2.3.1. Open bulk storage of maize meal

2.3.1.1. Materials

Freshly produced white roller maize meal was obtained from National Milling Corporation (Lusaka, Zambia). Roller maize meal is a partially degermed commercial brand on the Zambian market (Table 1.2). It is produced by dry milling at extraction rates between 80-85% (Jayne et al., 1996). The white roller maize meal was packaged in a white opaque polypropylene 10kg

sack and sent from Lusaka (Zambia) to Gent (Belgium) within 48 hours. The sack was rapped in two layers of polyethylene to minimize moisture loss and was stored in a cold room at 5^{o}C for 22 days before the storage study commenced.

2.3.1.2. Storage protocol

400g of the white maize meal was weighed into porcelain dishes. The dishes were placed in 4 desiccators, two with saturated salt solutions of $BaCl_2$ and the other two with K_2CO_3 solution. One desiccator of each solution was kept in an incubator at 45°C and the other two at room temperature (25°C). A saturated solution of $BaCl_2$ at 25 and 45°C represents a relative humidity of 90% (Simal et al., 2007) and a saturated K_2CO_3 solution represents 43% RH (Tunç & Duman, 2007). About 70g sample was drawn from each dissecator at 7 days intervals for analysis.

2.3.2. Analytical methods

2.3.2.1. Proximate analysis

Proximate analysis of the white maize meal was carried out according to AOAC methods: moisture content, crude protein, ash, and crude fiber (1998). The determinations were performed in triplicates and the data was calculated on wet basis, except for moisture which was presented on dry basis.

2.3.2.2. Moisture

After sampling, the moisture content was determined by drying in a forced air circulation oven at 130^{o}C for 1 h (AOAC, 1998). The moisture content was calculated on dry basis.

2.3.3. Results and discussion

2.3.3.1. Proximate composition

The maize meal used in this study was analysed for proximate composition and was found to have moisture 11.87 ± 0.12%, crude protein (N x 6.25) 10.83 ± 0.12%, crude oil 4.48 ± 0.09 %, crude fibre 2.08 ± 0.10 % wb, ash 1.27 ± 0.09 % and carbohydrates (by difference) 69.47% wb.

2.3.3.2. Changes in moisture content in open bulk storage

Figure 2.8 shows the changes in moisture content of white maize meal samples stored at different combinations of temperature – relative humidity conditions. The samples at 25°C-43%RH / 45°C-43%RH and 25°C-90%RH / 45°C-90%RH decreased and increased sharply, respectively, up to about 21 days, after which the change was marginal. The samples stored in the relative humidity of 90% adsorbed moisture whereas the samples stored in the relative humidity of 43% desorbed moisture in an attempt to reach an equilibrium. This means that given the same storage relative humidity, maize meal will absorb or loose more moisture and at a faster rate at a high storage temperature than at a low storage temperature. This has consequences for the storability of maize meal in that we expect the same trends in water activity under such storage conditions. Water activity is known to correlate well with storability of foods.

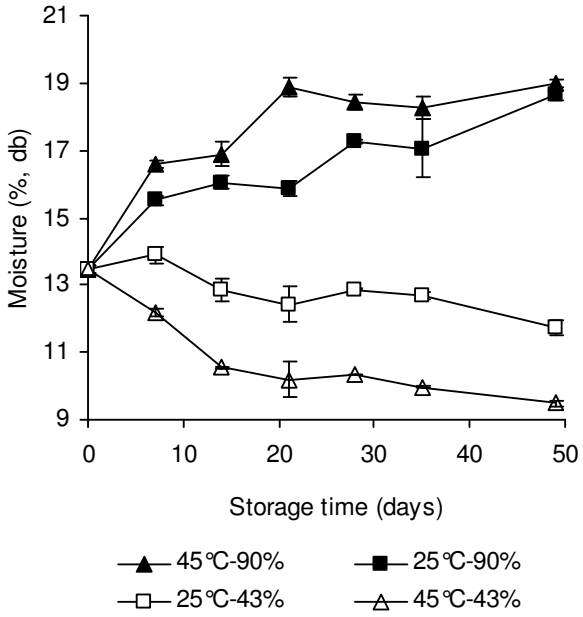

Figure 2.8 Changes in moisture content of white maize meal stored at temperatures and relative humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

2.4. Influence of storage conditions on water activity

2.4.1. Open bulk storage and storage in commonly used packaging material

2.4.1.1. Materials

Freshly produced 25 kg of white roller maize meal was obtained from National Milling Corporation (Lusaka, Zambia). Roller meal maize meal is a partially degermed commercial brand of on the Zambian market (Table 1.2). It is produced by dry milling at extraction rates between 80-85% (Jayne et al., 1996).

2.4.1.2. Storage protocol

250g of the white maize meal was weighed into 250ml beakers to just completely fill the beakers. Polypropylene interwoven sack packaging material and thick opaque polyethylene plastic packaging material were cut into circular shapes with circumferences larger than the beakers' openings. The openings of some beakers were covered with the polypropylene (PP) while other beakers were covered with the polyethylene (PE) materials by fastening the packaging materials to the beakers with elastic rubber bands several times. Another set of beakers with the maize meal were left uncovered to act as the controls. Four sets of dessicators were prepared, two with saturated salt solutions of barium chloride ($BaCl_2$) and the other two with potassium carbonate (K_2CO_3) solution. Three (3) beakers with maize meal (one covered with polypropylene packaging sack material, another covered with polyethylene plastic packaging material and the third without any covering) were placed in each dessicator. One desiccator of each solution was kept in an incubator at 45°C and the other two at 25°C. A saturated solution of $BaCl_2$ at 25 and 45°C represents a relative humidity of 90% (Simal et al., 2007) and a saturated K_2CO_3 solution represents 43% RH (Tunç & Duman, 2007). At least 35g sample was drawn from each beaker at 7 days intervals for analysis.

2.4.2. Analytical methods

2.4.2.1. Water activity

After sampling, the water activity of the white maize meal samples was determined at room temperature using an electronic dew-point water activity meter, Aqualab Model Series 3 (Decagon Devices Inc., Pullman, Washington, USA). The equipment was calibrated with saturated salt solutions as in the instrument manual. The samples were placed in Aqualab sample dishes and immediately well covered with aluminium foil. The samples at high temperatures were left for not more than 15 minutes to equilibrate to room temperature before measurements were performed. For each determination three replicates were obtained.

2.4.2.2. Water vapor transmission rate (WVTR) of the packaging

Water vapor transmission rate (WVTR) of the packaging material was measured according to Jongjareonrak et al. (2006), but with some modifications. The packaging materials were firmly fixed with elastic bands onto the opening of glass cups containing 3.0000g silica gel (0% relative humidity). The glass cups had internal diameter of 49.0 ± 1.0 mm and a depth of 58.00 ± 1.0 mm. The glass cups were placed in desiccators with distilled water maintained at 25 and 45°C in incubators (Memmert, Gmbh+Co.KG, Schwabach FRG, Germany). The cups were weighed at 24 h intervals over a 5 days period and WVTR of the packaging materials were calculated using the equation:

$$WVTR = \frac{w}{tA} \tag{2.11}$$

where w is the weight gain of the cup (g), t is the time of gain (days) and A is the area of exposed packaging material (m^2). A total of three determinations were made for each film. The term $\frac{w}{t}$ was calculated by linear regression from the points of weight gain and time, in the constant rate period. Packaging material thickness was determined from the mean of 4 measurements across circular cuttings of the packaging material using a digital micrometer (Mitutoyo Corp., England, UK).

2.4.2.3. Statistical analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

2.4.3. Results and discussion

2.4.3.1. Packaging properties

The packaging materials used in this study were chosen because of their widespread use in the packaging of maize meal for commerce. The water vapor transmission rates (WVTR) of the packaging materials were experimentally determined because this information was not available.

Table 2.4 shows the water vapor transmission rates (WVTR) and thicknesses of the polyethylene plastic (PE) and polypropylene interwoven sack (PP) materials used in this experiment.

Table 2.4. Water vapour transmission rates (WVTR) and thickness of the packaging materials

Packaging material type	**Thickness (μm)**	**WVTR (g m^{-2} day^{-1}) at 25°C and 100% RH**	**WVTR (g m^{-2} day^{-1}) at 45°C and 100% RH**
PE	128 ± 20	14 ± 1	45 ± 10
PP	277 ± 26	160 ± 13	631 ± 8

The PP packaging material was thicker than the PE packaging material. It can be observed that the WVTRs for PP were higher than for PE at both low and high temperatures. The WVTR at low temperature for PP was 11 times higher than for PE, whereas it was 14 times higher at high temperature. The WVTRs at high temperatures were higher than at low temperatures for both PE and PP. The WVTR for PP at high temperature was 4 times higher than at low temperature, whereas it was 3 times higher for PE.

2.4.3.2. Water activity

Figure 2.9 shows the changes in water activity as affected by packaging material, storage temperature and relative humidity during storage. Figure 2.9(a) illustrates the influence of storage temperature and relative humidity on A_w, and the patterns of evolution are as observed for moisture in section 2.3.3.2. Figures 2.9 (b) and (c) illustrate the influence of packaging material on A_w when maize meal is stored under the same four storage conditions. There was no significant difference in the evolution patterns of A_w for the control samples and samples in PP at all the storage conditions (Figure 2.9a and b). The water activity of the control samples and samples in PP stored at low relative humidity significantly ($p<0.05$) decreased while the samples stored at high relative humidity increased during the storage period. At low storage relative humidity for the control and samples in PP, the samples at 45°C-43%RH decreased to lower water activity values than for the samples at 25°C-43%. On the other hand for the control and samples in PP, the samples at 45°C-90%RH initially increased to higher water activity values than for samples at 25°C-90%RH, up to between 43 and 51 storage days. Thereafter, the water activity for the control and samples in PP at 25°C-90%RH was significantly higher than for the

samples at 45°C-90%RH. However, the equilibrium may not have been reached due to storage of large sample size.

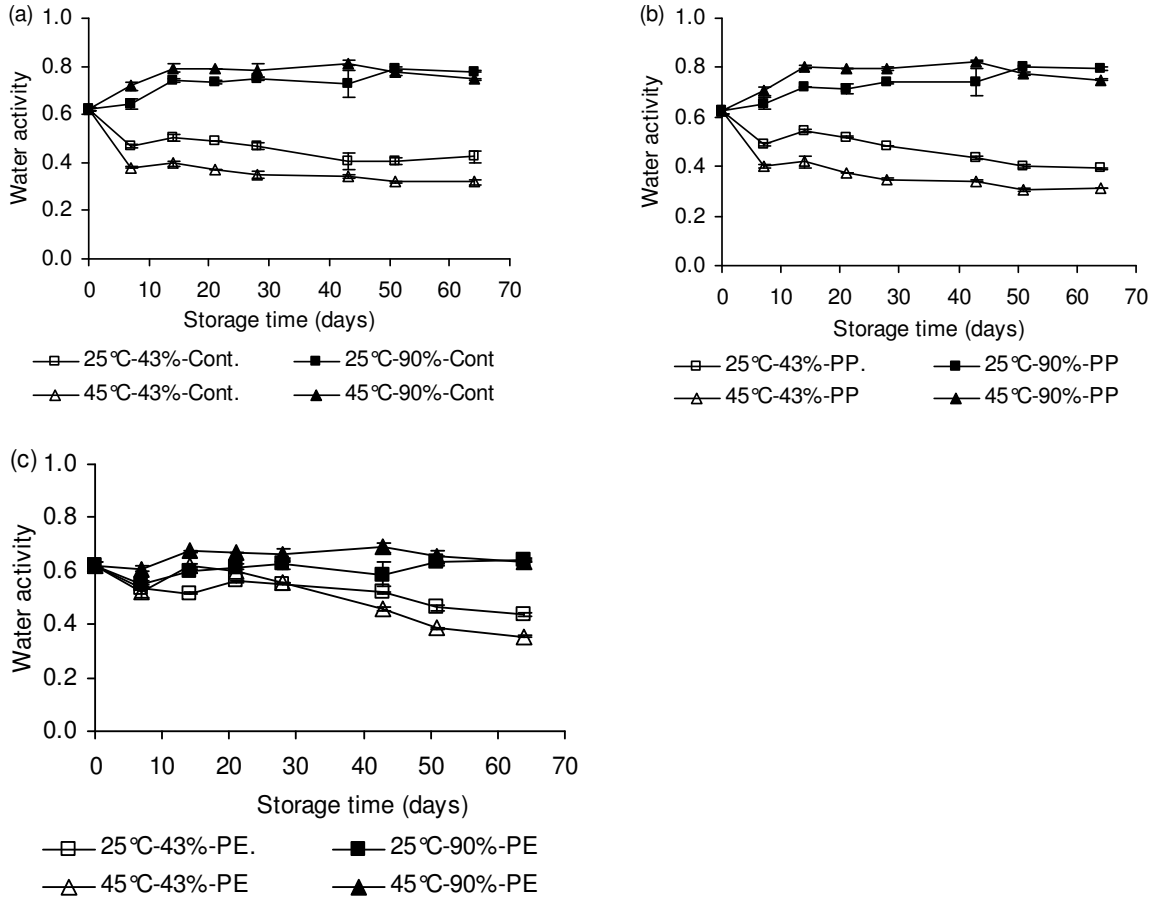

Figure 2.9 Changes in water activity of white maize meal during storage (a) without packaging (Cont: Control), (b) in Polypropylene (PP) and (c) Polyethylene (PE) packaging materials and exposed to temperature-humidity conditions of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH.

The samples in PE had rather a different pattern of water activity changes during the storage period (Figure 2.9c). The water activity of samples in PE at low relative humidity decreased while the samples at high relative humidity remained significantly ($p<0.05$) constant during the storage period. At low relative humidity for the samples in PE, the samples at 45°C-43%RH decreased to lower water activity values than at 25°C-43%RH after 28 days of storage.

In terms of magnitudes, the control samples at 45°C-43%RH and samples in PP at 45°C-43%RH did not significantly ($P>0.05$) differ and had the lowest water activity. The control samples at

45°C-90%RH and samples in PP at 45°C-90%RH did not significantly differ and had significantly (P>0.05) the highest water activity. The water activity of the following pairs of storage conditions: the control samples at 25°C-43%RH and samples stored in pp at 25°C-43%RH, samples in PE at 25°C-43%RH and in PE at 45°C-43%RH, the control samples at 25°C-90%RH and samples in PP at 25°C-90%RH, respectively, did not differ significantly (P>0.05). The water activity for the samples stored in PE at 25°C-90%RH and PE at 45°C-90%RH did not match any other conditions, and were fourth and fifth highest, respectively, from the lowest.

In summary, PP interwoven sack material showed poor barrier protection against A_w changes when maize meal is stored under varying temperature and humidity. The PE plastic material on the other hand showed good barrier protection against A_w change when maize meal is stored at high humidity for both low and high storage temperatures. On the other hand, PE plastic material had good protection for a limited storage period of time at low humidity storage for both low and high storage temperature. The differences in the water activity of the samples packaged in PP and PE, and the absence of differences between the control and PP could be attributed to the higher WVTRs in PP and lower WVTRs in PE observed in section 2.4.3.1 above.

2.4.4. Fortified-packaged-sunlight exposed storage

2.4.4.1. Materials

Freshly produced 25 Kg of unfortified white roller maize meal was obtained from National Milling Corporation, Lusaka, Zambia. Roller maize meal is a partially degermed commercial brand on the Zambian market (Table 1.2). It is produced by dry milling at extraction rates between 80-85% (Jayne et al., 1996). The maize meal was immediately delivered to the Department of Food Science and Technology Laboratory, University of Zambia. The sample was divided into two portions, one portion remained unfortified and the other portion was immediately delivered to National Institute for Scientific and Industrial Research (NISIR), Lusaka – Zambia, for fortification. Chemicals were supplied by Merck (South Africa), the maize meal fortificant was given by DSM (former Roche, South Africa).

2.4.4.2. Fortification Procedure

The maize meal was fortified at the National Institute for Scientific and Industrial Research of Zambia, the government institute in Zambia with the mandate to carry out fortification trials in collaboration with the National Food and Nutrition Commission of Zambia. The fortification was performed using the hand operated stainless steel ribbon blender. The fortification was carried out to have the following composition of the fortified nutrients mg/100g : vitamin A (0.08-0.12), vitamin B_1 – thiamine (0.43-0.63), vitamin B_2 – riboflavin (0.36-0.44), vitamin B_3 – niacin (3.02 – 3.66), vitamin B_6 – pyridoxine (1.04-1.46), vitamin B_{12} – cyanocobalamine (0.0004 – 0.0006), folic acid (0.143-0.237), iron (2.99-5.87) and zinc (3.08-3.98). The fortificant premix also contained butylated hydroxytoluene (BHT), which is an antioxidant. The homogeneity of the fortificant was verified by determining the iron content of the white maize meal taken from various positions of the blender.

2.4.4.3. Storage Protocol

The unfortified and fortified samples were repackaged into 150 g thin polyethylene plastic and polypropylene interwoven sack packages. The repackaged 150g pack sample sets were stored under two storage conditions; (i) in the dark in the cupboard at room condition until sampling for analysis (ii) exposed to sunlight from 08.00hrs to 17.00 hrs everyday until sampling**.** The storage period was from June to August i.e. the transition from dry-cold season and to dry hot season in Zambia. The experimental design was as summarized in Table 2.5. 2x150g packages were drawn at random from each treatment for analysis every one week for fortified samples and every two weeks for unfortified samples. The sample was immediately analyzed for water activity. The water activity was monitored for a total period of ten weeks.

2.4.5. Analytical methods

2.4.5.1. Proximate analysis

Proximate analysis (moisture, crude protein, ash and crude fiber) were determined according to AOAC methods (1998).

Table 2.5 Experimental design

RUN No.	FORTIFICATION	PACKAGING TYPE	SUNLIGHT EXPOSURE	ABREVIATIONS USED IN THE PAPER
1	Fortified	PE	Sunlight	FES
2	Fortified	PP	Sunlight	FPS
3	Fortified	PE	Dark	FED
4	Fortified	PP	Dark	FPD
5	Unfortified	PE	Sunlight	UES
6	Unfortified	PP	Sunlight	UPS
7	Unfortified	PE	Dark	UED
8	Unfortified	PP	Dark	UPD

2.4.5.2. Water activity

The water activity of the white maize meal samples was determined at room temperature using an electronic dew-point water activity meter, Aqualab Model Series 3 (Decagon Devices Inc., Pullman, Washington, USA). The equipment was calibrated with saturated salt solutions as in the instrument manual. For each determination three replicates were obtained and the mean was recorded.

2.4.5.3. Water vapor transmission rate (WVTR) of packaging material

WVTR was determined as described in section 2.4.2.2, except it was only determined at 45^{o}C

2.4.5.4. Light transmission and transparency of packaging material

The ultraviolet and visible light barrier properties of the films were measured at selected wavelengths, from 350 to 800 nm (350, 400, 500, 600 and 800), using a UV–visible recording spectrophotometer (UV-160, Shimadzu Co., Kyoto, Japan) according to Hamaguchi et al (2005). The light transmission of film was measured on the film specimens measuring 7x7 cm in size and the transparency of the films was calculated as follows:

$$Transparency = \frac{A_{600}}{x} \quad \text{or} \quad Transparency = \frac{-LogT_{600}}{x} \tag{2.12}$$

where A_{600} is absorbance at 600 nm, T_{600} is transmittance (%) at 600 nm, and x is film thickness (mm).

2.4.6. Statistical Analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

2.4.7. Results and discussion

2.4.7.1. Proximate composition

The maize meal sample was analyzed at the beginning of the experiment. It had a moisture content of 11.0 ± 0.4%, crude oil content 4.2 ± 0.5 %, crude protein content of 9.16 ± 0.01%, crude fiber content of 2.00 ± 0.14 %, and total ash content of 1.93 ± 0.014 %.

2.4.7.2. Packaging properties

The packaging materials used in this study were chosen because of their widespread use in the packaging and re-packaging of maize meal by open market vendors. The packaging materials were experimentally determined in this study for their water vapor transmission rates (WVTR) because this information was not available. Table 2.6 shows the water vapor transmission rates (WVTR) and thicknesses of the polyethylene plastic (PE) and polypropylene interwoven sack (PP) materials used in this experiment. The PP packaging material was 11.5 times thicker than the PE packaging material. It can be observed that the WVTRs for PP were more than 4 times higher than for PE.

Table 2.6 Water vapor transmission rates (WVTR) and thickness of the packaging materials

Packaging type	**Thickness (μm)**	**WVTR (g m^{-2} day^{-1}) at 45°C and 100% RH**
PE	24 ± 2	145 ± 13
PP	277 ± 26	631 ± 8

Table 2.7 presents the light transmission, at selected wavelengths from 350 to 800 nm, and transparency (A_{600}/mm) of the packaging material. The selected wavelength represents the UV-visible range. It is clear that light transmission, indicated by light transmittance in the table, of the PE is of greater magnitudes higher than the PP. The light transmission increased with increase in wavelength for the PE. The PE material is more transparent, as indicated by

transparency in the table, than the PP material. Physically, the PE material was very transparent and clear as a see-through packaging material, whereas the PP is not a see-through material.

Table 2.7. Light transmission and transparency of the packaging materials

Wavelength (nm)	Light transmittance (%)		Transparency ($A_{wavelength}$/mm)	
	PP	PE	PP	PE
350	1.60 ± 1.58	79.23 ± 0.96	-	-
400	1.76 ± 1.67	81.10 ± 0.99	-	-
500	1.96 ± 1.82	83.83 ± 0.94	-	-
600	2.15 ± 1.93	85.44 ± 0.97	6.57 ± 1.61	2.80 ± 0.20
800	1.87 ± 2.07	87.29 ± 0.91	-	-

2.4.7.3. Changes in water activity

Figure 2.10 below, shows that there was a decrease in water activity in all the samples during the 70 days of storage.

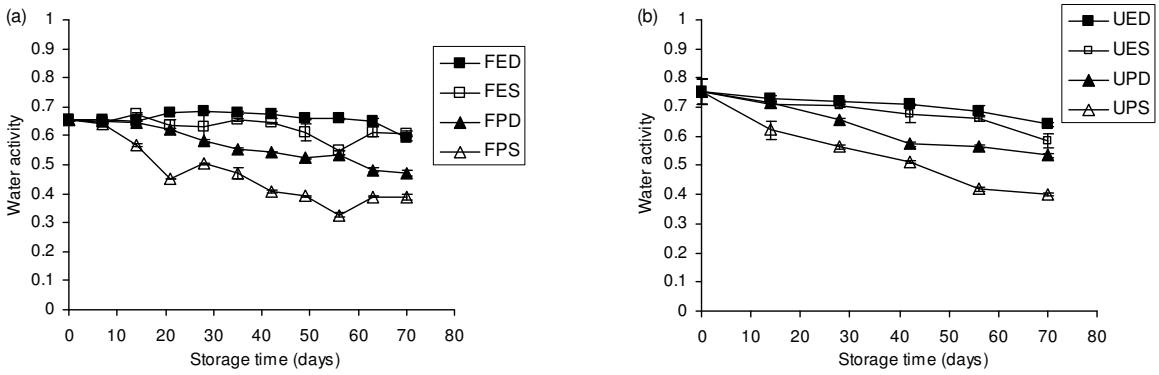

Figure 2.10 Changes in water activity of the fortified and non-fortified white maize meal packaged in polypropylene sack and polyethylene plastic packages with exposure and non-exposure to sunlight conditions. The three letter abbreviation in the legend gives the maize meal treatments: type of maize meal - packaging type - sunlight/darkness storage. FED: Fortified-PE-Darkness; FES: Fortified-PE-Sunlight; FPD: Fortified-PP-Darkness; FPS: Fortified-PP-Sunlight; UED: Unfortified-PE-Darkness; UES: Unfortified-PE-Sunlight; UPD: Unfortified-PP-Darkness and UPS: Unfortified-PP-Sunlight.

This means that both room conditions and outside - sunlight conditions, might had environments which had lower relative humidity than the samples. Hence, the samples were losing their moisture to the environment. It has been reported that differences among the water activities of food components, food domains and the external environment outside the package introduces a driving force for water transport (Labuza & Hyman, 1998; Risbo 2003). Risbo (2003) further noted that water transport ceases when the differences in water activity have levelled out, i.e., the water activities converge to a common equilibrium value.

From Figure 2.10, magnitudes of change in water activity based on the initial water activity between day zero and day 70 were calculated and expressed as percent water activity retention (WR):

$$WR = 100 - \left(\frac{C_0 - C_{70}}{C_0} \right) * 100 \qquad (2.13)$$

where C_0 is the initial water activity, C_{70} is the water activity on the 70th day. WR was mainly influenced by the packaging material. Samples stored in polyethylene had higher WR (ranging between 78 and 93%) than in polypropylene (53 – 72 %). PE had higher WR because of the low WVTR compared to PP as shown in Table 2.6. Dirim et. al., (2004) noted that PE is the mostly used polymer film for packaging as it offers the advantages of being inert and comparatively less permeable to water vapor. Therefore, in any application it is considered more like a barrier for water and/or its vapor on either side of the film. Within polyethylene, the fortified samples had WR of (FES = 93 % and FED = 91 % retention) while the unfortified samples had (UED = 85 % and UES = 78 %). On the contrary, at the beginning of the experiment fortified maize meal had lower A_w than the unfortified samples. The possible reason for the decrease in A_w of fortified maize meal is the change in particle size during blending of fortified maize meal. The fortificant levels used here may not have that immediate influence on the A_w.

For the samples stored in polypropylene, the samples in the dark room condition had WR of (FPD = 72 % and UPD = 71 % retention), while the samples exposed to sunlight had (FPS = 60% and UPS = 53 %). This indicates that, of all the three conditions, packaging type plays a significant role in retention of the water activity during storage of white maize meal. From Figure 2.10, it is also clear that, the difference in water activity for samples stored in the dark and samples exposed to sunlight was highly pronounced for PP packaging for the maize meal in PE.

2.5. Conclusions

- The adsorption isotherms determined at 25, 30 and 45^{o}C before and after defatting white maize meal, exhibited a sigmoidal shape, representing Type II isotherms. The temperature had an influence on adsorption isotherms, the EMC increased with decrease in temperature at the same A_w. Among the models evaluated, the data was better fitted to GAB, Oswin and Smith models for both non-defatted and defatted white maize meals, with the GAB model being the best. The models fitted much better for non-defatted than for defatted white maize meals. The differential heat of sorption and differential entropy of sorption increased with decreasing moisture content. Moisture adsorption was enthalpy-driven in the temperature range studied. The monolayer moisture content decreased with increase in temperature of sorption. Comparing non-defatted and defatted maize meals, at constant temperature, the defatted had higher EMCs than the non-defatted.

- The changes in moisture content of white maize meal have been found to be influenced by temperature and relative humidity during storage. At constant storage relative humidity, white maize meal will absorb or loose more moisture at high storage temperatures than at low storage temperatures.

- The packaging type was found to influence the changes in water activity of white maize meal during storage. PP interwoven sack material had poor barrier protection against A_w changes when maize meal was stored under varying temperature and humidity. The PE plastic material had good barrier protection against A_w change when maize meal was stored at high humidity for both low and high storage temperatures. On the other hand, PE plastic material had good protection against A_w change for a limited storage period of time at low storage humidity for both low and high storage temperature. The differences in the water activity of the samples packaged in PP and PE is attributed to the higher WVTRs in PP than in PE.

- In addition to relative humidity, which is the primary determinant, packaging type plays a significant role in maintaining the A_w during storage of both fortified and unfortified maize meals.

Chapter 3

Chemical and sensory properties of white maize meal during storage

Chapter 3. Chemical and sensory properties of white maize meal during storage

Abstract

This chapter involved studies on the influence of storage conditions on acidity, colour, lipolysis, lipid oxidation and sensory properties of white maize meal during storage. High storage temperature resulted in lower pH than low storage temperature in function of storage time, while titratable acids were only affected by storage time.

The colour of white maize meal during storage was monitored using L-, a- and b-values. The L-values decreased after a short period of storage at temperature-humidity of 45°C-43%RH and 45°C-90%RH, while at 25°C-90%RH after a longer storage period. The a- and b-values at 45°C-43%RH and 45°C-90%RH increased, while at 25°C-43%RH and 25°C-90%RH did not significantly change. The change in sensory properties was only established for colour scores, which decreased for maize meal storage at 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. The L-values at 25°C-90%RH and 45°C-90%RH decreased in polypropylene (PP) packaging material, while it decreased at 45°C-43%RH and 45°C-90%RH for polyethylene (PE). The a- and b-values increased at 45°C-43%RH and 45°C-90%RH for the PP and PE, with the L-, a- and b-values increasing at the same rate in PE for both storage conditions. The observed change in colour is attributed to discoloration of the maize meal by non-enzymatic browning.

Lipolysis was evaluated by determining the evolution of free fatty acid (FFA) contents. FFA at high storage temperatures had higher contents and evolved faster than at low storage temperatures. However, at constant storage temperature, samples at high storage relative humidity had higher increases in FFA contents and evolved faster than at low storage relative humidity. Packaging material type did not seem to have influence on lipolysis. Fortified maize meal had higher increases in FFA contents than the unfortified maize meal, while packaging and sunlight exposure did not seem to affect FFA contents.

Lipid oxidation was evaluated by determining peroxide and p-anisidine values, and both increased and then decreased to relatively constant values during the storage period. Higher peroxide values in unfortified than the fortified maize meal were recorded, while packaging and sunlight exposure did not seem to significantly influence the evolution of peroxide values. The influence of storage temperature on p-anisidine values was not significant.

Key words: *Chemical stability, Fortification, Lipid oxidation, Lipolysis, Maize meal, Packaging, Sensory, Storage*

3.1. Introduction

Chapter 1 has shown that there are numerous food products produced from maize meal. These products may contribute directly to human nutritional status or be utilised as relatively low cost, bulk nutrient and energy sources in industrial processes (Nelles et al., 2000). The distribution chains of the maize meal may vary from one country to another in Africa. However, taking a case of Zambia, as outlined in section 1.8, the distribution of maize meal from the commercial millers to the final consumer involves: (a) long life on the shelf (b) a variety of packaging and (c) exposure to sunlight. Moreover, tropical temperatures in Africa exceeding 45°C are not uncommon particularly for low-lying valleys coupled with high humidity (AQUASTAT, 2005).

Deterioration in the quality of maize meal during storage could be attributed to lipid hydrolysis (lipolysis) and lipid oxidation. The literature review has shown that storage of cereal and cereal products can lead to lipolysis (Castello et al., 1998; Sammon, 1999). Lipid oxidation in dehydrated foods (Pershem et al., 1995; Maskan & Karatas, 1998). Oxidation of lipids has been reported to be of great influence on the deterioration of foods, even if the lipid content is small (Rutgersson et al, 2000). Oxidation of lipids reduces the nutritional value of cereal products, affects the color, and the appearance of the products, and causes the formation of off-odors and off-flavors (Kaukovirta-Norja et al., 1998).

Color measurement is a critical objective quality parameter that can be used for analyses of quality changes as a result of food processing, storage, and other factors (Esteller et al., 2006). Browning of foods on storage due to Maillard reaction or non-enzymatic browning (BeMiller & Whistler, 1996) is considered an important factor influencing food nutritional value and quality (Tsen et al., 1982; Dexter et al., 1984; Sensidoni et al., 1999). In a study of maize meal by Bothast et al. (1981)**,** they investigated lipid oxidation by monitoring hexanal, but did not report on the browning. Bovel-Benjamin et al. (1997) evaluated the sensory quality and storability of whole maize fortified with novel iron and concluded that fortification compromises the sensory quality and oxidative stability of maize porridge, depending upon the nature of the fortificant. The role of packaging in stability of foods depends on how well the packaging protects the food from adverse environmental conditions (Ou et al., 2005).

From the literature review, it is evident that the chemical and sensory stability of quality properties such as lipolysis, lipid oxidation and the role of packaging material in white maize

meal produced in Africa are either scarce or non-existent. Therefore, the purpose of this chapter was to determine the influence of storage conditions on: (a) acidity (b) colour (c) lipolysis (d) lipid oxidation, and (e) sensory properties

3.2. Influence of storage conditions on bacteria, yeast and moulds

3.2.1. Materials and sampling

Regarding samples involving fortification, the materials, fortification procedure, storage protocol, WVTR and light transmission were as described in section 2.4.4.1, section 2.4.4.2, section 2.4.4.3, section 2.4.2.2 and section 2.4.5.4, respectively. However, the WVTR here was only determined at 45^{o}C. In case of samples involving storage at different temperature-humidity conditions, the materials and storage protocol were as described in section 2.3.1.1 and section 2.3.1.2, respectively. The samples for microbial analysis were taken prior to handling for other analyses.

3.2.2. Microbial counts

Total plate counts were determined on plate count agar pour plates and enumerated after an incubation period of 48–72 h at 30°C. Enumeration of yeast and moulds was done using oxytetracycline glucose yeast extract (OGYE) agar by the pour plate technique and incubated at 25^{o}C for 120 hours according to IDF-94B method (1990) using chloromphenicol as a selective supplement.

3.2.3. Results and discussions

Microbial growth was monitored by microbial counts and visual inspection of mould appearance. In Figure 3.1, fortified white maize meal recorded higher populations of yeast and moulds than the unfortified white maize meal in the first 21 days, both reaching a maximum in 14 days. This obviously is because the fortified maize meal had a better nutrient base than the unfortified maize meal, hence, the fortified maize meal offered better growth conditions for yeast and mould growth. Bothast et al. (1981) found that both bacteria and mold counts in maize meal increased during the storage period before finally decreasing. Within the fortified and unfortified maize meals, there was no significant difference in yeast and mould population changes in the first 21

days. After the peak growth periods up to termination of the storage study, fortification, packaging type and sunlight exposure had insignificant influence on the yeast and mould count changes. This could be due to the decreasing water activity during storage (See Figure 2.10)

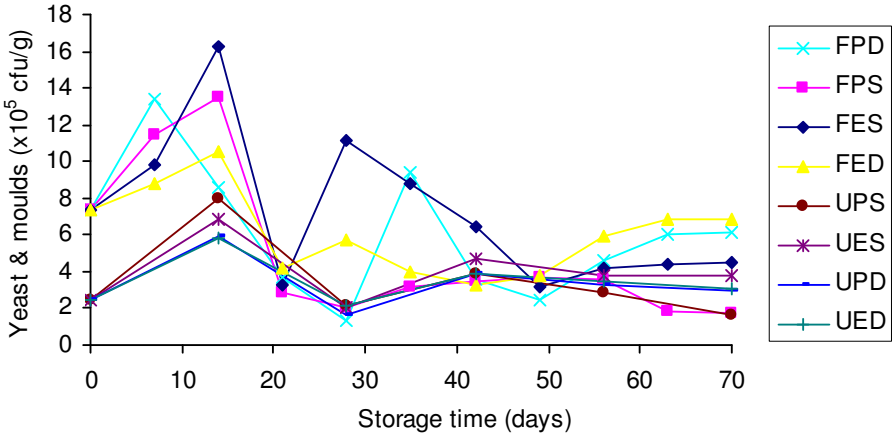

Figure 3.1 Changes in yeast & mould counts of fortified and non-fortified white maize meal packaged in PP and PE with exposure and non-exposure to sunlight conditions.The three letter abbreviations in the legend gives the maize meal treatments: type of maize meal - packaging type - sunlight/darkness storage. FPD: Fortified-PP-Darkness; FPS: Fortified-PP-Sunlight; FES: Fortified-PE-Sunlight; FED: Fortified-PE-Darkness; UPS: Unfortified-PP-Sunlight; UES: Unfortified-PE-Sunlight; UPD: Unfortified-PP-Darkness and UED: Unfortified-PE-Darkness.

Table 3.1 shows the total plate, yeast and mould counts for the fresh white maize meal and for the white maize meal stored at four different conditions for 49 days. The bacterial counts depicted by total plate counts were higher in the fesh maize meal than the stored maize meal. The white maize meal was more dominated by the moulds than the yeasts at all the four storage conditions for both fresh and stored maize meal.

Table 3.1 Total plate, yeast and mould counts of fresh white maize meal and white maize meal stored for 49 days at different temperature-humidity conditions

Storage condition	**Total plate counts (cfu/g)**	**Yeast counts (cfu/g)**	**Mould counts (cfu/g)**
Fresh	$1.2x10^7$	15	$1.8x10^4$
25°C-43%RH	$2.9x10^4$	<10	$2.0x10^4$
25°C-90%RH	$8.8x10^5$	$6.2x10^3$	$8.6x10^5$
45°C-43%RH	$2.9x10^4$	$2.0x10^2$	$9.2x10^3$
45°C-90%RH	$4.8x10^6$	<10	$5.4x10^6$

Moreover, the maize meal at 45°C-90%RH storage condition was visually observed to be caking and having whitish-like moulds by day 28 and, heavy caking and greenish-like moulds by day

35. At 25°C-90%RH storage condition, the caking was visually observed by day 35 and heavy caking coupled with blackish fungal/mould growth were observed by day 49. This was observed for the samples initially kept for 22 days at 5°C before commencing the experiments. Bothast et al. (1981) found that maize meal stored at 25°C became visibly moldy after 1.5 months (6 weeks) of storage, which is one week later than our observation. The growth of moulds in the maize meal samples may confound the results from the points were they proliferated. This is because growth of moulds requires nutrients, hence may be consuming some of the nutrients from the maize meal during storage. The moulds would also produce different kinds of enzymes which may begin to degrade the lipids, carbohydrates or proteins. This has consequences on the other quality parameters of the maize meal during storage.

3.3. Influence of storage conditions on acidity

3.3.1. Maize meal storage in closed bottles

3.3.1.1. Materials

Freshly produced white maize meal branded 'Super fine' was obtained from Superior Milling Company (Lusaka, Zambia). This brand belongs to the low extraction generic brands known as 'breakfast' maize meal (Table 1.2). White breakfast maize meal is a partially degermed commercial brand on the Zambian market. It is produced by dry milling at extraction rates between 60-70% (Jayne, et. al., 1996). The white breakfast maize meal was packaged in an opaque thick polyethylene 5kg plastic bag and sent from Lusaka (Zambia) to Gent (Belgium) within two days.

3.3.1.2. Storage protocol

230g of maize meal was weighed into bottles. The bottles were capped to make them air and moist-tight. The bottles were further wrapped on the exterior with aluminium foils. One set of bottles was stored in a cupboard at room temperature (≈25°C) and another at 43°C in an incubator until sampling day. Two bottles from each set were taken out of storage at random for analysis on days 0, 29, 42, 54, 68, 89 and 124 of the storage period.

3.3.1.3. Proximate, pH and Titratable acids Determinations

pH determinations were carried out in at least duplicates according to AOAC method (1984). Titratable acids were determined by titrating 25ml an aliquot from extracts obtained from pH determinations against standardized 0.05M NaOH and was calculated as mg NaOH per 100g (db) white maize meal.

3.3.2. Results and discussion

3.3.2.1. Acidity of white maize meal stored in closed bottles

pH decreased very fast within the first 30 days of storage for both 43°C and (≈25°C) storage (Figure 3.2a) and was followed by a period of minimal decrease. The maize meal stored at 43°C decreased faster and much lower than the maize meal stored at (≈25°C) throughout the storage period.

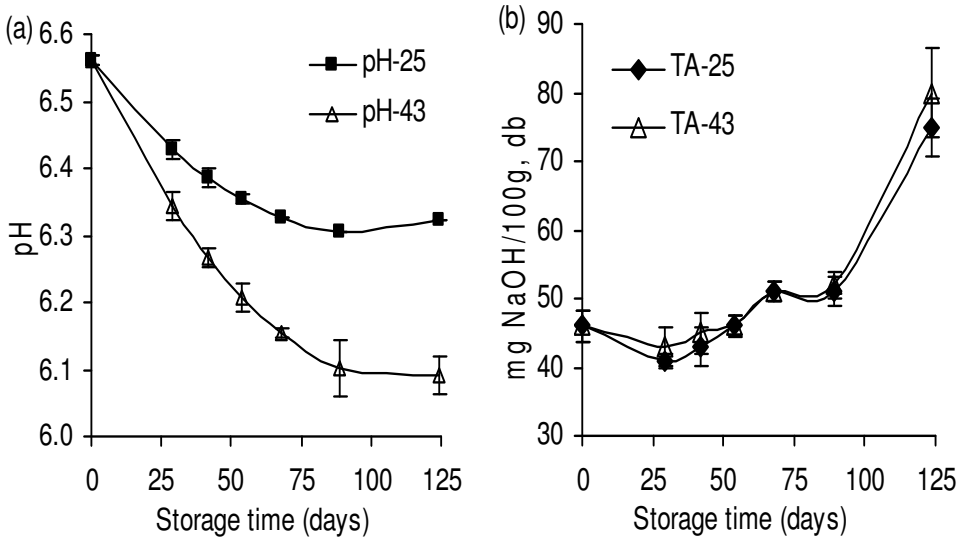

Figure 3.2 Changes in pH and titratable acids of white maize meal during storage at room temperature (≈25°C) and 43°C.

The faster decrease in pH at 43°C than at room temperature shows that storage temperature influences changes in pH of maize meal. Titratable acids, expressed as mg NaOH per 100g white maize meal, increased very slowly for both 43°C storage and 25°C storage, until after 90 days when there was a steep increase (Figure 3.2b). The titratable acidity is used to approximate total acidity. There was no significant difference in the titratable acids of maize meal at the two

storage temperatures. Zia-Ur-Rehman (2006) has reported a decrease in pH and an increase in titratable acids after three months of storage at 25^{o}C in maize grain. The increase in the acidity of the stored grains has been attributed to the increasing concentration of the free fatty acids and phosphate, which result from increased grain deterioration. The other possible cause of increased acidity in stored cereals has been attributed to the binding of the amino group of amino acids, short chain peptides, and protein, leaving the carboxylic ends free and the presence of acid byproducts of advanced Maillard reactions.

3.4. Influence of storage conditions on colour

3.4.1. Open bulk storage

3.4.1.1. Materials

Freshly produced 25 kg of white roller maize meal was obtained from National Milling Corporation (Lusaka, Zambia). Roller maize meal is a partially degermed commercial brand of on the Zambian market (Table 1.2) It is produced by dry milling at extraction rates between 80-85% (Jayne et al., 1996).

3.4.1.2. Storage protocol

1200g of the white maize meal was weighed into salad glass bowls. The bowls were placed in 4 dessicators, two with saturated salt solutions of $BaCl_2$ and the other two with K_2CO_3 solution. One desiccator of each solution was kept in an incubator at 45°C and the other two in an incubator at 25°C. A saturated solution of $BaCl_2$ at 25 and 45°C represented a relative humidity of 90% and a saturated K_2CO_3 solution represented 43%RH. 200g sample was drawn from each dissecator at 7 days intervals for analysis.

3.4.2. Maize meal storage in commonly used packaging material

The materials, storage protocol, WVTR and statistical analyses were as described in section 2.4.1.1, section 2.4.1.2, section 2.4.2.2 and section 2.4.2.3, respectively.

3.4.3. Analytical Methods

3.4.3.1. Colour (L, a and b-values)

The colour of the white maize meal during storage was measured with a hand-held tristimulus Konica Minolta Color Reader CR-10 (Konica Minolta Sensing Inc., Japan). The Minolta color reader allocates each sample a colour co-ordinate within the CIE (Commission Internationale l'Eclairage) three-dimensional (L,a,b) colour space. CIE L values represent brightness on a 0 (pure black) –100 (pure white) unit scale, CIE a values range from -60 (pure green) to +60 (pure red), and CIE b values range from -60 (pure blue) to +60 (pure yellow). 9g of the white maize meal was partially compacted in a cell provided by the manufacturer to the required level by gently tapping the cell on a laboratory bench. The glass cell containing the maize meal was placed against the light source and post-processing L, a, b values were recorded. Each CIE L, a, and b value was an average from three readings. From these values, total color difference ΔE was calculated using the formula:

$$\Delta E = \sqrt{(L_0 - L_i)^2 + (a_0 - a_i)^2 + (b_0 - b_i)^2} \qquad (3.1)$$

Where L_0, a_0 and b_0, denote the color parameters for the initial samples (fresh maize meal sample); and L_i, a_i and b_i-values denote the color parameters of the maize meal samples during storage.

3.4.3.2. Statistical analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

3.4.4. Results and Discussion

3.4.4.1. Changes in colour properties (L, a and b-values) in open bulk storage

The L a b color space (also referred to as CIELAB) was used to measure the colour changes in white maize meal during storage. Figure 3.3 shows the evolution of L-values for white maize meal exposed to a combination of temperature-humidity of 25°C-43%RH, 25°C-90%RH, 45°C-

43%RH and 45°C-90%RH. The L-values of samples at 25°C-43%RH remained essentially constant during the storage period (Figure 3.3a). At 45°C-43%RH and 45°C-90%RH storage, lightness decreased by 9.6 and 17.3% respectively, during the storage period. The L-values at 25°C-90%RH decreased by 12.8% after being constant for the first 28 days of storage.

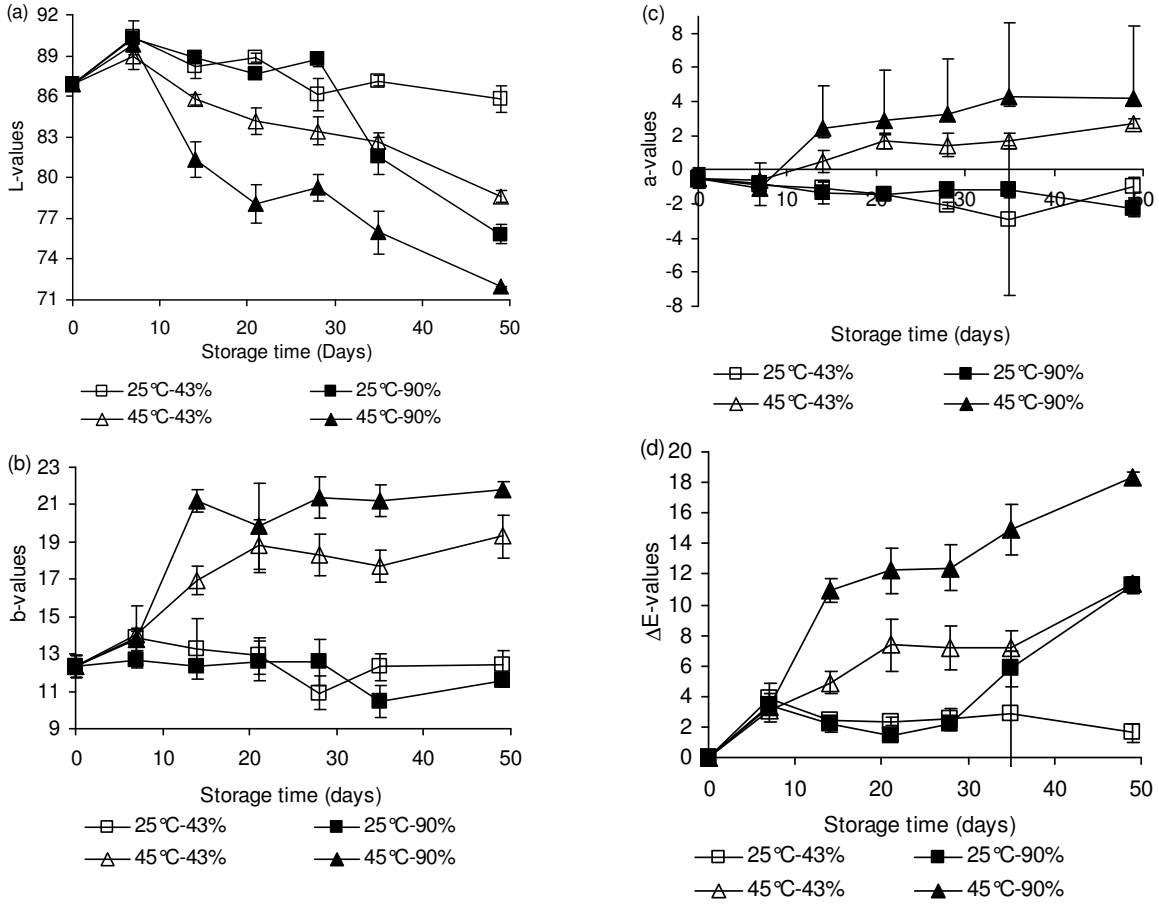

Figure 3.3. Changes in (a) L-values (b) a-values, (c) b-values and (d) ΔE-values of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

The a- and b-values of samples stored at 25°C-43%RH and 25°C-90%RH did not differ significantly ($p<0.05$) in their evolution, and were essentially constant (Figure 3.3 c and b). The maize meal pigments shifted towards the yellow colour by 56.1 and 76.5% at 45°C-43%RH and 45°C-90%RH, respectively during the storage period.

The ΔE-values of samples stored at 25°C-43%RH did not significantly change throughout the storage period (Figure 3.3d). After 28 days of storage, samples at 25°C-90%RH substantially increased up to the end of storage study. The ΔE of samples at 45°C-43%RH increased during the storage period and were higher than at 25°C-90%RH up to 28 days of storage. The ΔE of samples stored at 45°C-90%RH increased almost linearly and had the highest ΔE-values after 7 days of storage.

3.4.4.2. Changes in L-, a- and b-values in packaging commonly in use

Figure 3.4, 3.5, 3.6 and 3.7 shows the changes in L-, b-, a- and ΔE-values of white maize meal as affected by packaging material stored at four temperature-humidity conditions.

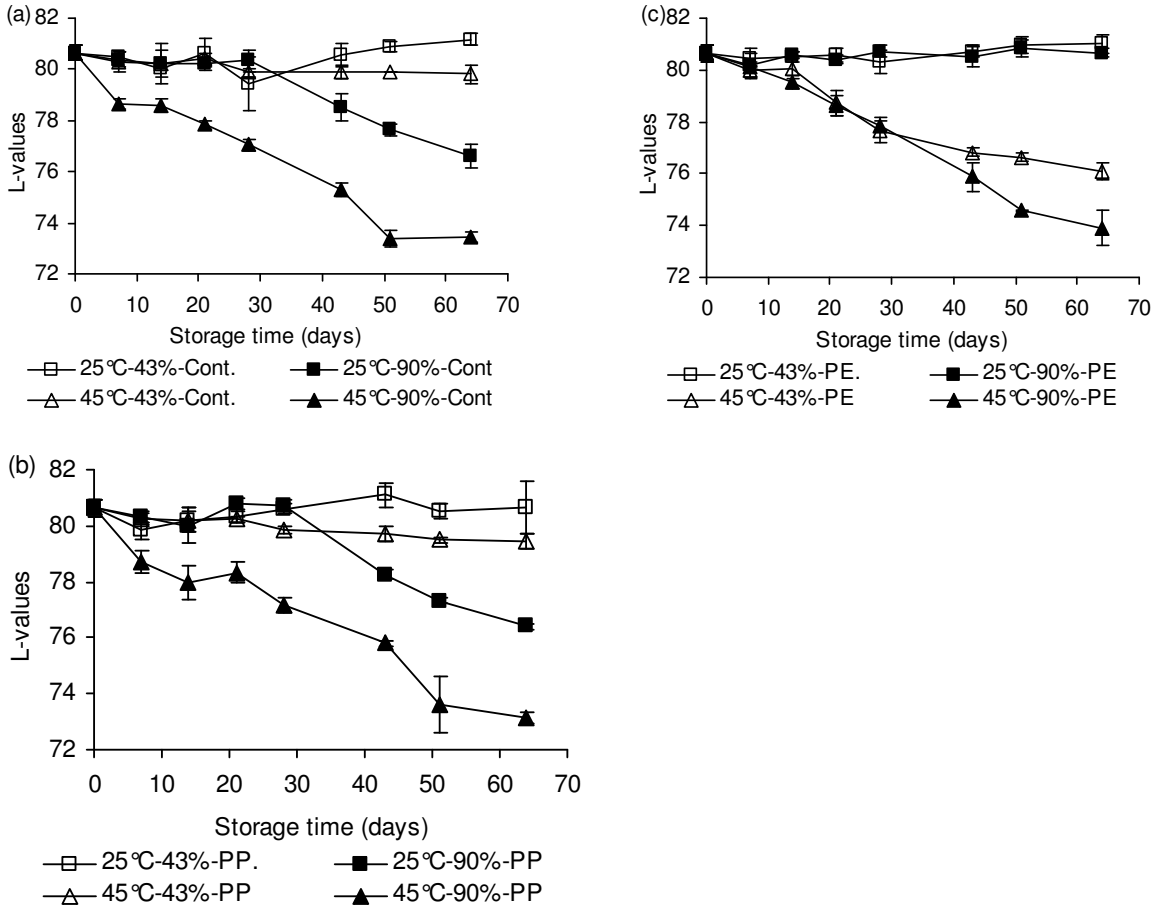

Figure 3.4 Changes in L-values of white maize meal during storage at different conditions: (a) without packaging (Cont: Control), (b) in polypropylene (PP) and (c) in polyethylene (PE) packaging materials with exposure to temperature-humidity conditions of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH.

Figure 3.4 (a), 3.5(a), 3.7(a) and 3.7(a) illustrates the influence of storage temperature-humidity on L-, b-, a- and ΔE-values, and the patterns of evolution are similar to those observed for Figure 3.3(a), (b), (c) and (d), respectively. Figures 3.4 (b) and (c) illustrate the influence of packaging material on L-values when packaged white maize meal is stored under the same four storage conditions. In terms overall quantitative differences, ANOVA revealed that L-values for the control at 25^{o}C-43%RH, PP at 25^{o}C-43%RH, PE at 25^{o}C-43%RH, and PE at 25^{o}C-90%RH remained high and did not significantly ($p>0.05$) differ. The L-values for the control at 45^{o}C-90%RH and PP at 45^{o}C-90%RH had the lowest values and did not significantly ($p>0.05$) differ. On the other hand, the L-values for the control samples at 25^{o}C-90%RH and PP at 25^{o}C-90%RH did not significantly differ just as the control at 45^{o}C-43%RH and PP at 45^{o}C-43%RH did not significantly differ. However, the L-values for PE at 45^{o}C-43%RH and PE at 45^{o}C-90%RH were appreciably low and, had the third and second lowest values, respectively.

Figures 3.5 (b) and (c) illustrate the influence of packaging material on b-values when packaged maize meal is stored under the same four storage conditions. ANOVA showed that b-values for the control at 25^{o}C-90%RH and PP at 25^{o}C-90%RH did not significantly differ and had the lowest values. The b-values for the control at 45^{o}C-90%RH and PP at 45^{o}C-90%RH did not significantly differ and had significantly the highest values. The b-values for the control at 25^{o}C-43%RH, PP at 25^{o}C-43%RH, PE at 25^{o}C-43%RH and PE at 25^{o}C-90%RH did not significantly differ and had the second lowest values. The b-values for the control at 45^{o}C-43%RH and PP at 45^{o}C-43%RH did not significantly differ and had the third highest values. On the other hand, the b-values for PE at 45^{o}C-43%RH and PE at 45^{o}C-90%RH did not significantly differ and had the second highest values.

Figures 3.6 (b) and (c) illustrate the influence of packaging material on a-values when packaged maize meal is stored under the same four storage conditions. Using ANOVA it was found that the control at 45^{o}C-90%RH had significantly the highest a-values followed by PP at 45^{o}C-90%RH, PE at 45^{o}C-90%RH and PE at 45^{o}C-43%RH, in that order. The a-values for the control at 45^{o}C-43%RH and PP at 45^{o}C-43%RH did not significantly differ and had the fifth highest values.

The evolution of ΔE for the control and PP at all the four storage conditions did not significantly differ during the storage period (Figure 3.7). The ΔE for the control and PP at 45^{o}C-90%RH,

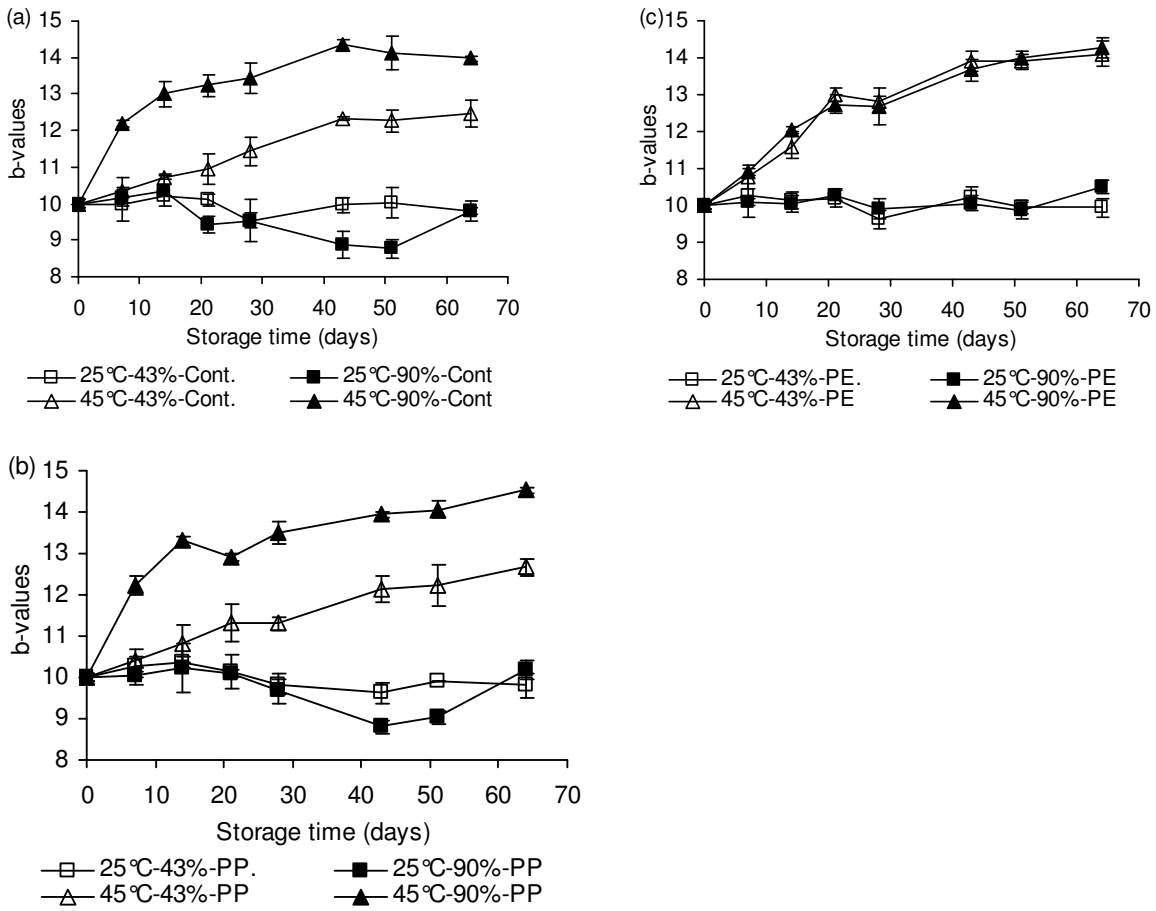

Figure 3.5 Changes in b-values of white maize meal during storage at different conditions: (a) without packaging (Cont: Control), (b) in polypropylene (PP) and (c) in polyethylene (PE) packaging materials with exposure to temperature-humidity conditions of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH.

45°C-43%RH and 25°C-90%RH increased during the storage period with samples at 45°C-90%RH having the highest ΔE –values (Figure 3.7a and b). The ΔE for control and PP at 25°C-90%RH were only higher than the ΔE at 45°C-43%RH after 43 days of storage, while ΔE at 25°C-43%RH was the lowest and was significantly constant during the storage period. The ΔE at high storage temperature (45°C-90%RH and 45°C-43%RH) for samples in PE were higher than the samples at low storage temperature (25°C-43%RH and 25°C-90%RH) during the storage period (Figure 3.7c). The ΔE for samples in PE at 45°C-90%RH and 45°C-43%RH did not significantly differ until after 43 days when the samples at 45°C-90%RH became significantly higher than at 45°C-43%RH. On the other hand the ΔE for samples in PE at 25°C-43%RH and 25°C-90%RH did not significantly differ throughout the storage period.

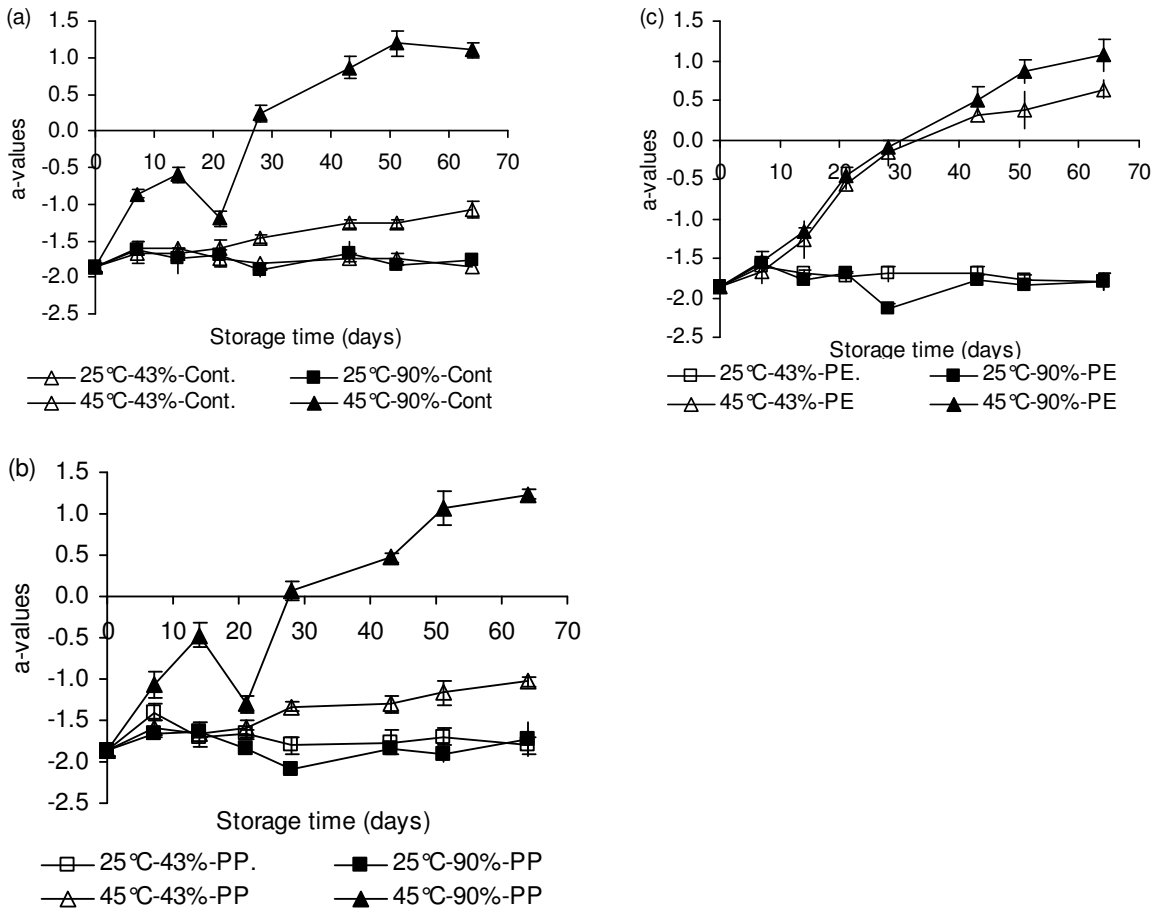

Figure 3.6 Changes in a-values of white maize meal during storage at different conditions: (a) without packaging (Cont: Control), (b) in polypropylene (PP) and (c) in polyethylene (PE) packaging materials with exposure to temperature-humidity conditions of 25^{o}C-43%RH, 25^{o}C-90%RH, 45^{o}C-43%RH and 45^{o}C-90%RH.

Overall, storing maize meal in PP interwoven sacks had poor barrier protection from effects of storage temperature and relative humidity on L-, a- and b-values. PE plastic maintained L-values (suppressed reduction in L-values) at low temperature-high humidity storage conditions. However, PE plastic decreased L-values faster than in PP interwoven sacks at high temperature-low humidity. Storing maize meal in PE plastic increasesd b- and a-values faster and to higher values than in PP interwoven sacks at high temperature-low humidity. The overall colour (ΔE-values) in the PE plastics changed faster and more intensely than in PP interwoven sacks at high temperature-low humidity. In fact, the rate of change in colour was equivalent to the rate of change at high temperature-high humidity.

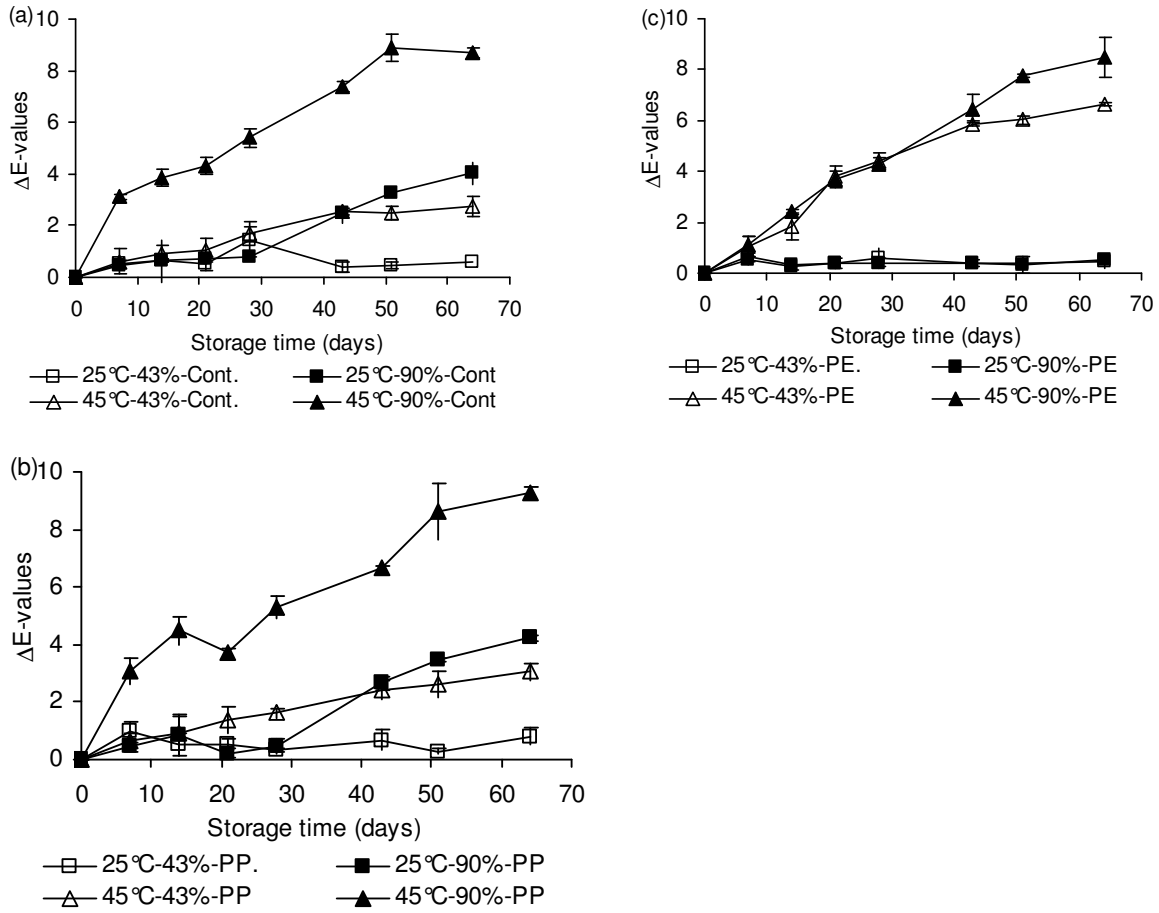

Figure 3.7 Changes in ΔE-values of white maize meal during storage at different conditions: (a) without packaging (Cont: Control), (b) in polypropylene (PP) and (c) in polyethylene (PE) packaging materials with exposure to temperature-humidity conditions of 25^{o}C-43%RH, 25^{o}C-90%RH, 45^{o}C-43%RH and 45^{o}C-90%RH.

The results have shown that low storage temperatures and low humidity maintains the color quality of maize meal for a longer storage time even without packaging. However, PE plastics could be used to slow down the browning at high humidity, if the storage tempearure can be maintained low. These results also indicate that at high storage temperatures and high humidity, neither the PP nor the PE would inhibit the browning in the white maize meal. It is clear that to avoid browning, high storage temperatures must be avoided. This is a big challenge for low lying regions of Africa like the valleys which record extreme high temperatures.

3.5. Influence of storage conditions on sensory properties

3.5.1. Open bulk storage of maize meal

3.5.1.1. Materials and storage protocol

The materials and the storage protocol were as described in Section 3.4.1.1 and section 3.4.1.2, respectively.

3.5.2. Sensory testing

3.5.2.1. Sample preparation and serving

Immediately after sampling, 5g maize meal samples were placed in small clear bottles (approx. volume = 40ml, internal diameter = 22mm and height = 70mm). The bottles were capped with a lid immediately to avoid loss in aroma/smell and were marked with a three digit code. The sample bottles consisted of a control (untreated sample), and the four treated samples. The samples were left to equilibrate overnight in the sample bottles at room temperature before sensory analysis. The control sample used in sensory evaluation was kept in hermetically closed glass bottles in the refrigerator maintained at 4 - 7^{o}C.

3.5.2.2. Sensory panel and training

Sensory analysis was accomplished by 11 panellists consisting of 4 males and 7 females aged between 20 and 50 years. The panellists were staff members from the faculty of Agricultural Sciences of the University of Zambia, Lusaka, Zambia. The panellists were selected on the basis of willingness to participate through out the study period, regular users (at least once a week) of maize meal and not allergic to maize meal. The sensory analysis was conducted in the Laboratory at the Department of Food Science & Technology of the University of Zambia, Lusaka, Zambia.

The panellists were familiarized in one 2-hour session with samples previously stored under similar conditions. The panellists were also familiarized with the attributes to be evaluated, the techniques to be used during the evaluation process, the use of the questionnaire and the terms used were explained in detail.

3.5.2.3. Sensory attributes and evaluation

Attributes evaluated included aroma, colour and texture of the maize meal and were evaluated in that order. For aroma, the panellists were instructed to open the sample bottle and smell the maize meal provided in the bottle. The panellists were asked to rank the maize meal based on the intensity of maize meal aroma of the reference/control sample using the scale (1 = Extreme off-odor, 5 = Typical Maize meal Aroma, and 9 = No maize meal aroma). For colour, the panellists were instructed to place the samples on a white disposable plate and using the scale (1 = Extremely more browned, 5 = Typical 'white' roller meal, and 9 = Extremely more whiter), they were asked to rank the colour of the maize meal based on the intensity of the colour of the reference sample. For the texture, the panellists were asked to examine the maize meal sample by picking and pressing a small amount of it in between their thumb-finger and the middle-finger, for a few seconds. By comparing with the reference/control sample, they were then asked to rank the texture (stickiness or agglomeration to itself) of the maize meal using the scale (1 = extremely more sticky, 5 = typical stickiness of roller maize meal, and 9 = extremely less sticky).

3.5.2.4. Statistical analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

3.5.3. Results and discussions

The white maize meal was evaluated for three sensory properties during storage; aroma, colour and texture. The sensory properties were only significantly ($p<0.05$) established for colour. In this study, low colour scores means that the colour of the maize meal deteriorated, in fact became browner. The sensory mean colour scores of the maze meal at 25^{o}C-43%RH slightly but significantly ($p<0.05$) increased during the storage period (Figure 3.8). This means that the maize meal was perceived by the panellists to become whiter during storage at 25^{o}C-43%RH. The sensory mean colour scores of the maze meal at 25^{o}C-90%RH significantly ($p<0.05$) decreased from the 28th day of storage up to the end of the storage period. The colour scores of the maze meal at 45^{o}C-43%RH and 45^{o}C-90%RH significantly ($p<0.05$) decreased between 7th and 14th days of storage and remained constant during the rest of the storage period. However, the colour of the maize meal at 45^{o}C-90%RH reduced significantly ($p<0.05$) to lower mean colour scores than at 45^{o}C-43%RH.

This entails that the panellists perceived browner colour development with storage time at 25°C-90%RH, 45°C-43%RH and 45°C-90%RH storage conditions. However, the rate of brown colour development at these storage conditions were perceived by the panellists to be different, with 45°C-90%RH having the highest rate and 25°C-90%RH having the least while 45°C-43%RH was intermediate.

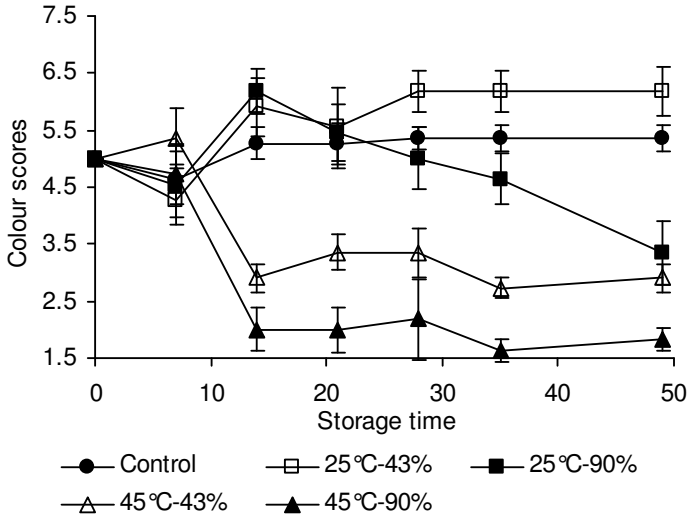

Figure 3.8 Mean colour scores of white maize meal during storage at temperature – relative humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH.

Table 3.2 shows the correlation coefficients between L-, a- and b-values obtained by a Minolta camera and the mean sensory colour scores obtained by panellists during storage of white maize meal. The samples at low storage temperature only showed a significant ($p<0.05$) negative correlation for ΔE (overall colour change) and the mean sensory colour scores. On the contrary, high temperature storage had all the Minolta colour values significantly correlating with the mean sensory colour scores. At high storage temperatures, L-values positively correlated with mean sensory colour scores while b-, a- and ΔE-values negatively correlated with mean sensory colour scores. The b- and a-values at high temperature storage increased during storage, meaning that the maize meal pigments became more reddish and yellowish in colour in the course of storage. A combination of these colours is what the panellist scored as brownish hue. From table 3.2, it is also evident that the correlation values were higher for 45°C-90%RH than for 45°C-43%RH storage conditions. This means that the storage relative humidity also influenced the changes in colour during storage. Higher relative humidity at high storage temperature increased the intensity of discoloration or browning of the maize meal during storage.

Table 3.2 Correlation coefficients between sensory colour scores and Minolta colour values of white maize meal during storage at temperature – relative humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH*

Minolta colour values	**Sensory colour scores**			
	25°C-43%RH	**25°C-90%RH**	**45°C-43%RH**	**45°C-90%RH**
Storage time (days)	0.77*	-0.59	-0.77*	-0.79*
L-values	-0.75	0.75	0.77*	0.89*
b-values	-0.64	0.40	-0.87*	-0.98*
a-values	-0.60	0.41	-0.84*	-0.96*
ΔE-values	-0.09	-0.80*	-0.78*	-0.94*

*Significant at $p<0.05$

It seems that even though there was a change in the aroma during storage of the white maize meal, the changes were not at a level perceivable for differentiation by the panelists. In a study of cornmeal, Bothast et al. (1981) also found that with respect to flavor and ordor scores, storage time did not appear to be a factor in low-temperature storage of either product at 11 and 13% moisture. Probably, the aroma and texture attributes of the maize meal needed a well elaborate training for the panelists, unlike the level of familiarization/training given in this study. For aroma, the researcher's observation was that the off-flavours could be sensed on the first time of opening the product under the storage conditions, but not afterwards. Therefore, it seems that in order to capture the aroma trend during maize meal storage, a real time aroma sensory evaluation is required.

The decrease in the lightness (decrease in L-values), the shift towards red (increase in a-values) and yellow (increase in b-values) hue in colour at high storage temperature conditions were principally due to pronounced browning which was visually observed. No browning was observed at low temperature – low humidity conditions. On the other hand, the browning at low temperature – high relative humidity storage condition was only manifested in decreasing L-values (lightness) but no shifts in the a- and b-values. A decline in lightness has been associated with darkening in irradiated maize flour (maize meal) due to Maillard (Rombo et al., 2001), enhanced Maillard browning reactions in rice (Wootton et al., 1988; Wang et al., 1983) and in dry bean flours (Cunha et al., 1993; Rombo et al., 2001).

In white maize meal, the L-values clearly depicted the increase in browning at 45°C-43%RH and 45°C-90%RH after 7 days of storage, and after 28 days of storage for 25°C-90%RH storage conditions (Figure 4.5).

Common browning of foods during storage has been attributed to Maillard reactions (BeMiller & Whistler, 1996). The white maize meal became brown during storage due to the reaction between sugars and free amino proteins. Total soluble sugars have been reported at 3.6% in maize grain. A decrease in total soluble sugars has been reported in maize grain during six months of storage at 45°C while an increase has been observed at 25°C. The increase in the soluble sugars has been attributed to activity of endogenous amylases whereas the decrease in soluble sugars at 45°C has been attributed to their involvement in Maillard reactions (Zia-Ur-Rehman, 2006).

Browning was not observed at low temperature – low humidity conditions during the storage of the white maize meal. The white maize meal at this storage condition decreased to low water activities during the storage period. It has been suggested that the decrease of Maillard reaction rate in low water activity systems is due to higher viscosity, which reduces the mobility of reagents (Sensidoni et al., 1999).

The white maize meal increased in browning at 45°C-43%RH and 45°C-90%RH after 7 days of storage and after 28 days of storage for 25°C-90%RH. Some researchers (Eichner & Karel, 1972; Sensidoni et al., 1999) have reported that the maximum rate of the non-enzymatic browning reaction appears when dry food materials are humidified. The region where the maximum occurs is usually near water activity = 0.65 – 0.70, which corresponds to the water activity of intermediate moisture foods. The water activities in the white maize meal for the high humidity storage were falling between 0.6 and 0.8 (section 2.4.3.2, Figure 2.9) which is within the stated range. These researchers (Eichner & Karel, 1972; Sensidoni et al., 1999) have further suggested that the differences in reactivity with increasing water activity can be explained by considering the non-enzymatic browning reaction as a diffusion limited reaction. Increasing water activity generally leads to higher reaction rates due to higher mobility of reactants.

However, the white maize meal stored at high temperature-low humidity conditions resulted in high amounts of non-enzymatic browning and yet the water activities in this storage condition decreased to below 0.6, with the lowest water activities around 0.4 (section 2.4.3.2, Figure 2.9).

Assuming equilibrium, water activities of 0.4 for the white maize meal gives moisture content of 7.5% which is slightly above the estimated monolayer moisture content obtained. This indicates, however that increasing temperature even with low water activities causes browning in white maize meal during storage. Goddard (1999) has indicated that, in general, as with all chemical reactions, heat accelerates and in many cases initiates the browning reaction.

The degradation of the Amadori product formed from the reaction of sugars and amino protein is dependent on the pH of the system. At pH 7 or below, the Amadori product mostly rearranges through the 1,2-enolisation to form furfural (when pentoses are involved) or hydroxymethylfurfural (HMF) (when hexoses are involved) (Martins et al., 2001). The pH of the white maize meal in this study decreased during storage at both low and high temperatures. In light of this observation and referring to the Maillard pathways presented in Figure 1.3, one would postulate that the browning mechanism in white maize meal during storage would proceed via schiff's base of hydroxymethylfurfural (HMF) or furfural. The HMF or furfural would probably react with amino compounds to produce melanoidins (brown nitrogenous polymers).

Brown colors obtained during long-term storage of foods containing reducing sugars are undesirable (BeMiller & Whistler, 1996). Browning or discoloration is undesirable among white maize meal consumers too. Maillard reaction is also known to be an important factor influencing food nutritional value and quality. This must be of concern in white maize meal because it is a product that is already low in protein quality, particularly, lysine and tryptophan. If the small amounts in essential amino acids in the maize meal react in Maillard reactions, this further lowers the nutritional quality of this staple food.

3.6. Influence of storage conditions on lipolysis

3.6.1. Maize meal storage in closed bottles

The materials and storage protocol were as described in section 3.3.1.1 and section 3.3.1.2, respectively.

3.6.2. Open bulk storage of maize meal

The materials, storage protocol and statistical analysis were as described in section 2.3.1.1, section 2.3.1.2 and section 2.4.2.3.

3.6.3. Maize meal storage in commonly used packaging material

The materials, storage protocol, WVTR and statistical analyses were as described in section 2.4.1.1, section 2.4.1.2, section 2.4.2.2 and section 2.4.2.3, respectively.

3.6.4. Fortified-packaged-sunlight exposed storage

The materials, fortification procedure, storage protocol, WVTR, light transmission and statistical analyses were as described in section 2.4.4.1, section 2.4.4.2, section 2.4.4.3, section 2.4.2.2, section 2.4.5.4 and section 2.4.6, respectively. However, the WVTR here was only determined at 45^{o}C.

3.6.5. Free fatty acids determination

For the maize meal storage in closed bottles, open bulk storage and fortified-packaged-sunlight exposed storage, the oil extraction procedure was as follows: Maize meal oil was extracted by shaking 5g of maize meal in 100ml chloroform-methanol (2:1 v/v) mixture for 8 hours at room temperature according to Folch et al. (1957). The mixture was passed through filter paper to remove the insoluble material. The extract was evaporated to dryness in a rotary evaporator at 40°C under reduced pressure.

For the maize meal storage in commonly used packaging material, the oil extraction procedure was as follows: Oil was extracted by shaking 5g of maize meal in 100ml *n*-hexane for 8 hours at room temperature. The mixture was passed through filter paper to remove the insoluble material. The filtrate was evaporated to dryness in a rotary evaporator at 65°C under reduced pressure.

The dry oil extracts were weighed. Free fatty acid contents were determined in duplicates according to DGF-Standard methods (1984).

3.6.6. Results and discussion

3.6.6.1. Maize meal storage in closed bottles

Figure 3.9 shows the evolution of free fatty acids for the samples stored in capped bottles at low and high temperature. The fats in this section were extracted using choloroform:methanol (2:1) mixture. The use of a mixture of chloroform and methanol (2:1, 1:1, 1:2 by volume) is used to extract non-starch total lipids at room temperature. In cereals, the sum of free lipid and bound lipid is termed the non-starch total lipids (Chung & Ohm, 2000). Free fatty acid contents increased almost linearly throughout the 124 days of storage at both room temperature (≈25°C) and 43°C. The gradient for the 43°C storage graph was steeper than the room temperature (≈25°C) storage graph. The results show that both storage temperature and time have a profound effect on the free fatty acid contents in maize meal. This could be due to increased lipase activities with an increase in storage temperature.

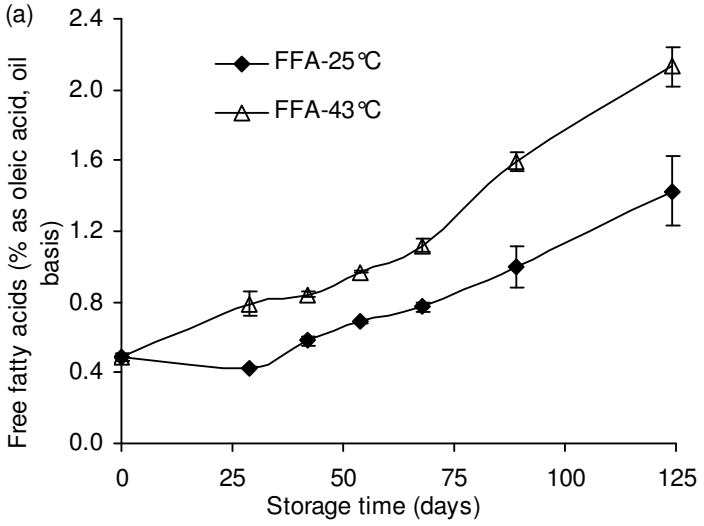

Figure 3.9 Changes in free fatty acids of white maize meal during storage at room temperature (≈25°C) and 43°C

Castello et al. (1998) reported that wheat lipases have been implicated in the increase of free fatty acid contents during long term storage of flour.

3.6.6.2. Open bulk storage of maize meal

Figure 3.10 shows the changes in free fatty acid contents of maize meal stored at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. The fats in this section were extracted using choloroform:methanol (2:1) mixture. The free fatty acid contents of samples stored at 25°C-90%RH increased slowly the first 30 days and thereafter increased sharply. The free fatty acid contents of samples stored at 45°C-90%RH increased very sharply in the first 35 days before decreasing sharply again up to the 49th day of the storage study. There was mould or fungal growth from 28 days and 49 days at 45°C-90%RH and 25°C-90%RH, respectively. At low humidity storage no fungal growth was observed throughout the storage period. Castello et al. (1998) reported that wheat and fungal lipases have been implicated in the increase of free fatty acids during long term storage of flour.

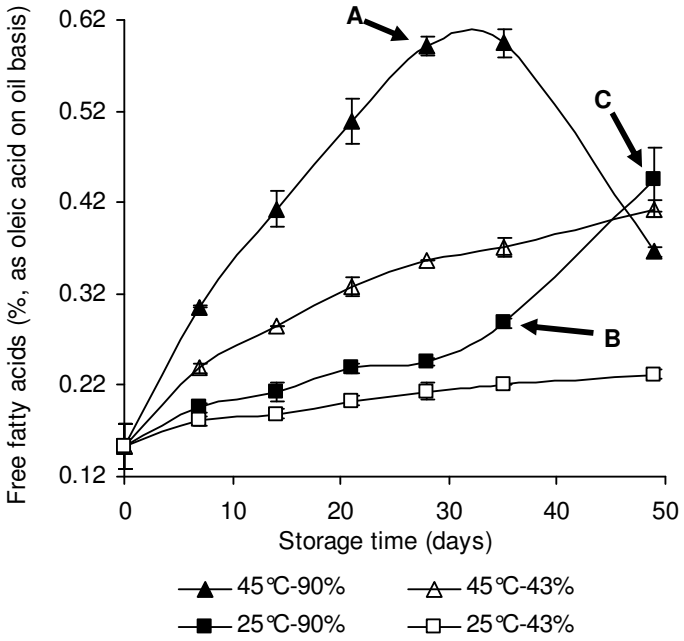

Figure 3.10 Changes in free fatty acid contents of white maize meal stored at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. A – Caking and mould appearance; B – Caking; C- Mould appearance

Storage temperature has a higher influence on the changes in free fatty acid contents than storage relative humidity. Free fatty acid contents at high storage temperatures were higher and evolved faster than at low storage temperatures. However, it is also clear that at constant storage temperature, samples at high storage relative humidity had faster and higher increases in free fatty acid contents than at low storage relative humidity.

This effect is more pronounced at high storage temperatures than at low storage temperatures. This phenomenon could be explained on the basis of moisture content. In section 2.3.3.2, high storage relative humidity was associated with higher moisture contents and higher water activity in section 2.4.3.2. Higher moisture contents could have increased substrate mobility hence, enhanced lipolytic reactions. Water activity affects chemical reactions in foods.

3.6.6.3. Maize meal storage in commonly used packaging material

The properties of the packaging materials used were as reported in section 2.4.3.1. In order to determine the influence of packaging on lipolysis the white maize meal was stored in polypropylene interwoven sacks and polyethylene plastic materials together with samples without packaging as a control at different temperature-humidity conditions. The two packaging materials were used in the study because they are in common use in the packaging of maize meal in Zambia. Free fatty acids (FFA) are a measure of the extent of lypolysis. In this study FFA was expressed as % oleic acid on oil basis. The fats in this section were extracted using hexane. Unlike the chloroform:methanol mixture which extracts non-starch total lipids, hexane is a nonpolar solvent and only extracts free lipids. Figure 3.11 (a) illustrates the influence of storage temperature and relative humidity on FFA. Figures 3.11 (b) and (c) illustrate the influence of packaging material on FFA when maize meal is stored under the same four storage conditions.

The FFAs for the control samples increased during the storage period and did not significantly differ particularly the first 20 days, for all the four storage conditions (Figure 3.11a). However, the FFA at high storage temperatures were significantly higher than for the samples at low storage temperatures for the control after 20 days of storage. At high storage temperature, the FFAs for the samples at 45^{o}C-90%RH were significantly higher than at 45^{o}C-43%RH after 28 days of storage. Similarly, at low storage temperature, the FFAs for the samples at 25^{o}C-90%RH were significantly higher than at 25^{o}C-43%RH after 28 days of storage.

The FFAs for the samples in PP also increased during the storage period for all the four storage conditions (Figure 3.114b). However, the FFAs at high storage temperatures were significantly higher than for the samples at low storage temperatures for the samples in PP particularly after 28 days of storage.

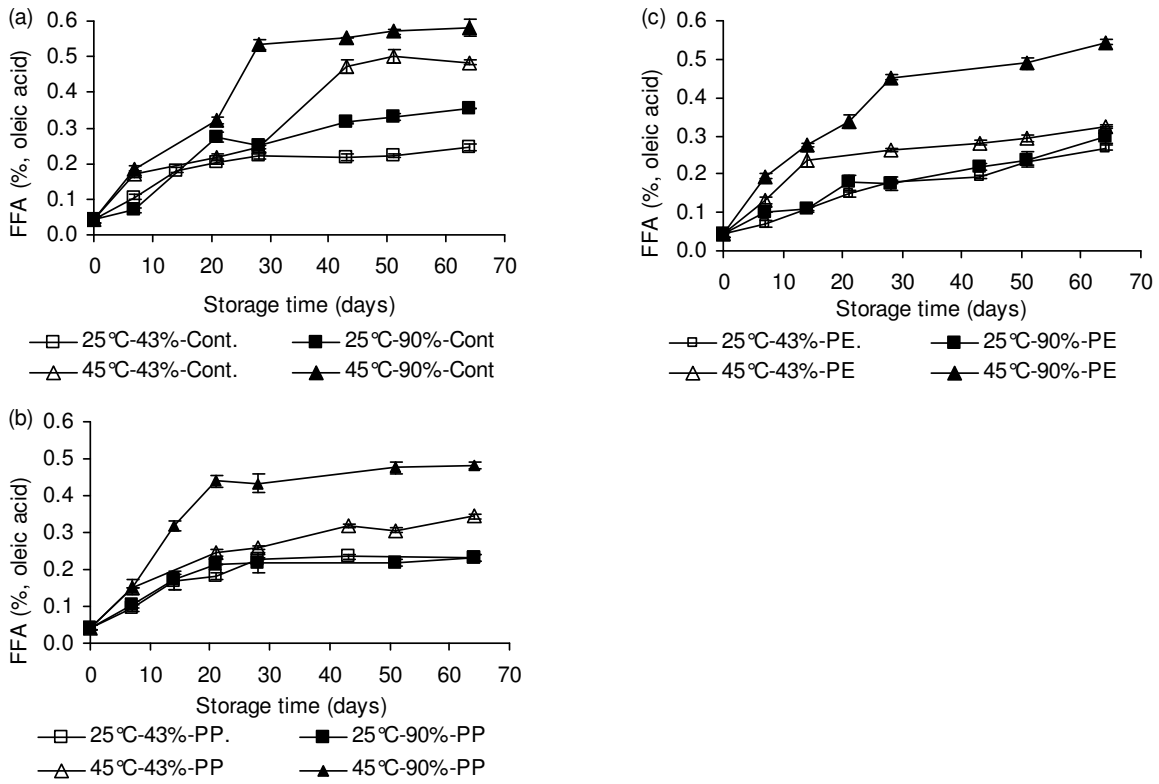

Figure 3.11 Changes in free fatty acid (FFA) contents of white maize meal during storage at different conditions: (a) without packaging (Cont: Control), (b) in polypropylene (PP) and (c) in polyethylene (PE) packaging materials with exposure to temperature-humidity conditions of 25^{o}C-43%RH, 25^{o}C-90%RH, 45^{o}C-43%RH and 45^{o}C-90%RH.

At high storage temperature, FFAs for the samples at 45^{o}C-90% were significantly higher than at 45^{o}C43%RH just after 7 days of storage. The FFAs for the samples stored in PP at 45^{o}C-43%RH did not significantly differ from the samples at low storage temperature until after 28 days of storage. On the contrary, at low storage temperature, FFAs for the samples at 25^{o}C-90%RH and at 25^{o}C-43%RH did not significantly differ during the storage period.

The FFAs for the samples stored in PE also increased during the storage period with samples at high storage temperature being higher than at low storage temperatures (Figure 3.11c). At high storage temperature, FFAs at 45^{o}C-90%RH were significantly higher than at 45^{o}C-43%RH. However, the FFAs for the samples in PE at 25^{o}C-43%RH and 25^{o}C-90%RH did not significantly differ during the storage period.

Quantitatively, ANOVA showed that the control samples stored at 45°C-90%RH had significantly the highest FFAs. The free fatty acids of samples stored in PP at 45°C-90%RH and in PE at 45°C-90%RH did not significantly differ and had the second highest FFAs. The control samples stored at 25°C-43%RH, the samples stored in PP at 25°C-43%RH and stored in PE at 25°C-90%RH did not significantly differ and had the second lowest FFAs after samples in PE at 25°C-43%RH which had significantly the lowest. The control samples at 45°C-43%RH and the samples in PP at 45°C-43%RH had the third and fourth highest. The control samples at 25°C-90%RH and the samples in PE 45°C-43%RH did not significantly differ though they had significantly higher FFAs than samples in PP at 25°C-90%RH. In essence, it seems that packaging material has no direct influence on the evolution of FFA. The increase in free fatty acid contents in the white maize meal during storage could be an implication of lipases. Sammon (1999) reported that freeing of fatty acids takes place from the time of milling, presumably due to mixing of natural lipases with esterified fatty acids.

3.6.6.4. Fortified-packaged-sunlight exposed storage

The fat in this section was extracted using chloroform:methanol (2:1) mixture. When maize meal was fortified, packaged and exposed to sunlight, there was an increase in free fatty acids in all the samples during the 70 days storage period (Figure 3.12). All the fortified samples had higher free fatty acids contents than the unfortified samples, throughout the storage period, except for FSP which had the same as the unfortified in the first two weeks, but crossed on the higher side thereafter. Quantitatively, ANOVA showed that FED and FES had significantly ($P<0.05$) the highest FFA followed by FPD and FPS, in that order. On the contrary, there was no significant ($P<0.05$) difference in FFA among UPS, UES, UPD and UED which had the lowest FFA. This indicates that, of all the three conditions, fortification was a major determinant of the FFA during storage.

The magnitudes of change in FFA between day zero and day 70 were also calculated from Figure 3.12. The calculations were based on the initial free fatty acids as:

$$\Delta C_{FFA} = \left(\frac{C_{70} - C_0}{C_0} \right) * 100 \qquad (3.2)$$

where ΔC_{FFA} is the percentage change in FFA, C_0 is the initial concentration of FFA, C_{70} is the concentration of FFA on 70th day.

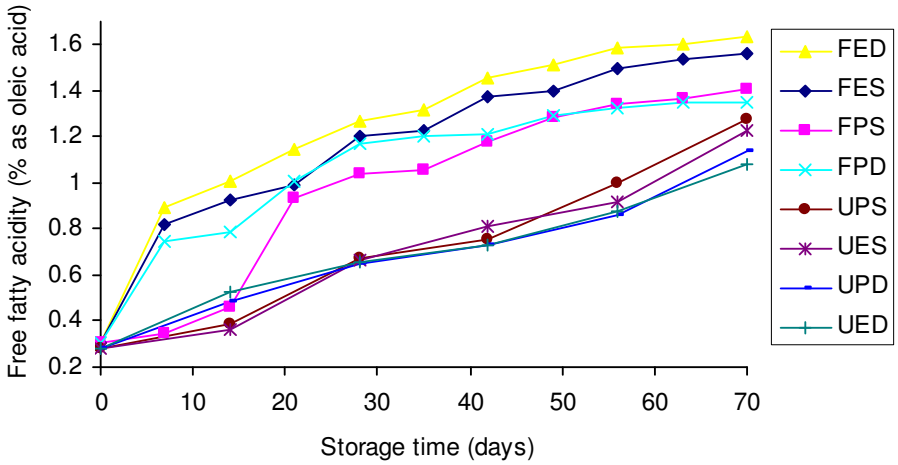

Figure 3.12 Changes in free fatty acid contents of fortified and non-fortified white maize meal packaged in polypropylene sack and polyethylene plastic packages with exposure and non-exposure to sunlight conditions. The three letter abbreviation in the legend gives the maize meal treatments: type of maize meal-packaging type-sunlight/darkness storage. FED: Fortified-PE-Darkness; FES: Fortified-PE-Sunlight; FPS: Fortified-PP-Sunlight; FPD: Fortified-PP-Darkness; UPS: Unfortified-PP-Sunlight; UES: Unfortified-PE-Sunlight; UPD: Unfortified-PP-Darkness and UED: Unfortified-PE-Darkness.

The fortified samples' increase in free fatty acid contents ranged between 342 and 433 %, whereas the unfortified ranged between 284 and 354 %. Within fortified samples, the samples packaged in polyethylene (FED = 433 % and FES = 411 %) had a higher increase in free fatty acids than the samples in polypropylene (FPS = 358 % and FPD = 342 %). Within the unfortified samples, samples stored in sunlight had higher increase in free fatty acids (UPS = 354 % and UES = 334 %) than samples in the dark room condition (UPD = 305 % and UED = 284 %), although ANOVA has shown that these were not statistically different. The higher magnitudes of increase in free fatty acid contents in the fortified samples than unfortified could be attributed to increased yeast & mould growth. The yeast & moulds are capable of producing lipases which increases the free fatty acid contents. Among the fortified samples, polyethylene increased free fatty acids more than polypropylene because of the good water activity retention properties in polyethylene than polypropylene, as reported in Table 2.6 section 2.4.7.2.

Lipolysis may be of great concern in maize meal as it is now being associated with oeasphagus cancer. Squamous cancer of the esophagus is endemic in Southern Africa and consumption of maize meal has been shown to be strongly associated with cancer of the esophagus (Van

Rensburg et al., 1985; Sammon, 1999). The effect of milling is the mixing of esterified fatty acids with natural lipases, resulting in release of the non-esterified form. It has been suggested that an aetiological link exists between maize meal and cancer of the esophagus by means of elevated Prostaglandin E2 (PGE2) levels in the stomach (Sammon, 1999). Linoleic acid is a precursor of PGE2. A diet high in linoleic acid leads to a high level of PGE2 production in the stomach, the production of PGE2 apparently rising steadily as the dietary linoleic acid rises (Grant et al., 1988; Schepp et al., 1988; Sammom, 2006). This means that the longer the maize meal stays on the shelf, the higher the risk to the consumers. Therefore, to minimize the occurrence of non-esterified fatty acids in maize meal, storage temperature and humidity are major factors to be addressed. In fact, Sammon (2006) has recommended that health measures including poverty alleviation, health education, and monitoring and control of maize meal storage and content may be required to reduce the incidence of this disease in Africa.

However, proponents of mycotoxins also have a strong view that oesophagus cancer in the high maize consumption regions is due to fumonisins intake. Fumonisins have been proven to cause cancer in experimental animals. Experimental evidence proving or disapproving suspected effects on human subjects cannot be found in literature because of ethical considerations (Samapundo, 2006). However, evidence from experimental animals gives fumonisins a stronger association between oesophagus cancer and maize consumption.

3.7. Influence of storage conditions on lipid oxidation of maize meal during storage

3.7.1. Fortified-packaged-sunlight exposed storage

3.7.1.1. Materials and methods

The materials, fortification procedure, storage protocol, WVTR, light transmission and statistical analyses were as described in section 2.4.4.1, section 2.4.4.2, section 2.4.4.3, section 2.4.2.2, section 2.4.5.4 and section 2.4.2.3, respectively. However, the WVTR here was only determined at 45^{o}C. Oil extraction procedure was performed as in section 3.6.5 using chloroform:methanol mixture.

3.7.2. Maize meal storage in closed bottles

The materials and the storage protocol were as described in section 3.3.1.1 and section 3.3.1.2, respectively. Oil extraction procedure was as in section 3.6.5 using chloroform:methanol mixture.

3.7.3. Analytical methods

3.7.3.1. Peroxide value determination

Peroxide value was determined according to Egan et al. (1981). The peroxide value was calculated as mEq/kg (based on oil content).

3.7.3.2. p-Anisidine value determination

The dry oil extract was weighed and was used to determine p-anisidine value according to DGF-Standard methods (1984).

3.7.4. Results and discussion

3.7.4.1. Fortified-packaged-sunlight exposed storage

The properties of the packaging material used were as reported in section 2.4.7.2. The evolutions of peroxide value were highly influenced by whether the maize meal was fortified or unfortified. Figure 3.13 shows that the fortified samples reached their peak peroxide values in the second week, whereas the unfortified samples reached their peak peroxide values in the fourth week. The mean peak peroxide values of the unfortified samples were higher (15.4 mEq/kg) than the fortified mean peak peroxide values (8.8 mEq/kg). Thereafter, all the samples decreased in the peroxide value contents, although the unfortified still maintained higher peroxide values than the fortified samples up to the termination of storage. Peroxide value provides a clear indication of the initial oxidation potential of different lipids since hydroperoxides are the primary products of lipid oxidation (Wanasundara et al., 1995).

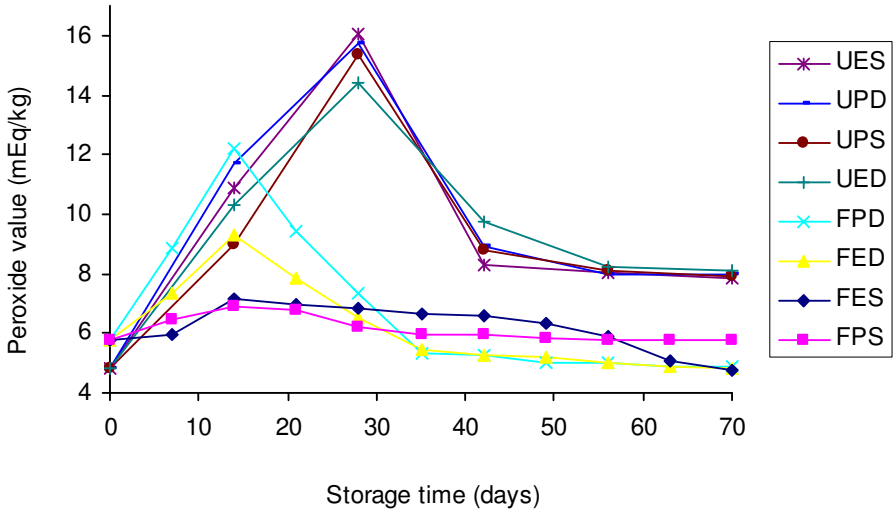

Figure 3.13 Changes in peroxide value of fortified and non-fortified maize meal packaged in polypropylene sack and polyethylene plastic packages with exposure and non-exposure to sunlight conditions. The three letter abbreviation in the legend gives the maize meal treatments: Type of maize meal - Packaging type - Sunlight/darkness storage. UES: Unfortified-PE-Sunlight; UPD: Unfortified-PP-Darkness; UPS: Unfortified-PP-Sunlight; UED: Unfortified-PE-Darkness. FPD: Fortified-PP-Darkness; FED: Fortified-PE-Darkness; FES: Fortified-PE-Sunlight and FPS: Fortified-PP-Sunlight.

The unfortified white maize meal contains metals such as iron and vitamins such as riboflavin. However, the metals in the white maize meal may be found in complexed states with compounds such as phytates. Fortification raises the concentration of iron and riboflavin in the white maize meal. In terms of lipid oxidation, white maize meal stored in the dark would be initiated only by thermal dissociation of hydroperoxides initially present in the maize meal and decomposition of hydroperoxides catalysed by iron. The two mechanisms would also dominate the initiation of lipid oxidation in the white maize meal stored in opaque PP material and exposed to sunlight.

In addition to these two lipid oxidation iniation mechanisms, the lipid oxidation of white maize meal stored in transparent PE plastics and exposed to sunlight would be initiated by riboflavin photosensitized reactions. The riboflavin photosensitized initiation reactions are not inhibited by *chain breaking* antioxidants like BHT. The presence of BHT in the fortified white maize meal could not therefore inhibit this mechanism of lipid oxidation initiation. This lipid oxidation initiation mechanism would thus contribute more towards free radical production in fortified white maize meal than in the unfortified white maize meal in transparent PE exposed to sunlight.

In addition, iron in the fortified maize meal would equally highly contribute towards free radical production in lipid oxidation of the fortified than in unfortified white maize meal.

The *chain-breaking* antioxidants inhibit or retard lipid oxidation by interfering with either chain propagation or initiation by hydrogen-atom transfer and readily donating hydrogen atoms to lipid alkyl, alkoxyl and peroxyl radicals. Phenolic compounds such as BHT are effective *chain-breaking* antioxidants (Frankel, 2005). Therefore, the presence of BHT in the fortified white maize meal could have inhibited the lipid oxidation initiation by thermal dissociation of hydroperoxides and decomposition of hydroperoxides catalysed by iron. The BHT could have also inhibited the chain propagation stage of lipid oxidation reactions thereby reducing the secondary products in fortified maize meal.

Therefore, sunlight exposure in fortified samples had lower maximum peak peroxide value and appeared earlier than in unfortified maize meal probably due to increased rates of oxidation. The hydroperoxides formed in fortified white maize meal could have been lost at a faster rate than what the method of determination of peroxides used could capture due to a combination of catalysis by sunlight energy (photosensitized reactions), iron and thermal decomposition lipid oxidation initiation reactions. It has been argued that the peroxide value method is limited by the transitory nature of the peroxides which are intermediate products in the formation of carbonyl compounds (Fernández et al., 1997). It is further argued that hydroperoxides decompose rapidly during storage (Wanasundara et al., 1995).

3.7.4.2. Maize meal storage in closed bottles

The evolution of p-anisidine value for the samples stored in capped bottles at low and high temperature is shown in Figure 3.14. The peak para-anisidine value of 23 for the sample stored at room temperature (≈25°C) appeared around the 29th day. On the other hand, the peak para-anisidine value for the sample stored at 43°C was not detected. The para-anisidine values after the peak value were almost constant and there was no significant ($P<0.05$) difference between the two storage temperatures.

The para-anisidine value measures secondary products of lipid oxidation, namely carbonyl compounds (Wanasundara et al., 1995). Measuring secondary oxidation products is important in

the determination of lipid oxidation in food products for human consumption because they are generally odour-active, whereas primary oxidation products are colourless and flavourless.

Unlike hydroperoxides, carbonyls do not decompose rapidly and thus allow the history of an oil to be determined by the para-anisidine value (Osborn & Akoh 2004). The peak para-anisidine value for samples stored at 43°C was not detected most probably because it occurred much earlier than the chosen sampling interval.

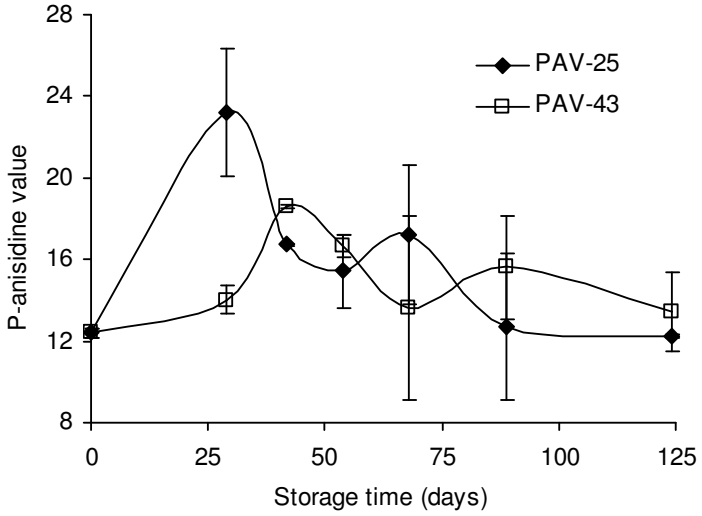

Figure 3.14 Changes in para-anisidine value of white maize meal during storage at room temperature (≈25°C) and 43°C

3.8. Storage life markers for white maize meal

3.8.1. Use of lipid oxidation indices

Among the lipid related properties, the use of peroxide value and para-anisidine value to assess the freshness or the storage life of maize meal must be used with caution. This is because in the determination of peroxide value, there are two storage time points that one can get the same peroxide value during the storage of maize meal. For instance, results in section 3.7.4.1, Figure 3.13, shows that a value of about 11 mEq/kg can be obtained around the 14 and 35th day of storage for unfortified maize meal during storage. A similar observation can be made concerning the use of para-anisidine values as seen in section 3.7.4.2, Figure 3.14. This makes this primary

(peroxide value) and the secondary lipid oxidation (anisidine value) indices unusable as storage life indicators or markers for maize meal during storage.

3.8.2. Use of lipolytic index

On the other hand, lipolysis has shown that it has a better potential of easily being used as a storage life marker for maize meal. This is because FFA increased at all storage conditions in this study for most of the storage period, except for the case of high temperature – high relative humidity storage. In other words, lipolytic index (free fatty acids) seems to be sensitive to storage time at all the storage conditions studied in this research. Moreover, even for the high temperature – high humidity storage, by the time the free fatty acids begin to decrease, the maize meal would have been visually/physically noticed rancid.

3.8.3. Use of colour indices

The sensory colour change produced trends which could be used to determine the shelf life of maize meal. When the colour becomes significantly different (negatively) from the typical (control/reference sample) then the end of shelf life has been reached. The mean colour scores at 45^{o}C-43%RH and 45^{o}C-90%RH were consistently below the mean scores of the control after 7 to 14 days, where as they were consistently below for 25^{o}C-90%RH after 28 days of storage (Section 3.5.3, Figure 3.8). On the other hand, the colour mean scores at 25^{o}C-43%RH were consistently slightly above the control after 28 days of storage. Therefore, it can be interpreted that the shelf life of the maize meal at 45^{o}C-43%RH and 45^{o}C-90%RH using colour as a shelf life marker is between 7 and 14 days, whereas the shelf life at 25^{o}C-90%RH would be about 28 days. On the other hand, the shelf life of the maize meal at 25^{o}C-43%RH was beyond the 49 days of storage. However, this analysis is invalid in the absence of data on other chemical and microbiological storage life markers, which might be more sensitive and of more food safety concern to storage of maize meal than colour. What is of interest is also the fact that the correlations between sensory colour and instrumental colour were quiet high although for high storage temperatures only. This offers an opportunity for the use of instrumental colour to easily determine the storage life of maize meal as it is a rapid method.

3.9. Conclusions

- At increased storage temperature decreased evolution of pH in function of time is observed. Storage period affected the evolution of titratable acids but storage temperature did not. Titratable acids increased in function of storage time.

- The colour of white maize meal changed depending on the storage conditions. The L-values decreased after a short period of storage at high storage temperature conditions, while at low storage temperature-high humidity after a longer storage period. The L-values at low storage temperature-low humidity conditions did not significantly change over the storage period. The a- and b-values at high storage temperatures increased, while at low storage temperature conditions did not significantly change during the storage period. These changes depicted the browning of white maize meal during storage as collaborated by sensory analysis.

- Storing maize meal in PP interwoven sacks had no barrier protection from effects of storage temperature and humidity on L-, a- and b-values. Storing maize meal in PE plastic maintained the colour at low temperature-high humidity storage conditions. On the contrary, storing maize meal in PE plastic deteriorated colour of white maize meal faster and more intense than in PP interwoven sacks at high temperature-low humidity. Infact, the rate of change in colour at high temperature-low humidity was equivalent to the rate of change at high temperature-high humidity.

- Storage temperature had a higher influence on the changes on lipolysis than storage relative humidity. Free fatty acids contents at high storage temperatures were higher and evolved faster than at low storage temperatures. At constant storage temperature, samples at high storage relative humidity had higher increases in free fatty acid contents and evolved faster than at low storage relative humidity. However, at high storage temperature-high humidity, the free fatty acid contents were confounded by mould growth after 28 days storage. Fortification had great influence on the evolution of FFA, with fortified maize meal evolving higher FFA than unfortified maize meal during storage. Packaging and sunlight exposure did not seem to play a significant role in the evolution of FFA during storage of maize meal.

- Lipid oxidation as observed in changes of peroxide value increased and then decreased to relatively constant values during the storage period. Unfortified maize meal generated higher peroxide values than the fortified maize meal, while packaging and sunlight exposure did not significantly influence the evolution of peroxide values. P-anisidine value also increased and then decreased to relatively constant values during the storage period, while the influence of storage temperature was not significant.

Chapter 4

Pasting and rheological properties of white maize meal during storage

Chapter 4. Pasting and rheological properties of white maize meal during storage

Abstract

This chapter evaluates the influence of storage conditions on gelatinization, pasting and rheological behaviours of white maize meal during storage. Starch in maize meal had significantly ($P<0.05$) higher gelatinization onset temperature (T_o) and gelatinization peak temperature (T_p) than the isolated starch for maize meal stored at both low and high temperature. On the contrary, starch in maize meal had significantly ($P<0.05$) lower gelatinization enthalpy (ΔH) than the isolated starch. Storage temperature had no significant ($P>0.05$) effect on the evolution of T_p and ΔH. The gelatinization properties only significantly ($P<0.1$) changed in the T_o for the isolated starch and gelatinization end temperature (T_E) ($P<0.05$) for maize meal, with both decreasing during the storage period.

In terms of pasting behaviour, low storage humidity increased peak viscosity (PV), initial hot-paste viscosity (V_{95i}) and final hot-paste viscosity (V_{95f}) at both low and high storage temperatures. High storage temperature resulted in higher cold-paste viscosity (V_{50}), total setback (SB_t) and cold-paste:hot-paste viscosity ratio (C:H) than low storage temperature. At constant storage temperature, high storage humidity resulted in higher SB_t and C:H than low storage humidity and this phenomenon was more pronounced at high storage temperature than at low storage temperature.

Storing maize meal at higher temperature and for a long period increased the peak elastic modulus (G'_p) while it decreased the peak viscous modulus (G''_p) of the isolated starch during heating. The white maize meal exhibited shear-thinning behaviour at all storage conditions throughout the storage period. The Herschel-Bulkley and Mizrahi-Berk models best predicted flow behaviour for low temperature storage conditions throughout the storage period, while only for a limited storage period at high storage temperatures. The stress overshoot at low storage temperature conditions decreased during storage while it increased at high storage temperatures. The flow behaviour indices and yield stress decreased while the consistency indices increased at all storage conditions, except at low storage temperature-low humidity conditions.

Key words: *Flow behaviour, Functional properties, Gelatinization, Maize meal, Oscillatory rheology, Pasting behaviour, Stability, Starch, storage*

4.1. Introduction

Almost any application of starch involves the gelatinization or melting of the granule structure (Thiewes & Steeneken, 1997). Differential Scanning Calorimetry (DSC) is used to detect enthalpy changes in the phase transition of starch (Chaiwanichsiri et al., 2001). At 30% or higher moisture contents, starches are analogous to other natural and synthetic polymers where the degree of crystalline order and polymer-solvent/plasticizer interactions are major factors in determining their melting behaviour and other properties (Zobel et al., 1988).

Dynamic rheology has been used in the past to study the rheological properties of corn starches by monitoring of elastic modulus (G′) and viscous modulus (G″) of starch granule dispersions (Yoshimura et al., 1988; Navarro et al., 1997; Rosalina & Bhattacharya, 2002; Singh et al., 2002; Freitas et al., 2003; Wang et al., 2003; Sandhu et al., 2004). Dispersion of cereal flour or starch in water results in a suspension whose rheology depends largely on the type and composition of the cereal, the concentration of the soluble and insoluble solids, heat treatment (such as extent of gelatinization and retrogradation) and the temperature of measurements (Bhattacharya & Bhattacharya, 1996). Cooked maize starches were found to possess yield stresses, and exhibited shear-thinning, pseudoplastic behaviour (Doublier, 1987; Bhattacharya & Bhattacharya, 1996). Further, it is also necessary to know to which the rheological model, or models, the cooked corn (or maize) flour suspensions conform (Bhattacharya & Bhattacharya, 1996).

In chapter 1 it has been shown that maize meal is consumed in many parts of Africa and is a major ingredient in the preparation and production of food products. Heating of maize meal suspensions or cooking in these processes is a major unit operation. Cooked maize flour and starch suspensions are often used in the food industry (Bhattacharya & Bhattacharya, 1996). Therefore, gelatinization and rheology of starch contained in the maize meal are important phenomena. Generally, a concern for the food industry is the production and maintenance of the product while preserving the proper consistency and texture properties of the food in question. Gelatinization and rheological properties of maize meal suspensions and pastes may change during food processing and storage due to the changes in composition of maize meal. The changes in gelatinization and rheological properties of maize meal may affect its processibility as a major ingredient in food products and indeed the quality of the products made from such affected maize meal. Hence, the objective of this chapter was to investigate the influence of storage conditions on: (a) gelatinization and pasting properties, and (b) rheological properties.

4.2. Influence of storage conditions on gelatinization and pasting properties

4.2.1. Gelatinization properties

4.2.1.1. Maize meal storage in closed bottles

The materials used were as in section 3.3.1.1. 230g of maize meal was weighed into bottles. The bottles were capped to make them air and moist-tight. The bottles were further wrapped on the exterior with aluminium foils. One set of bottles was stored in a cupboard at room temperature (≈25°C) until sampling day. Another set of bottles was stored at 43°C in an incubator until sampling day. Two bottles from each set were taken out of storage at random for analysis on days 0, 54 and 124 of the storage period. The content of each bottle was divided into two portions. One portion was used for the starch granule isolation whereas the other portion was analyzed as maize meal.

4.2.1.2. Starch granule isolation for gelatinization properties

Starch granules were isolated using method of Tester & Morrison (1990) with slight modifications. The white maize meal (100g) was steeped in water, kept at 3-5°C for 24 hours, then ground in a kitchen blender to release a suspension of starch that was passed through a 90-μm aperture sieve. The crude starch that was recovered by centrifuging (1,550 g, 15 minutes) at room temperature was slurried in 20ml of 80% (w/v) CsCl and centrifuged at 10,000 g for 20 min at 15°C. The starch granules were then washed six times with water and centrifuged for 5 min at 1,550 g to recover starch at each stage. The starch was dried in an air convection oven at 40°C. The isolated starch for DSC and oscillatory rheological analyses were defatted by shaking the starch granules in chloroform-methanol (2:1 v/v) mixture for 8 hours at room temperature. The starch granule to solvent ratio was maintained at 1:20. The mixture was passed through filter paper to remove the solvent. The defatted starch granules were dried at 40°C in an oven for 1 hour.

4.2.1.3. Defatting maize meal for DSC analysis

Maize meal was defatted by shaking 5g of maize meal in 100ml chloroform-methanol (2:1 v/v) mixture for 8 hours at room temperature. The mixture was passed through filter paper to remove

the insoluble material. The defatted maize meal residual was dried at 40°C in an oven for 1 hour and was used for DSC analysis.

4.2.1.4. Gelatinization by DSC

The gelatinization was performed on a 2010 CE DSC with a refrigerated cooling system (Texas Instruments, New Castle, DE, USA). The DSC was calibrated with indium (TA Instruments, New Castle, DE, USA), azobenzene (Sigma–Aldrich, Bornem, Belgium) and undecane (Acros Organics, Geel, Belgium) prior to analyses. Gelatinization of the samples was investigated using a method adopted from Singh et al. (2001) with slight modifications. Defatted isolated starch granule/maize meal samples (3.5mg db) and water (8 µl) were weighed in aluminium pans, sealed and allowed to equilibrate for 1 hour at room temperature. The pans were then heated from 25 to 120°C at a rate of 10°C/min in the DSC heating chamber, using an empty sealed pan as a reference pan. To evaluate whether the sample materials (particularly maize meal) were completely gelatinized during the DSC scan, several samples were rescanned immediately after being cooled to 25°C after the first scan (Fan & Marks, 1998). No endothermic transition was observed in these rescan thermograms, indicating fully gelatinized starches during the first DSC run. Because of the unsymmetrical and slanting baseline of the endotherms obtained, T_o and T_E were determined using the method of Foubert et al. (2003) using excel spreadsheets. The gelatinization enthalpy change (ΔH) was obtained using the software of the DSC by in-putting the obtained T_o, T_p and T_E values. The analyses were performed in duplicates.

4.2.2. Pasting properties

4.2.2.1. Open bulk storage of maize meal

The materials, storage protocol and statistical analysis were as described in section 2.3.1.1, section 2.3.1.2 and section 2.4.2.3.

4.2.2.2. Pasting properties measurements

Pasting properties of the white maize meal were determined on an AR2000 rheometer (TA Instruments, England, UK) attached with computer control software (Rheology Advantage Data Analysis Program, TA Instruments, England, UK). The AR 2000 rheometer was equipped with a Starch Pasting Cell and an impeller which attaches to the rheometer spindle and was

supplemented with an efficient Peltier temperature control system and the sample temperatures were precisely controlled and monitored. A white maize meal sample of 3.25g (db) was transferred into the starch pasting cup cell and distilled water was added accordingly to bring the total weight to 25.00g thereby giving a maize meal dispersion of 13% (w/w). The suspension was stirred rapidly at 900 rev/min (94.28 rad/s) and temperature raised from 20 – 50°C at 10°C/min, before decreasing the shear input and holding it constant at 160 rev/min (16.76 rad/s) for the heating and cooling cycles. The slurry was heated from 50°C to 95°C at 5°C/min and held at 95°C for 5 min, and finally cooled to 50°C at 5°C/min. Simultaneously, the attached computer software recorded the experimental conditions and the resulting viscosity profiles. The data was captured from the software and the viscosity profiles representing pasting curves were made in excel. The determinations were performed in triplicates. Five of the primary pasting properties were obtained from pasting curves: SR – slope of the pasting curve (McDonough et. al., 2004) between 75 and 90°C, PV, V_{95i}, V_{95f} and V_{50}. Thereafter, four derived viscosity indices calculated from the primary viscosity values were obtained: BD, SB, SB_t and $C:H$. For definition of these properties see section 1.6.5.

4.2.3. Statistical analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

4.2.4. Results and discussion

4.2.4.1. Gelatinization properties

First of all, the rationale behind determining the gelatinization properties in maize meal and its isolated starch granules was that, the effect of rancidity/storage breakdown products during the gelatinization process would be eliminated in the isolated starch. This would give a rough idea of the effect of rancidity/storage breakdown products on the evolution of the gelatinization process. However, the interpretation must be taken with caution due to the compositional complex nature of the maize meal. Figure 4.1 shows the changes in the T_o, T_p, T_E, and ΔH of a suspension of maize meal and its isolated starch granules during storage at room temperature ($\approx$25°C) and 43°C. Storage temperature had no significant ($P>0.05$) effect on the T_o. Maize meal stored at 25°C and 43°C were not significantly ($P>0.05$) different, just as the isolated starch. Starch in

maize meal had significantly ($P<0.05$) higher T_o than the isolated starch from the maize meal at both storage temperatures. In terms of evolution, the T_o for the maize meal slightly increased at both room and 43°C storage temperatures, respectively (Figure 4.1a), although the increases were not statistically significant ($P>0.1$).

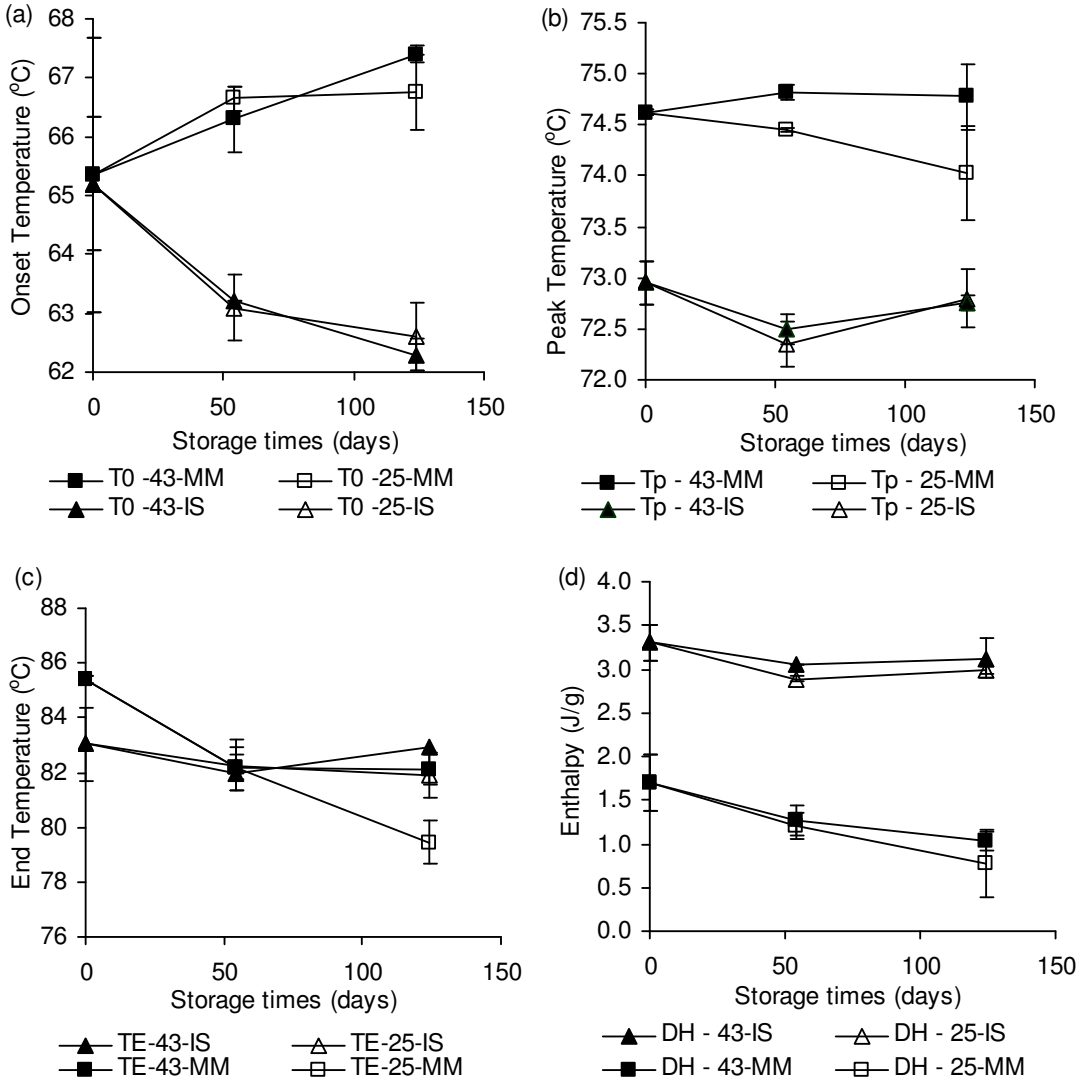

Figure 4.1 Changes in the gelatinization (a) onset temperature (T_o), (b) peak temperature (T_p), (c) end temperature (T_E) and, (d) enthalpy change (ΔH) of a suspension of white maize meal and its isolated starch granules during storage of white maize meal at room temperature (≈25°C) and 43°C. MM : Maize meal and, IS: Isolated starch

On the other hand, the T_o for the isolated starch significantly ($P<0.1$) decreased at both room and 43°C storage temperatures during the storage period. This signifies that the isolated starch

behaved differently from the starch in the maize meal. This also indicates that the storage period had affected the starch granules. The decrease in T_o in the isolated starch may be due to the amorphous background material being affected by storage conditions. It may have become more porous due to the degradation effects of storage on the amorphous material components.

Starch in maize meal had significantly ($P<0.05$) higher T_p than the isolated starch from the maize meal. On the other hand, storage temperature did not significantly ($P>0.05$) affect the T_p. T_p for maize meal at 25°C and 43°C were not significantly ($P>0.05$) different just as the isolated starch. In addition, T_p of both maize meal and isolated starch granules remained essentially constant during the storage period (Figure 4.1b). This indicates that the integrity of the three dimensional crystal structure and the double helicity was unaffected by the storage conditions. Yeh & Li (1996) reported that most granules lose their molecular order at T_p. Jenkins & Donald (1998) found that there is an initial gradual drop in crystallinity index from room temperature until somewhere between onset and peak temperature of the DSC endotherm. After this point the rate of crystallinity loss increases. Around the peak of the DSC endotherm, the rapid swelling and water uptake of the amorphous background region ceases. After this point, the crystalline packing of the double helices within the crystalline lamellae starts to be lost.

The T_E for maize meal significantly ($P<0.05$) decreased during the storage period at both room and 43°C storage temperatures (Figure 4.1c). On the other hand, the T_E for the isolated starch seemed to decrease, although this decrease was not statistically significant ($P>0.1$) at both room and 43°C storage temperatures. On the other hand, the T_E of isolated starch remained unaffected during the storage period. This could suggest that the deterioration products could have affected the gelatinization of maize meal, since T_E for isolated starch did not change.

Starch in maize meal had significantly ($P<0.05$) lower ΔH than the isolated starch from the maize meal. On the other hand, storage temperature did not significantly ($P>0.05$) affect the ΔH. However, neither the ΔH of maize meal nor the isolated starch significantly ($P>0.05$) changed during the storage period (Figure 4.1d). The endothermic enthalpy of gelatinization has been proposed to primarily reflect the loss of molecular order (Cooke & Gidley 1992; Hoover & Vasantha, 1994; Yeh & Li, 1996) and of the double-helical order (Cooke & Gidley, 1992; Fredriksson et al., 1998). It has been shown that the endothermic transition observed during the melting of granular starches reflects the melting of both crystalline and molecular ordered structures (Yuryev et al., 1996; Matveev et al., 2001).

In this study, both the ΔH for maize meal and isolated starch granules were not significantly affected during storage. Like the Tp, ΔH reflects that the crystalline and molecular ordered structures were probably affected by the storage conditions.

An attempt has been made to explain theoretically these findings on gelatinization properties. This is based on the research findings by other researchers and theory known so far about starch gelatinization. The T_o for the isolated starch significantly decreased at both high and low storage conditions. The decrease in T_o in the isolated starch has been attributed on the amorphous background material as being affected by storage conditions. The beginning of starch granule swelling has been proposed to be related to the region of the DSC curve when the endothermic peak is just beginning to form (Miller et al., 1973; Gallant et al., 1997). This phase can, therefore, also be considered as the stage where the amorphous regions have been swollen due to water absorption and crystallite melting is just starting to occur (i.e. the beginning of the irreversible swelling process). At this point, SEM observation of cassava starch granules showed the presence of groups of pores which divide the surface of the granule into polygonal areas of about one micron diameter (Miller et al., 1973; Gallant et al., 1997).

The isolated starch granules of the stored white maize meal may have become more porous due to the degradation effects of storage on the amorphous material components. This rendered easy access of water to the amorphous background region, hence decreasing the onset temperature. The cause of this phenomenon could be hypothesized on enzymatic attack of starch which involves hydrolysis of the bonds in the starch polymers probably taking place during storage. In enzymatic attack, the semi-crystalline (soft layers) of the granule are more easily and rapidly hydrolyzed than the crystalline (hard) layers (Gallant et al., 1997). Gallant et al. (1997) hypothesized that the hydrolysis rate of starch granules depends to a great extent on the distribution of the semi-crystalline and crystalline layers and on the size, identity and interaction of their constituents. Several researchers have shown that α-amylases can simultaneously solubilize both amorphous and crystalline regions of starch granules (Colonna et al., 1988; Lauro et al., 1999). While the cause of the decrease in T_o of the isolated starch and the decrease of T_E of maize meal observed in this study have been hypothesized on the rancidity/storage breakdown products, it might be very difficult to pin point the real cause due to the compositional complex nature of the maize meal.

The second possible explanation of the observation is based on the storage conditions which were an annealing-like process. The storage conditions where characterized by the low moisture content and exposure to moderately high temperatures of white maize meal over a long period of time. The gelatinization temperature range of the white maize meal decreased in a similar manner as the T_E (results not shown). For annealed starches, a narrowing of the gelatinization temperature range has been observed at higher temperature. It has been pointed out that the alterations in the DSC curve are sensitive indicators of the type of hydrothermal treatment the starch has undergone. For annealed starches, the narrower peaks have been interpreted to indicate greater homogeneity during melting of crystallites (Collado & Corke, 1999; Hormdok & Noomhorm, 2007). The decrease or narrowing of the gelatinization temperature in the white maize meal could be due to shifting of the starch granule structure towards a more perfect structure. Collado & Corke (1999) have broadly described annealing as a condition in which granules assume a more stable configuration. This is viewed as the realignment of polymer chains within the non-crystalline regions of the granule as well as in the crystallites or change in the coupling forces between the crystallites and the amorphous matrix.

4.2.4.2. Pasting properties

4.2.4.2.1. Pasting curve characteristics

The pasting viscosity properties may be classified into two major groups: primary viscosity values and derived viscosity indices. Primary viscosity values are properties obtained straight from the viscosity profile graphs during the heating and cooling of the sample suspensions as illustrated in section 1.6.5. On the other hand, derived viscosity indices are calculated values using primary viscosity values, sections 1.6.5 (Sowbhagya & Bhattacharya, 2001).

Figure 4.2 shows the pasting curves of the cooking of a 13% suspension of the white maize meal during storage on days 7 and 35 at 45^{o}C-90%RH storage condition. Figure 4.2 (a) represents the type of pasting curves also obtained for 25^{o}C-43%RH, 25^{o}C-90%RH and 45^{o}C-43%RH storage conditions. Figure 4.2 (b) gives the same curve when one zooms in the curve (Figure 4.2a) between 85 and 95^{o}C. These curves are typical for starch pasting curves.

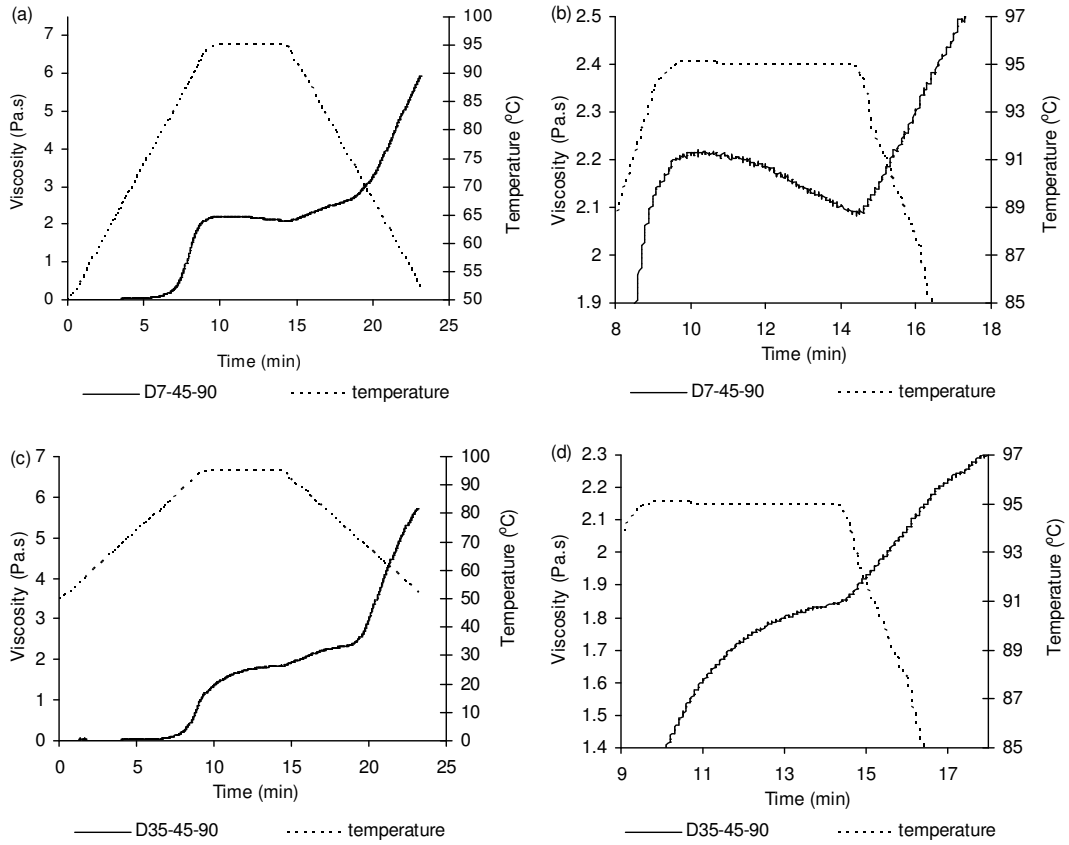

Figure 4.2 Pasting curves of white maize meal during storage: (a) and (b) storage on day 7 at 45°C and 90% relative humidity; (c) and (d) storage on day 35 at 45°C and 90% relative humidity

Typically the resulting pasting curve for maize starch shows a rapid increase in viscosity due to granule swelling and amylose leaching, with a peak in viscosity above the starch gelatinization temperature. Then a decline in viscosity (viscosity breakdown) follows due to soluble starch molecules orienting themselves in the direction that the system is being stirred and the break up of starch granules (Nelles et al., 2000). Thereafter, viscosity increases due to a decrease of energy in the system and subsequent hydrogen bond formation between starch chains (setback) when the starch product is cooled (Hoseney, 1998; Nelles et al., 2000).

Sowbhagya & Bhattacharya (2001) have reported three types of starch and flour viscograms (see section 1.6.5, Figure 1.7). The first type is characterized by the PV appearing before the V_{95i}, the second type by PV appearing between the cooking period i.e. between V_{95i} and V_{95f} and the third by the absence of a well defined PV. In the third type, the viscosity continues to rise until V_{95f}, where the V_{95f} is taken as PV. The type of pasting curves obtained for 25°C-43%RH,

25°C-90%RH and 45°C-43%RH storage conditions as illustrated in Figure 4.2 (b) in this study are representative of the second type described by Sowbhagya & Bhattacharya (2001).

However, pasting curves at 45°C-90%RH storage conditions were only of the Sowbhagya & Bhattacharya (2001) second type, up to 21 days of storage. From 28 days of storage, the curves obtained were as shown in Figures 4.2(c). This type of pasting curves never showed a peak viscosity and a trough viscosity, even when one zooms in the curve between 85 and 95°C as illustrated in Figure 4.2(d). They were of the Sowbhagya & Bhattacharya (2001) third type, in which the viscosity continues to rise until V_{95f} with no distinct PV. This observation could be attributed to the mould growth observed from day 28.

4.2.4.2.2. Primary viscosity indices: swelling rate and peak viscosity

Figure 4.3 shows the changes in swelling rate (SR) and peak viscosity (PV) of starch granules in the white maize meal stored at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. The SR was calculated as slopes of the pasting curves (McDonough et al., 2004) between 75 and 90°C. The SR at 25°C-90%RH, 45°C-43%RH and 45°C-90%RH decreased whereas SR at 25°C-43%RH increased during the storage period (Figure 4.3a).

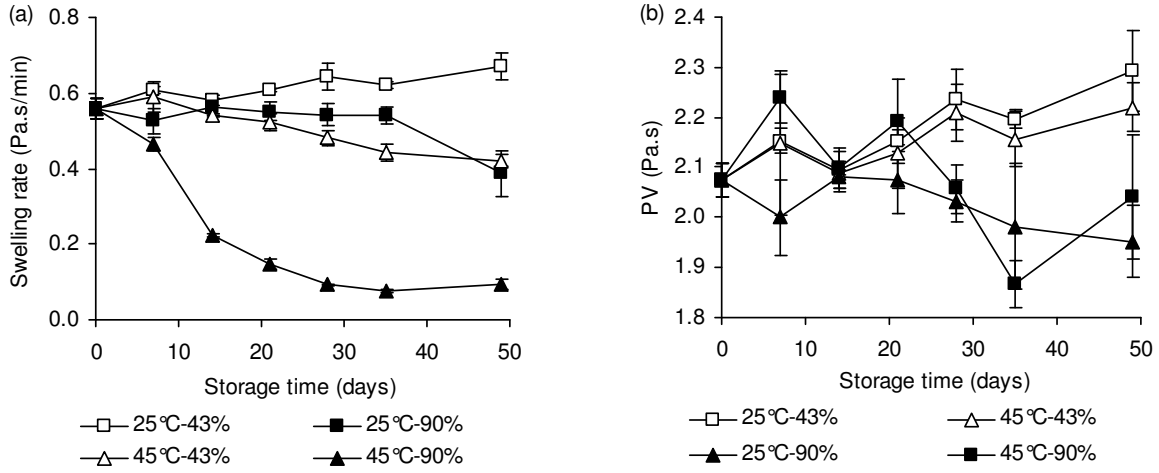

Figure 4.3 Changes in (a) swelling rate, and (b) peak viscosity of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

The initial pasting slope decreased by 30.8% at 25°C-90%RH, 24.6% at 45°C-43%RH and the highest decrease of 82.9% was at 45°C-90%RH, while it increased by 19.8% at 25°C-43%RH

after 49 days of storage and all evolved significantly different (P<0.05). McDonough et al. (2004) found that aging of maize decreased the rate of swelling of starch granules by 22% after 15 days of storage, as measured by the slope of the pasting curve. Decreased pasting slope has been interpreted by McDonough et al. (2004) as indicating that, as materials aged, more time and energy were required to increase the viscosity of the gelatinized starch. The cause of the decreased starch granule swelling in aged samples was reported to probably related to changes in protein and starch.

The PV for all storage conditions was essentially constant and evolved essentially the same the first 21 days of storage (Figure 4.3b). After 21 days, the samples at 25^{o}C-43%RH and 45^{o}C-43%RH gradually but significantly (p<0.05) increased by 10.6 and 7.0% respectively, at the termination of the storage study. However, the evolution at the two storage conditions were not significantly different (P<0.05). Oluwamukomi et al. (2005) have interpreted high PV as reflecting fragility of the swollen granules, which first swell and then break down under the continuous mechanical stirring conditions. Lim & Narsimhan (2006) have found that starch granules that seemed to swell more as temperature increased, were solubilized or rearranged more easily during shearing thus resulting in higher peak viscosity. Equally, Wang et al. (2000) found that rigid and hard starch granules do not rupture immediately when they are subjected to heating and shearing and that such starch granules displayed high peak viscosity as a result of the swelling of starch granules. Further more, Zhou et al. (2002) have interpreted the increase in peak viscosity of stored rice as showing that the starch granules of stored rice are more resistant to swelling than those of fresh rice which showed lower peak viscosity. All these interpretations suggest that PV can be used as a swelling index for starch granule.

On the contrary, after 21 days of storage, the peak viscosity of samples stored at 25^{o}C-90%RH and 45^{o}C-90%RH gradually decreased by 5.9 and 1.6% respectively, but this decrease was not significant (p>0.05). The peak viscosity could have also been confounded by the mould growths at 45^{o}C-90% from day 28. The evolution of 25^{o}C-43%RH and 45^{o}C-43%RH were significantly different (P<0.05) from 25^{o}C-90%RH and 45^{o}C-90%RH. Generally, at low storage humidity PV of the white maize meal increased for both low and high storage temperatures.

4.2.4.2.3. Primary viscosity indices: Initial hot-paste and final hot-paste viscosities

Figure 4.4 shows the evolution of the initial hot-paste viscosity (V_{95i}) and final hot-paste viscosity (V_{95f}) during storage of the white maize meal at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. There were no major differences in the evolution of V_{95i} in the first 14 days (Figure 4.4a). The differences began to emerge on the 21st day of sampling. The samples at 25°C-43%RH and 45°C-43%RH storage significantly ($p<0.05$) increased by 15.6 and 10.9% respectively after 49 days of storage, although the difference between them was not significant ($P<0.05$). The V_{95i} for samples stored at 25°C-90%RH remained significantly ($p<0.05$) constant but lower than 25°C-43%RH and 45°C-43%RH throughout the storage period. The V_{95i} for samples stored at 45°C-90%RH reduced to lower V_{95i} values than other three storage condition. However, there was mould growth from day 28 at 45°C-90%RH storage.

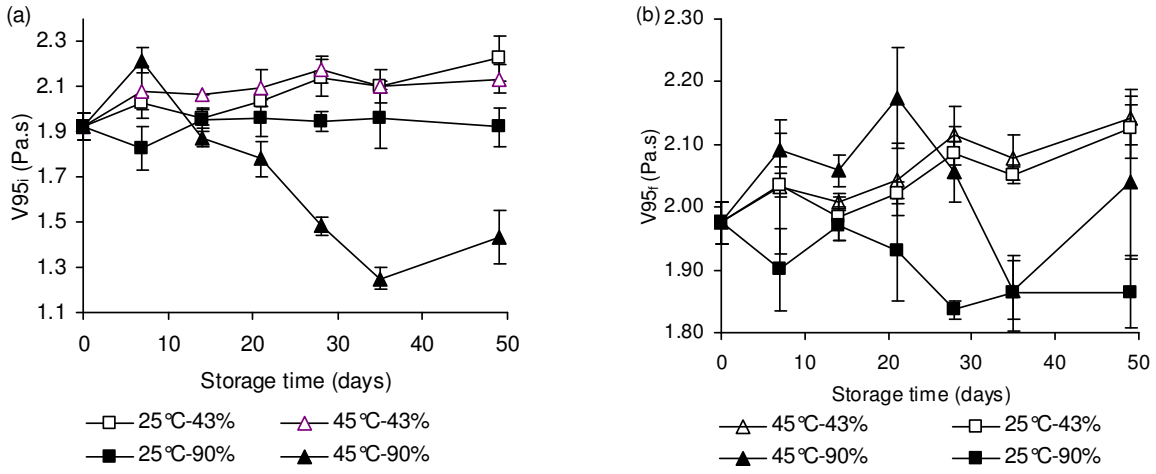

Figure 4.4 Changes in (a) initial hot-paste viscosity and (b) final hot-paste viscosity of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

There was no difference in the evolution of V_{95f} the first 21 days of storage as well (Figure 4.4b). The evolution of V_{95f} at 25°C-43%RH and 45°C-43%RH were not significantly different ($P<0.05$) although they both evolved significantly different from 25°C-90%RH. Storage conditions at 25°C-43%RH and 45°C-43%RH increased V_{95f} significantly ($p<0.05$) by 7.7 and 8.5% respectively. The increase in V_{95f} indicates that the white maize meal starch granules were becoming more resistant to fragmentation during cooking (Wang et al., 2000) in function of storage time. On the contrary, storage at 25°C-90%RH affected V_{95f} by decreasing it by 5.5%.

Decrease in V_{95f} illustrates that starch granules became fragile and broke down easily during cooking at these storage conditions (Wang et al., 2000). The V_{95f} for the samples stored at 45°C-90%RH increased up to 21 but not statistically significant. There was mould growth after 28 days at this storage condition which could have cuased the uncharacteristic trend.

4.2.4.2.4. Primary viscosity index - Cold-paste Viscosity (V50)

The changes in cold-paste viscosity (V_{50}) during storage for 49 days of white maize meal at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH, is shown in Figure 4.5.

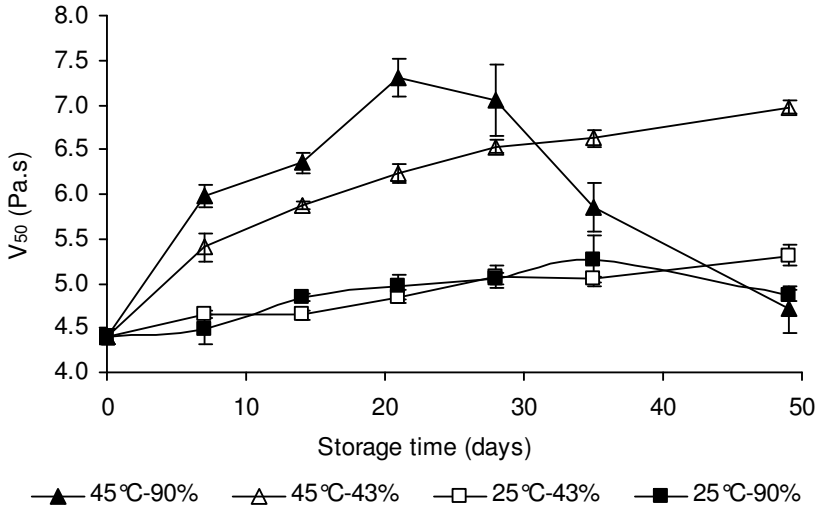

Figure 4.5 Changes in cold-paste viscosity of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

Cold-paste viscosity indicates the extent of starch retrogradation that occurs during the cooling process. When hot pastes are cooled, the extent of increase in viscosity is governed by the re-association tendency of the starch (Hagenimana et al., 2006). The V_{50} values of samples stored at 25°C-43%RH and 25°C-90%RH increased up to the termination of the storage study. The two evolved significantly the same till about 35 days of storage. By the end of storage however, samples at 25°C-43%RH had increased by 20.7% and was higher than for samples at 25°C-90%RH which increased by 10.7%. However, on the overall, statistically there was no significant difference ($P<0.05$) in the evolution at the two storage temperatures. The V_{50} values of samples stored at 45°C-43%RH increased sharply and were significantly ($P<0.05$) higher than for samples stored at 25°C-43%RH and 25°C-90%RH throughout the storage study. The V_{50} values of samples stored at 45°C-43%RH increased by 58.5% at the end of storage study.

The V_{50} values of samples stored at 45°C-90%RH increased sharply and were the highest up to 21 days were it increased by 66%, before rapidly reducing. The unusual drastic decrease could be attributed to the mould growth observed from 28th day of storage. It is however clear that all storage conditions experimented here increased the V_{50} during storage. Storage temperature had a higher influence on the changes in V_{50} than storage relative humidity. V_{50} values at high storage temperatures were higher than at low storage temperatures. However, at constant high storage temperature, samples at high storage relative humidity evolved higher than at low storage relative humidity.

4.2.4.2.5. Derived viscosity index - Breakdown index (BD)

Figure 4.6 shows the evolution of Breakdown (BD) index during storage of white maize meal at various storage temperature – relative humidity conditions. The BD index was essentially the same for all storage conditions until after 7 days of storage. The samples stored at 25°C-43%RH had minimal but significant ($p<0.05$) increases in BD and evolved higher than 45°C-43%RH and 45°C-90%RH from about 14th day of storage. The BD index at 45°C-43%RH decreased minimally but the decrease was not significant ($p<0.05$) during the storage study. Breakdown index has been defined as a measure of resistance to shear and disintegration of starch during cooking (Lawal, 2005). It has also been defined as a measure of the ease with which the swollen starch granule can be disintegrated and as an indication of the degree of its organization (Olayinka et al., 2008).

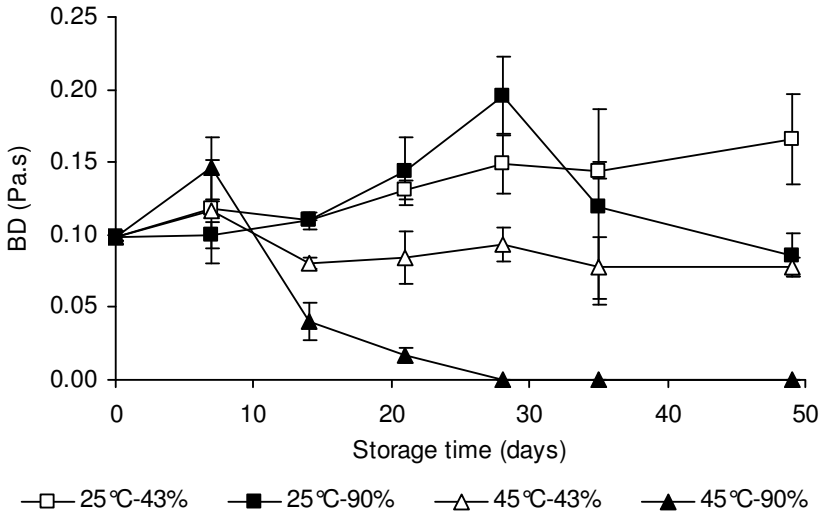

Figure 4.6 Changes in Breakdown of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

However, the BD index for 25°C-90%RH significantly ($p<0.05$) increased only up to 28 days of storage but thereafter decreased sharply to the same final values as 45°C-43%RH. The BD index for samples stored at 45°C-90%RH significantly (<0.05) decreased sharply from the 7th day to lower values than all the other storage conditions. However, the BD index for samples at 45°C-90% from day 28 could have been confounded by mould growth.

The decrease in BD indicates that the capacity of the starch granules to rupture after cooking was reduced significantly (Noomhorm et al., 1997; Zhou et al., 2003) during storage. Sowbhagya & Bhattacharya (2001) and Zhou et al. (2003) explained the steady decrease in paste BD during storage of rough rice on the basis of the granule surface as representing the primary barrier to processes such as hydration that may depend on the charge characteristics of the starch granule surface. They proposed that pasting may be influenced by the presence, orientation and nature of surface lipids and proteins. The changes at the granule surface could contribute to the change in hydrophilicity that would affect granule hydration and swelling.

4.2.4.2.6. Derived viscosity indices: Total Setback and Cold-paste:Hot-paste Viscosity Ratio

Figure 4.7 shows the evolution of total setback (SB_t) and cold-paste:hot-paste viscosity ratio (C:H) during storage of white maize meal at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH storage conditions for a storage period of 49 days. Setback value is the recovery of the viscosity during cooling of the heated starch suspension (Singh et al., 2006a).

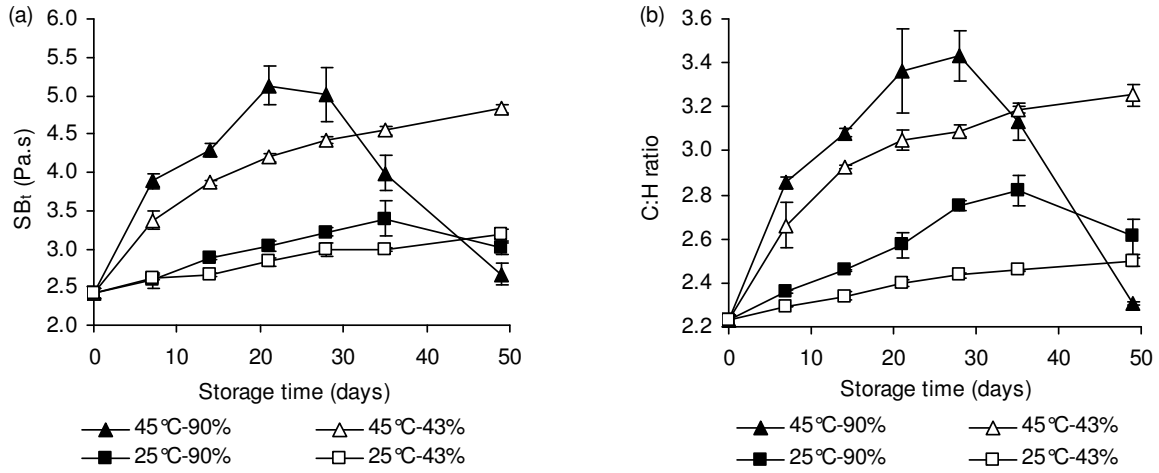

Figure 4.7 Changes in (a) total setback and (b) Cold-paste: Hot-paste viscosity ratio of white maize meal during storage at 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

During cooling, re-association between starch molecules, especially amylose, will result in the formation of a gel structure and, therefore, viscosity will increase to a final viscosity. This phase is commonly described as the setback region and is related to retrogradation and reordering of starch molecules (Ragaee & Abdel-Aal, 2006). The SB_t at all the storage conditions of this study increased during the storage period (Figure 4.7a). There was significant differences ($p<0.05$) in the evolution of SB_t when all the four storage conditions are compared. Equally, there was clear distinction in SB_t between samples stored at 45°C-43%RH / 45°C-90%RH, and, 25°C-43%RH / 25°C-90%RH, where the former were higher than the later right from the beginning of storage studies.

The graph shows that the samples stored at 25°C-43%RH and 25°C-90%RH had minimal and steady increases in SB_t. The differences between the two storage conditions in SB_t was statistically ($p<0.05$) but very small, with 25°C-90%RH evolving higher than 25°C-43%RH. The SB_t of 45°C-43% increased sharply and higher than 25°C-43% and 25°C-90% throughout the storage period. However, the SB_t for 45°C-90%RH increased sharply and had the highest SB_t up to 21 days before decreasing sharply. This decrease is attributed to the mould growths observed after 28 days of storage. Oluwamukomi et al. (2005) interpreted flours having higher setbacks as having higher retrogradation tendency. Higher setback was attributed to increased formation of not only thermally reversible hydrogen bonds but also thermally irreversible hydrophobic and/or covalent bonds (Luck et al., 2002; Roesch & Corredig, 2002; Singh et al., 2003a; Tolstoguzov, 2003; Lim & Narsimhan, 2006). These intermolecular bonds contribute to a higher final paste viscosity upon subsequent cooling (Lim & Narsimhan, 2006).

Sowbhagya & Bhattacharya (2001) have defined C:H ratio as the true reflection of retrogradation during cooling. The C:H ratio at all storage conditions increased during storage and there was clear differences in C:H ratio at all the storage conditions (Figure 4.7b). The samples stored at 25°C-43%RH slightly increased and had the lowest C:H ratio throughout the storage period. The samples stored at 25°C-90%RH increased up to about 35 days and evolved significantly ($p<0.05$) higher than samples stored at 25°C-43%RH, thereafter it reduced to the same final value of samples at 25°C-43%RH. It is worth noting that, while V_{50} and SB_t at 25°C-43%RH and 25°C-90%RH storage were not very indistinguishable in their evolution, the C:H at these storage conditions are much more distinguishable in their evolution. This means that C:H might be a better retrogradation index than V_{50} and SB_t alone. Probably, this agrees with Sowbhagya & Bhattacharya's (2001) definition of C:H.

However, the C:H ratio for 45°C-90%RH increased sharply and had the highest C:H ratio up to 28 days. The decrease thereafter is attributed to the mould growth observed on the same day. The C:H ratio of 45°C-43%RH increased sharply and higher than 25°C-43%RH and 25°C-90%RH throughout the storage period. Storage temperature has a higher influence on C:H ratio than storage relative humidity. High storage temperature had higher C:H ratios than low storage temperature. Nevertheless, given the same storage temperature, high relative humidity had higher C:H ratio than low relative humidity.

Sowbhagya & Bhattacharya (2001) found that the C:H ratio is relatively unaffected by the paste concentration but is species specific. They interpreted this as showing that C:H ratio might be a fundamental property and a characteristic index of various starches. Contrary to the white maize meal findings, Sowbhagya & Bhattacharya (2001) further found that C:H ratios were largely unaffected by the storage time during storage of rice grain despite the large and sustained change in all other viscogram parameters. At this point it is also worth noting that the evolution of C:H, SB_t and V_{50} were very similar, probably, confirming that they are all indices showing the changes of the same property i.e. retrogradation and/or syneresis.

4.2.4.2.7. An overview on pasting properties

Like for gelatinization, the pasting parameters during the cooking period of the pasting cycle may be explained on the observation that the storage conditions may be considered as an annealing-like process. The storage conditions of the white maize meal where characterized by low moisture content to moderately high moisture content with exposure to moderately high temperatures of white maize meal over a long period of time.

The PV, V_{95i} and V_{95f} of the white maize meals stored at low humidity for both storage temperatures increased during storage. High swelling starches usually show high pasting peak (Adebowale et al., 2005). On the other hand, the PV, V_{95i} and V_{95f} at high humidity either decreased or remained essentially constant. Reduction in PV, V_{95i} and V_{95f} after heat moisture treatment and annealing of starch from different types of foods has been observed (Hoover & Manuel, 1996a; Hoover & Manuel, 1996b; Adebowale & Lawal, 2003; Adebowale et al., 2005; Lawal, 2005; Hormdok & Noomhorm, 2007). Reduction in V_{95f} after annealing rice starch has been interpreted as indicating less stability of swollen granules (Hormdok & Noomhorm, 2007). Reduction in peak viscosity has been attributed to reorganization within the granule of the

modified starches. Enhancement of crystallinity after hydrothermal treatments leads to limited starch swelling and structural disintegration, which contribute significantly to starch viscosity (Adebowale et al., 2005). Reduction in swelling power after heat moisture treatment and annealing of starch from different types of foods has also been observed (Lawal, 2005; Adebowale & Lawal, 2003; Hoover & Manuel, 1996a; Hoover & Manuel, 1996b).

Storage of white maize meal at 25°C-43%RH and 45°C-43%RH reduced the moisture content overtime. This could have enhanced the starch granule to shift more towards a structure consistent with dry starch granules (Section 1.6.3, Figure 1.5a). The starch granules thus became more rigid and increased the ability to swell more as observed in the increase in PV, V_{95i} and V_{95f} for the low humidity storage conditions. On the other hand, storage of white maize meal at 25°C-90%RH and 45°C-90%RH increased the moisture content overtime. This shifted the starch granule towards a more perfect structure (Section 1.6.3, Figure 1.5b). The mobility of the amorphous and crystalline regions were enhanced and probably decreased the ability to swell during cooking.

The V_{50}, SB_t and C:H of the white maize meal increased at all the four storage conditions. The three parameters are indices of retrogradation of starch after gelatinization. Annealing has been reported to make the granules resistant to deformation by strengthening the intra-granular binding forces. It has also been speculated that, in annealed starch, swollen gelatinized granules are more rigid, contributing significantly to high cold paste viscosities (Collado & Corke, 1999). But this explanation is not consistent with the observed V_{50}, SB_t and C:H in white maize meal in this study. Therefore, the more plausible reason for the increase in V_{50}, SB_t and C:H for the white maize meal at all the four storage conditions has to do with FFA-amylose complexation. Free fatty acids at 25°C-43%RH and 45°C-43%RH positively correlated with PV, V_{95i}, V_{95f}, V_{50}, SB_t and C:H. Kaur and Singh (2000) found that peak viscosity (PV), viscosity at 95°C (V_{95i}) and viscosity at 50°C (V_{50}) of rice flour increased with the increase in levels of fatty acids. They attributed the change in peak viscosity, viscosity at 95 and 50°C with the addition of fatty acids to the formation of amylose-lipid complexes. Therefore, the increase in the retrogradation properties of the pastes reported in this study could be attributed to lipolysis which enhanced the formation of FFA-amylose complexes during cooking. The increase in V_{50}, SBt and C:H pasting properties can lead to increased energy consumption during stirring or mixing of white maize meal pastes in function of maize meal storage time.

4.3. Influence of storage conditions on rheological properties

4.3.1. Viscoelastic properties

4.3.1.1. Maize meal storage in closed bottles

The materials and storage protocol used were the same materials as in section 3.3.1.1 and 3.3.1.2, respectively. Then, starch granules were isolated from the sampled maize meal on days 0 and 124 of the storage period. Starch granules were isolated from maize meal as outlined in section 4.2.1.2.

4.3.1.2. Viscoelastic measurements

Rheological measurements were carried out on a Bohlin CVO50 (Bohlin Instruments Ltd, United Kingdom) controlled stress rheometer, equipped with a circulating water bath for temperature control (± 0.1^{o}C), using a parallel plate-plate geometry (diameter 40mm). The strain and frequency were set at 1.0% and 1 Hz, respectively, for all determinations. The dispersions were prepared by addition of the isolated dry starch granules to the required amount of distilled water to make a 20% starch suspension with continuous stirring in a small beaker for 1hour at room temperature at the same rpm for all samples. To maximize homogeneity, the suspension was sampled with a small syringe while stirring. 1.3ml of the suspension from the syringe was immediately loaded onto the centre of the lower plate of the rheometer which was maintained at 25^{o}C and the upper plate was lowered to give a gap size of 1000µm. The sides of the gap exposing the sample to the outside environment were covered with a thin layer of low-density silicon oil to minimize evaporation losses. The starch samples were then subjected to temperature sweep testing by heating from 25 to 90^{o}C at the rate of 1^{o}C/min. The dynamic rheological properties, storage modulus (G′) and loss modulus (G″) were recorded automatically by the instrument. All analyses were done in at least duplicate i.e. separate suspensions were prepared and each was run once.

4.3.2. Flow behaviour properties

4.3.2.1. Open bulk storage of maize meal

The materials, storage protocol and statistical analysis were as described in section 2.3.1.1, section 2.3.1.2 and section 2.4.2.3.

4.3.2.2. Flow behaviour measurements

The first part of the flow behaviour measurement was as described under pasting measurements, section 4.2.2.2. After the heating and cooling cycle, the resulting paste was held at 50°C for 5min without shear input. Then, the steady shear flow properties (stress/viscosity) of the paste were determined in the shear rate range of 0.1-1000 s^{-1} at 50°C and were timed for 10 points per decade. Determinations were performed in triplicates for the samples sampled at 7 days intervals. Rheological values (shear stress, viscosity and shear rate) were obtained from the software. Five rheological flow models based on shear stress–shear rate (Bingham, Herschel-Bulkley, Power law, Mizrahi-Berk and Casson models) as obtained from Bhattacharya & Bhattacharya (1996), were fitted to the data obtained. The goodness of fit of the models was evaluated by the mean relative error (MRE) as a percentage as given in Eqation. 2.1. A model is considered acceptable if it has a MRE value less than 10% (Kaymak-Ertekin & Gedik, 2005).

4.3.4. Statistical analysis

ANOVA statistical comparisons were performed with Duncan tests at a level of $\alpha = 0.05$ using SPSS® Version 11.0 (SPSS Inc., Chicago).

4.3.5. Results and discussion

4.3.5.1. Viscoelastic properties

Figure 4.8 below illustrates the evolution of elastic modulus (G′) and viscous modulus (G″) as a function of temperature during heating in a dynamic rheometer of a 20% starch isolated from maize meal stored at room temperature (≈25°C) and 43°C. The peak elastic modulus (G'_p) of starch isolated from maize meal stored at 43°C on Day124 (6046 ± 122 Pa) was significantly ($P<0.1$) higher than for starch isolated on Day0 (5468 ± 118 Pa), whereas there was no significant difference for the starch from fresh maize meal (5468 ± 118 Pa) and for the starch of maize meal stored at room temperature for 124 days (5670 ± 72 Pa) (Figure 4.8a). On the contrary, the peak viscous modulus (G''_p) of starch isolated from maize meal on Day0 (690 ± 54

Pa) was significantly (P<0.1) higher than starch isolated from maize meal stored at 43°C on Day124 (570 ± 6 Pa) (Figure 4.8b).

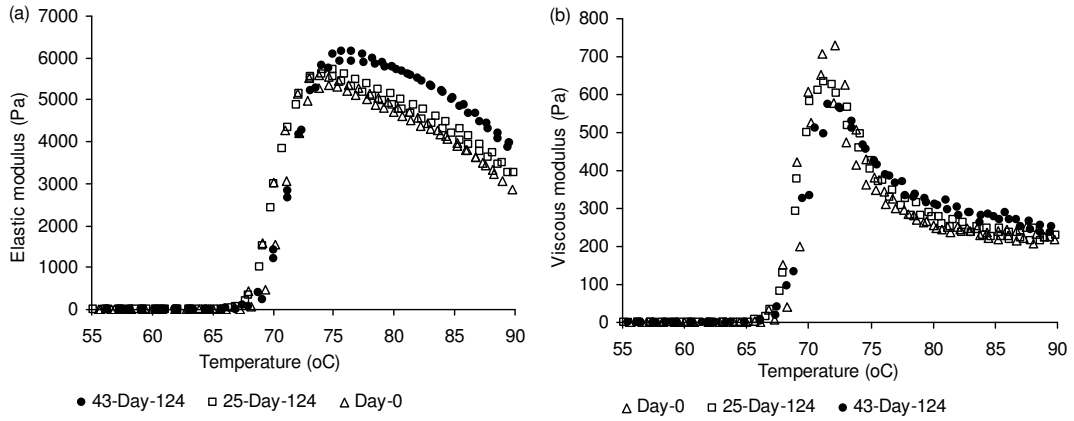

Figure 4.8 Evolution of (a) elastic modulus (G′) and (b) viscous modulus (G″) during heating of a 20% dispersion of starch isolated from fresh maize meal (Day-0) and maize meal stored for 124 days at 25°C (25-Day-124) and 43°C (43-Day-124).

Similar to an observation made in elastic modulus, there was no significant (P>0.05) difference between starch isolated from maize meal on Day0 (690 ± 54 Pa) and starch isolated on Day124 (630 ± 6 Pa) for peak viscous modulus (G''_p) at room storage temperature. The higher G'_p of isolated starch from a stored maize meal than a fresh maize meal, and a higher G''_p of isolated starch from a fresh maize meal than a stored maize meal indicates that starch pastes of stored maize meal became more solid-like with storage time at higher storage temperatures.

In terms of the rheometer instrument, the rise in G′ upon heating starch suspension is on the basis that with further increase in temperature during heating of the starch dispersion, the G′ increases to a maximum value termed peak elastic modulus (G'_p). This increase in G′ has been attributed to the closely packed network of swollen starch granules (Hsu et al., 2000; Singh et al., 2002). It has been stated that the swollen granules fully occupy the available volume at the moment the moduli reach their maximum, G'_p (Van Vliet et al., 1996). In a bid to explain the observed increase in G'_p upon high temperature storage, one can interpret this as; at a higher storage temperature of maize meal, the isolated starch appears to loose its ability for rapid swelling, leading to the requirement of additional heating to achieve close packing and rupturing of the starch granules. Hence the starch isolated from fresh maize meal had a lower G'_p than the starch isolated from maize meal stored at 43°C for 124 days.

4.3.5.2. Flow behaviour properties

4.3.5.2.1. Flow behaviour

Fig. 4.9 shows the viscosity against shear rate for the fresh maize meal dispersion and for the maize meal stored for 7, 21 and 49 days at temperature–humidity conditions of 45°C-90%RH and gives a good representation of curves at all the other storage conditions. The curves for the maize meal were experimentally obtained at concentration of 13% (w/w, dry basis). It is obvious from these figures that the viscosity for all storage conditions were changing with shear rate, which means that the examined maize meal dispersion systems are non-Newtonian. A sharp decrease in viscosity with increase in shear rate is a clear indication of shear-thinning behaviour exhibited by the maize meal used in this study.

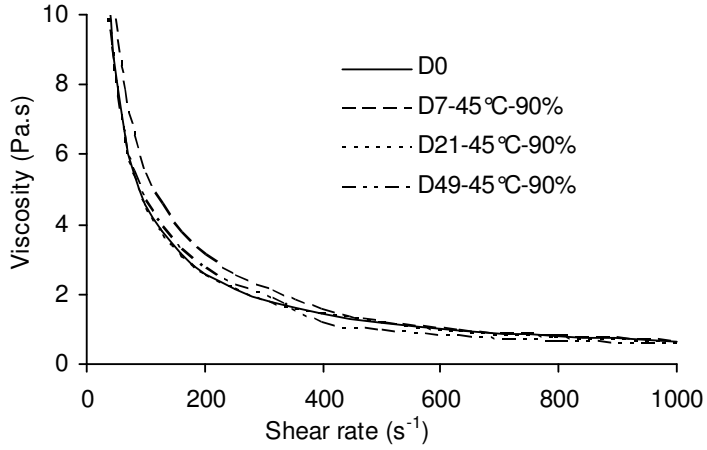

Figure 4.9 Viscosity against shear rate of a 13% (w/w, dry basis) white maize meal during storage at temperature-humidity of 45°C-90%RH. D0, D7, D21 and D49 denote storage times: Day 0 (fresh sample), day 7, day 21 and day 49, respectively.

4.3.5.2.2. Modeling of the flow curves

The shear stress/shear rate data depicting the flow behavior of the white maize meal dispersions at temperature-humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH storage conditions were examined using five rheological models for non-Newtonian fluids. The models included the Bingham, Herschel-Bulkley, Power law, Mizrahi-Berk and Casson models.

The goodness of fit over the storage period at all the four storage conditions was assessed using mean relative error [MRE (%)] (Table 4.1). According to Kaymak-Ertekin & Gedik (2005), a model is considered acceptable if MRE values are below 10%.

Table 4.1 MRE(%) and r^2 ranges for flow behaviour models during 49 days storage of white maize meal stored at temperature-humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH

Model*	25°C-43%RH		25°C-90%RH		45°C-43%RH		45°C-90%RH	
	MRE(%)	r^2	MRE(%)	r^2	MRE(%)	r^2	MRE(%)	r^2
HB	7.7-9.0	0.94-0.96	7.7-9.2	0.94-0.97	7.7-12.0	0.92-0.95	7.7-20.2	0.70-0.95
MB	7.8-9.2	0.93-0.96	7.8-9.4	0.94-0.97	7.8-12.1	0.91-0.95	7.8-22.6	0.67-0.95
C	8.0-9.9	0.93-0.96	8.0-14.1	0.90-0.95	8.9-15.5	0.84-0.94	8.9-22.7	0.70-0.93
B	10.7-13.8	0.87-0.91	11.9-20.5	0.80-0.90	11.9-20.4	0.73-0.90	11.9-27.8	0.69-0.90
PL	11.3-15.5	0.80-0.88	10.9-14.1	0.83-0.96	10.9-14.9	0.83-0.92	10.8-23.3	0.62-0.96

*HB: Herschel-Bulkley; MB: Mizrahi-Berk; C: Casson; B: Bingham; PL: Power law

At 25°C-43%RH storage, the Herschel-Bulkley, Mizrahi-Berk and Casson models gave MRE (%) less than 10 throughout the storage period. At 25°C-90%RH storage, the Herschel-Bulkley and Mizrahi-Berk gave MRE (%) less than 10 throughout the storage period. At 45°C-43%RH and 45°C-90%RH storage, the Herschel-Bulkley and Mizrahi-Berk models were within acceptable ranges up to about 21 and 14 days of storage, respectively. Generally, only the Herschel-Bulkley and Mizrahi -Berk models best predicted the flow behaviour of the white maize meal throughout the storage period, but this was only for low storage temperatures. For high storage temperatures, all the models tested here were not acceptable to predict the experimental data throughout the storage period. Bhattacharya & Bhattacharya (1996) also found the Herschel-Bulkley and Mizrahi-Berk models to best fit cooked maize flour suspensions at concentrations between 2 and 10%.

4.3.5.2.3. Stress overshoot

Figure 4.10 (a) shows the shear stress against shear rate for fresh white maize meal dispersions and for white maize meal stored for 7, 21 and 49 days at temperature–humidity condition of 25°C-43%RH for shear rates up to 5 s^{-1}. These curves represent the type of curves obtained at 25°C-90%RH, 45°C-43%RH and 45°C-90%RH. The curves for the white maize meal were experimentally obtained at concentration of 13%, w/w dry basis. The shear stress initially increased and then reduced.

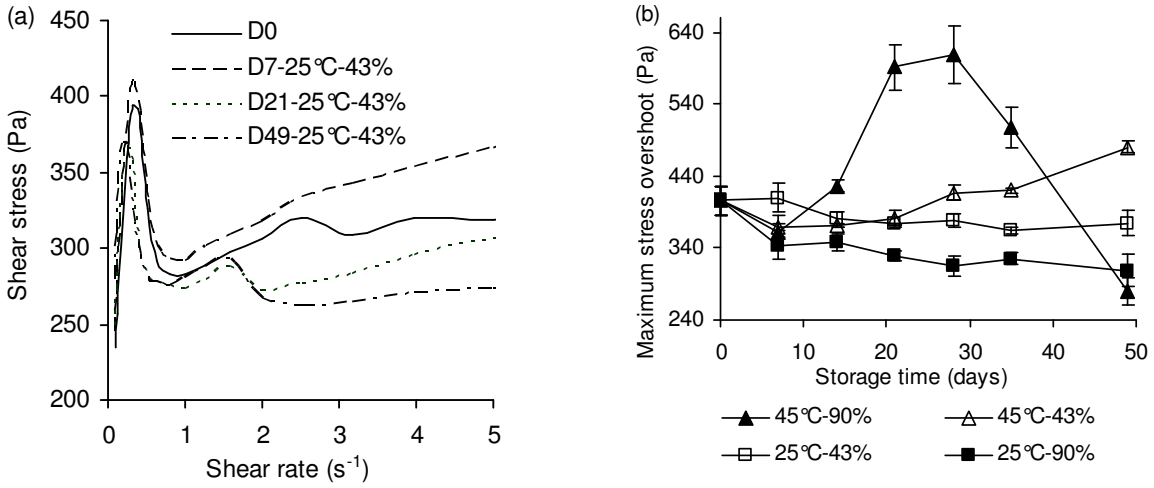

Figure 4.10 (a) Shear stress against shear rate for white maize meal during storage at temperature-humidity of 25°C-43%. D0, D7, D21 and D49 denote storage times: Day 0 (fresh sample), day 7, day 21 and day 49, respectively. (b) Evolution of maximum stress overshoot values of white maize meal during storage at temperature and relative humidity of 25°C-43%RH, 25°C-90%RH, 45°C-43%RH and 45°C-90%RH.

During the elongational flow studies of set yoghurt, Raphaelides & Gioldasi (2005) obtained similar kind of data. They described these kinds of curves as being a shape characteristic for a structured material such as a gel which is subjected to a large deformation. Starting with undisturbed material, on applying a constant deformation rate (the lowest possible to avoid inertia effects), the stress will increase initially about proportional to the deformation. On further deformation, a large and increasing structural breakdown occurs until it reaches to a maximum overshoot value. The stress overshoot is a property of non-linear viscoelastic materials. During structure rupturing, crosslinks continuously break and reform. At the maximum overshoot value, called sometimes yield value, reformation can no longer compete with structure breakdown. After a transition period of lower stress level, further deformation leads to a region where flow is dominant.

The maximum stress overshoot values of these curves for all the four storage conditions were obtained at 7 days storage intervals. The changes in mean maximum stress overshoot values at different temperature-relative humidity storage conditions during storage of the white maize meal are given in Figure 4.10(b). From the graph, the maximum stress overshoot values were essentially the same the first 7 to 14 days of storage and generally decreased during that period

of storage of the white maize meal at all the four storage conditions. The maximum stress overshoot values of samples stored at 25°C-43%RH slightly but significantly (P = 0.03) decreased while maximum stress overshoot values at 25°C-90%RH significantly ($p<0.05$) decreased during the storage period. There was also a significant difference ($p<0.05$) in the evolution of the maximum stress overshoot values between 25°C-43%RH and 25°C-90%RH. The maximum stress overshoot values at 25°C-43%RH decreased by 8%, whereas, at 25°C-90%RH the maximum stress overshoot values decreased by 24% after 49 days of maize meal storage. Stress overshoot at 45°C-43%RH and 45°C-90%RH generally increased during the storage period. The rapid drop in stress overshoot at 45°C-90%RH from day 28 could be attributed to the appearance of moulds. The decrease in stress overshoot observed at low temperature storage could be due to weaker gel formation, while the increase at high storage temperatures could be due to stronger gel formation after the resting period. As observed under pasting, low temperature storage had lower retrogradation indices than high storage temperatures. Higher retrogradation is due to higher bond formation which leads to stronger gels.

4.3.5.2.4. Yield stress

The two best fitting models, Herschel-Bulkley and Mizrahi-Berk, with a yield stress parameter were used for extrapolation to estimate the yield stresses. The Herschel-Bulkley and Mizrahi-Berk yield stress values had similar trends of evolution during the storage period and the two were not statistically different ($p<0.05$). The change in the yield stress values at 25°C-43%RH storage condition was not statistically significant ($p>0.05$) (Figure 4.11a). After 49 days of maize meal storage, the yield stress at 25°C-90%RH significantly ($P<0.05$) decreased by an average of 53% (Figure 4.11b). At 45°C-43%RH and 45°C-90%RH storage, there was significant ($p<0.05$) reduction in Herschel-Bulkley and Mizrahi-Berk yield stress by an average of 33% and 73% during the 21 and 14 days, respectively, of valid model prediction period (Figure 4.11c and d). Loisel et al. (2006) indicated that the decrease in yield stress is an indication of the increasing fluidity of the paste. High temperature storage had a faster decrease in yield stress than low storage temperature. At constant high temperature storage, high humidity storage had a more pronounced decrease in yield stress. At low storage temperature, humidity effect was only significant at high storage humidity. Yield stress is an important quality control parameter to process industries. Yield stress could be beneficial for the optimal design of food-processing systems such as those required during thermal processing (Steffe, 1992; Ahmed et al., 2007), and is important in preventing flow (Bhattacharya & Bhattacharya, 1996).

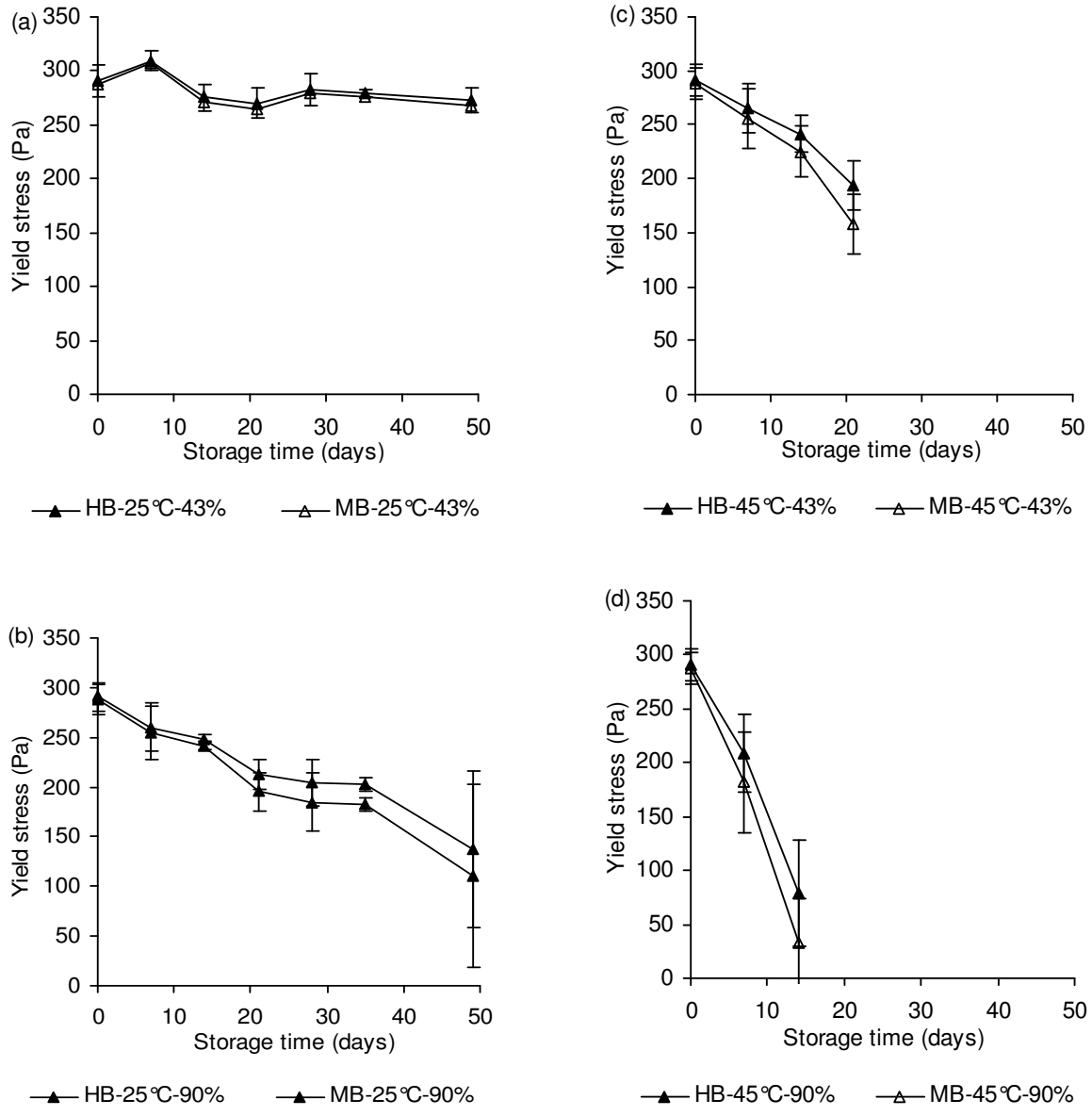

Figure 4.11 Changes in Herschel-Bulkley (HB) and Mizrahi-Berk (MB) yield stress for white maize meal during storage at temperature-humidity of: (a) 25°C-43%RH, (b) 25°C-90%RH, (c) 45°C-43%RH and (d) 45°C-90%RH.

4.3.5.2.5. Flow behaviour index

The change in the flow behaviour index (*n*) of the Herschel-Bulkley (n_{HB}) and Mizrahi-Berk (n_{MB}) models during storage of the white maize meal at different temperature – relative humidity conditions is shown in Figures 4.12. The observations and explanations of the flow behaviour indexes has been restricted to the Herschel-Bulkley and Mizrahi-Berk models

since the two gave better predicted flow behaviour data. However, it must be remembered that even these two models gave acceptable predictions only for 25°C-43%RH and 25°C-90%RH, for data throughout the storage period.

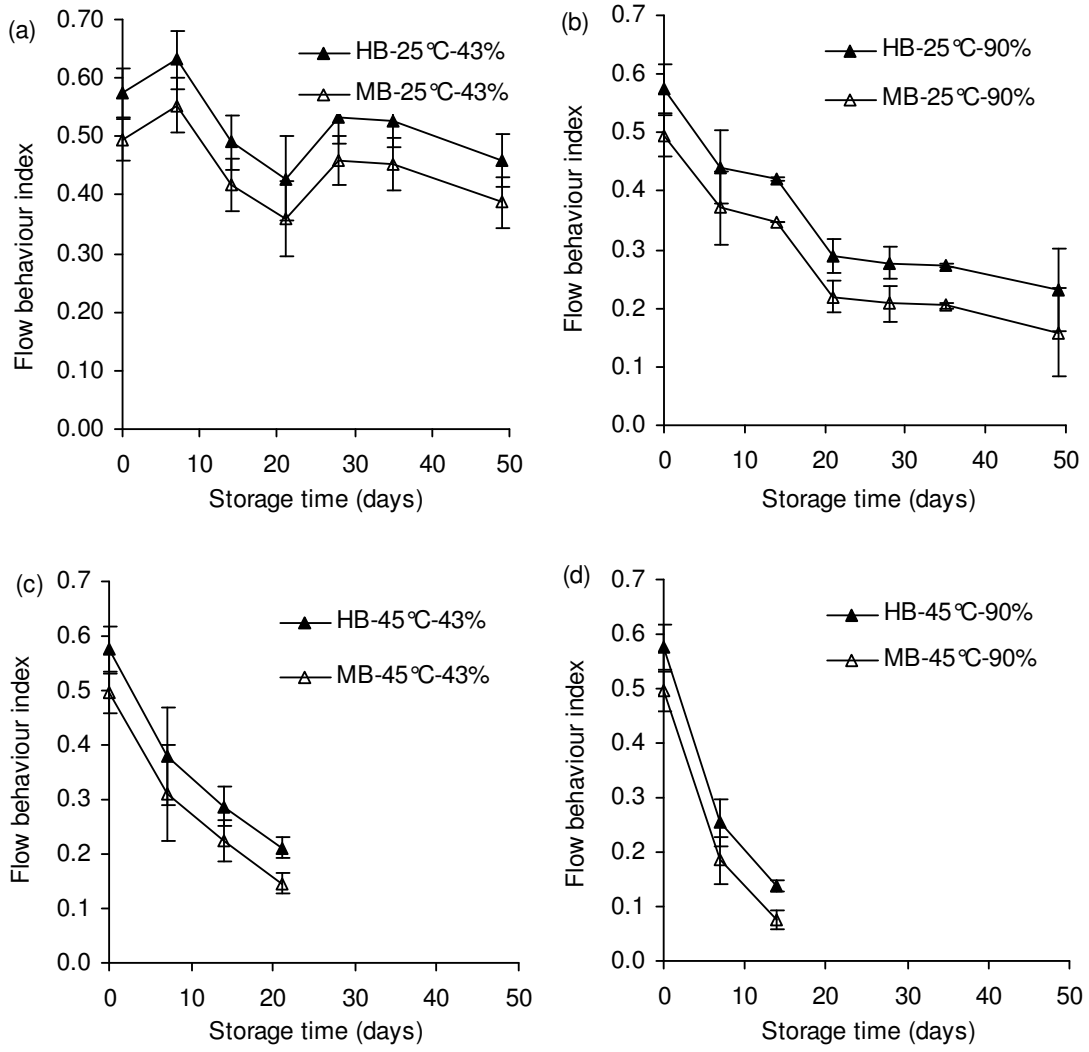

Figure 4.12 Changes in flow behaviour index of Herschel-Bulkley (HB) model and of Mizrahi-Berk (MB) model for white maize meal during storage at temperature and relative humidity of: (a) 25°C-43%RH, (b) 25°C-90%RH, (c) 45°C-43%RH and (d) 45°C-90%RH.

The Herschel-Bulkley and Mizrahi-Berk flow behaviour indices had similar trends of evolution throughout the storage period. Although the Herschel-Bulkley model shows numerically higher mean flow behaviour indices than Mizrahi-Berk in the graphs, the two were not statistically different ($p<0.05$). However, Bhattacharya & Bhattacharya (1996) found that, for cooked maize

flour with concentrations between 2 and 10%, the flow behaviour index calculated from the Herschel-Bulkley model were higher than the corresponding values of the Mizrahi-Berk model.

The mean flow behaviour indices for all storage conditions, ranged between 0.71 and 0.14 for Herschel-Bulkley model. Values of *n* less than unity means that the substance exhibits a shear-thinning behavior, while a greater than unity value means that the substance exhibits a shear-thickening behaviour (Al-Malah et al., 2000). It is obvious from these results that *n* values were less than 1. The *n* values obtained in this study, also confirms the pseudo-plasticity behaviour of the white maize meal during storage at all storage conditions. At 25^{o}C-43%RH storage, both the Herschel-Bulkley and Mizrahi-Berk mean flow behaviour indices seemingly marginally reduced from about 0.55 on the 7th day of storage up to about 0.4 on the 21st day of storage, where it remained almost constant up to the end of storage study (Figure 4.12a).

Although the n_{HB} at 25^{o}C-43%RH storage condition decreased, by 11% after 49 days of storage, the reduction was not statistically significant ($p<0.05$). At 25^{o}C-90%RH storage, there was a nearly linear and significant ($p<0.05$) decrease from about 0.55 to about 0.2 in Herschel-Bulkley and Mizrahi-Berk flow behaviour indices throughout the storage period (Figure 4.12b). After 49 days of maize meal storage, the n_{HB} significantly ($P<0.05$) decreased by an average of 44%. At 45^{o}C-43%RH storage, there was significant ($p<0.05$) reduction in Herschel-Bulkley and Mizrahi-Berk flow behaviour indices from about 0.55 to about 0.15 during the 21 days of valid model prediction period (Figure 4.12c). Equally, at 45^{o}C-90%RH storage, the Herschel-Bulkley and Mizrahi-Berk flow behaviour indices significantly ($p<0.05$) decreased from about 0.55 to about 0.1 during the 14 days of valid model prediction period (Figure 4.12d). The reduction in the *n* values for the samples stored indicates that the white maize meal dispersions exhibited more pseudoplasticity or shear thinning behaviour with storage time.

4.3.5.2.6. Consistency Index

Figures 4.13 shows the changes in the consistency index (*k*) of the Herschel-Bulkley (k_{HB}) and Mizrhi-Berk (k_{MB}) models during storage of the white maize meal at different temperature – relative humidity conditions. Similar to the flow behaviour index, the observations and explanations of the consistency indices are restricted to the Herschel-Bulkley and Mizrahi-Berk models. The Herschel-Bulkley and Mizrahi-Berk consistency indices had similar trends of evolution throughout the storage period.

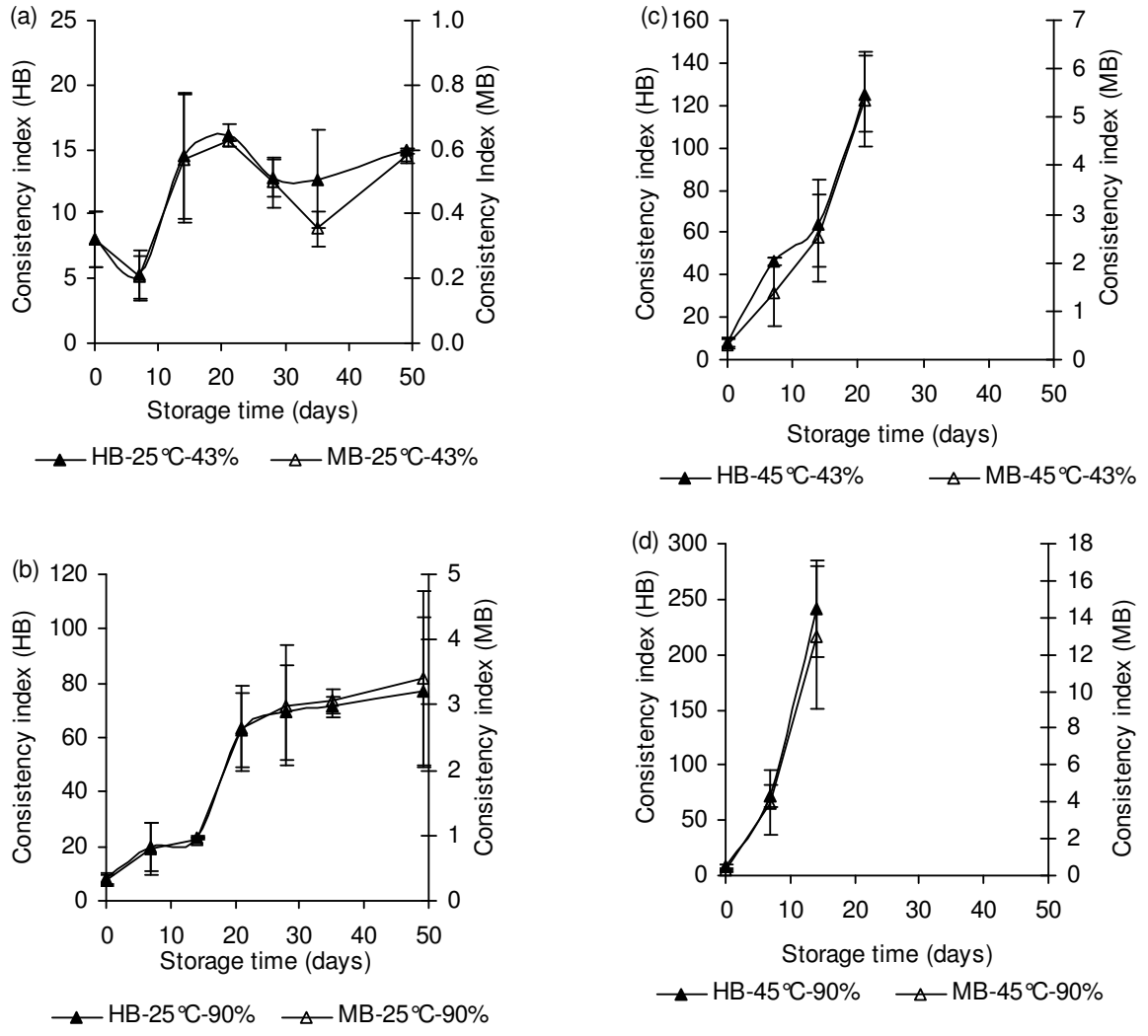

Figure 4.13 Changes in consistency index of Herschel-Bulkley (HB) model and Mizrahi-Berk (MB) Model of white maize meal during storage at temperature and relative humidity of: (a) 25°C-43%RH, (b) 25°C-90%RH, (c) 45°C-43%RH and (d) 45°C-90%RH. Units for consistency index in HB and MB models are Pa s^n and $Pa^{0.5}.s^n$

On the other hand, the Herschel-Bulkley model had significantly ($p<0.05$) higher consistency indices than Mizrahi-Berk. Similar to the flow behaviour index, Bhattacharya & Bhattacharya (1996) also found that the consistency index calculated from the Mizrahi-Berk model were lower than the corresponding values of the Herschel-Bulkley model.

At 25°C-43%RH storage, the Herschel-Bulkley and Mizrahi-Berk consistency indices marginally increased during storage period, but this increase was not statistically ($p<0.05$) significant

(Figures 4.13a). The Herschel-Bulkley and Mizrahi-Berk consistency indices significantly ($p<0.05$) increased during the storage period at 25°C-90%RH (Figure 4.13b). Similarly, the Herschel-Bulkley and Mizrahi-Berk consistency indices significantly ($p<0.05$) increased during the storage period at 45°C-43%RH (Figure 4.13c) and 45°C-90%RH (Figure 4.13d) within their valid periods of model prediction of 21 and 14 storage days, respectively. Flow behaviour index decreased during the storage period while the consistency index increased at all storage conditions. In a study of rice pastes, Kaur & Singh (2000) also found that the consistency coefficients of cooked rice pastes increased with the increase in fatty acid contents. They also found that addition of fatty acids decreased the flow behaviour values. They attributed the increase in consistency values with the addition of fatty acids to the formation of inclusion complexes with starch. In the white maize meal, free fatty acid contents increased during storage at all storage conditions just as the flow behaviour index decreased during the storage period while the consistency index increased at all storage conditions. Therefore, this observation could also be attributed to lipolysis, which resulted in formation of FFA-amylose complexes.

4.4. Conclusions

- Gelatinization properties were affected by the storage period, while storage temperature had no significant effect ($P<0.05$). Starch in maize meal had significantly ($P<0.05$) higher $T_{o,}$ and T_p than the isolated starch. On the contrary, starch in intact maize meal had significantly ($P<0.05$) lower ΔH than the isolated starch. The gelatinization properties only significantly ($P<0.1$) changed in the T_o for the isolated starch and T_E ($P<0.05$) for maize meal which both decreased at both storage temperatures during the storage period.

- Both primary and derived pasting properties of white maize meal have been found to change during storage. Low storage humidity increased PV, V_{95i} and V_{95f} at both low and high storage temperatures. High storage temperature evolved V_{50}, SB_t and C:H higher than low storage temperature. At the same storage temperature, high storage humidity had higher SB_t and C:H than low storage humidity and this phenomenon was more pronounced at high storage temperature than at low storage temperature.

- Storing maize meal at higher storage temperature and for long a period increased the peak elastic modulus (G'_p) while it decreased the peak viscous modulus (G''_p) of the isolated starch during heating.

- The white maize meal has been found to exhibit shear-thinning behaviour at all storage conditions throughout the storage period. The Herschel-Bulkley and Mizrahi-Berk models predicted flow behaviour for low temperature – low humidity and low temperature – high humidity storage conditions throughout the storage period, while it was only for a limited period at high storage temperatures. The stress overshoot at low temperature storage conditions decreased during storage while it increased at high temperature storage. The flow behaviour indices and yield stress also decreased while the consistency indices increased during storage.

Conclusions and recommendations

5. Conclusions and recommendations

5.1. Conclusions of the research

This research has shown through literature search that maize is a staple food in many parts of Africa, of which maize meal is the major form of maize utilization. Maize meal is produced by a dry milling process – degerming and non-degerming processes. In Africa, the degerming processes are used by large commercial milling firms and produces varying types of superior (refined) maize meals depending on the extraction rates. Consumer preference of the maize meal types is much more dependent on the color and level of refining the product, although no much research has been done in this area. The new trends in maize meal production underway in Africa include fortification. The socio-economic importance of maize meal to Africa lies in its home to industrial food applications. The climatic conditions in Africa do pose a challenge for storage of white maize meal during distribution. Despite white maize meal being a staple food for many parts of Africa with high involvement in commerce, literature is either scarce or non-existent on the stability of functional properties of the African maize meal types during storage or distribution. This major finding led to this research on the functional properties of white maize meal stored under tropical conditions. The study was based on chosen storage conditions taken as case study conditions. The properties studied included moisture sorption, lipolysis, lipid oxidation, colour, gelatinization, pasting, viscoelastic and flow properties.

The research has found that the adsorption isotherms before and after defatting white maize meal, exhibited sigmoidal shapes, representing Type II isotherms. Temperature influenced the adsorption isotherms, with the EMC increasing with decreasing temperature at the same A_w. GAB, Oswin and Smith models acceptably fitted the adsorption isotherms for both non-defatted and defatted white maize meal, with the GAB model being the best. The monolayer moisture content decreased with increase in temperature of adsorption. The differential heat of sorption and differential entropy of sorption increased with decreasing moisture content. Moisture adsorption has been found to be enthalpy-driven in the temperature range studied.

When stored at constant storage relative humidity, white maize meal would absorb or lose more moisture at high storage temperatures than at low storage temperatures. Storing white maize meal in polypropylene interwoven sack material under varying temperature and humidity conditions did not protect it against water activity changes. Polyethylene plastic material had

good barrier protection against water activity change when maize meal is stored at high humidity for both low and high storage temperatures. On the other hand, polyethylene plastic material had good protection against water activity change for a limited storage period of time at low storage humidity for both low and high storage temperature. The differences in the water activity of the samples packaged in polypropylene and polyethyelene was attributed to the higher water vapour transmission rates in polypropylene than in polyethylene.

Storage temperature and storage time had significant effects on the evolution of pH. At increased storage temperature decreased evolution of pH in function of time was observed. Storage period affected the evolution of titratable acidity, as it increased during storage, while storage temperature was not found to influence evolution of titratable acids.

The L-values decreased after a short period of storage at high storage temperature conditions, while at low storage temperature-high humidity after a longer storage period. The L-values at low storage temperature and low humidity conditions were significantly stable over the storage period. The a- and b-values at high storage temperatures increased, while at low storage temperature conditions were stable. These observations paralleled colour by sensory evaluation, for which colour deteriorated for low storage temperature-high relative humidity and high storage temperature conditions. The colour however, remained essentially constant for low storage temperature-low relative humidity. The observed change in colour was attributed to discoloration of the maize meal by non-enzymatic browning.

Storing maize meal in polypropylene interwoven sacks had poor barrier protection from effects of storage temperature and relative humidity on L-, a- and b-values. Storing maize meal in polyethylene plastic maintained L-values (suppressed reduction in L-values) at low temperature-high humidity storage conditions. Maize meal in polyethylene decreased L-values faster than in polypropylene at high temperature-low humidity during storage.

Storing maize meal in polyethylene increased b- and a-values faster and to higher values than in polypropylene at high temperature-low humidity. Storing maize meal in polyethylene changed the overall colour (ΔE-values) faster and more intensely than in polypropylene at high temperature-low humidity. In fact, the rate of change in all these properties at high temperature-low humidity was equivalent to the rate of change at high temperature-high humidity.

Storage temperature had a higher influence on lipolysis than storage relative humidity. Free fatty acids at higher storage temperatures had higher contents and evolved faster than at lower storage temperatures. However, at constant storage temperature, samples at high storage relative humidity had higher increases in free fatty acids contents and evolved faster than at low storage relative humidity. Fortification had great influence on the evolution of FFA, with fortified maize meal evolving higher FFA contents than unfortified maize meal during storage. Packaging and sunlight exposure did not play a significant role in the evolution of FFA contents during storage of maize meal.

Lipid oxidation determined by peroxide value, increased and then decreased to relatively constant values during the storage period. Fortification seemed to suppress the evolution of peroxide value, and this was attributed to high rates of lipid oxidation due to a combination of thermal, iron and photosensitized catalyzed lipid oxidation. Lipid oxidation as determined by p-anisdine value initially increased and then decreased to relatively constant values during the storage period, but the influence of storage temperature seemed not to be significant

Gelatinization properties of white maize meal and its isolated starch were inherently different due to the compositional difference. The $T_{o,}$ $T_{p,}$ and T_E of maize meal were higher, while ΔH was lower in maize meal than in its isolated starch. The $T_{o,}$, T_p and ΔH maintained this status quo during the storage period, while the T_E changed with time. The evolutions of the T_p and ΔH gelatinization parameters were not affected by storage temperature nor storage period. However, the T_o for the isolated starch decreased at both storage temperatures, while the T_E for maize meal also decreased at both storage temperatures. The changes in gelatinization properties during storage period have been hypothesized on the storage effects on the amorphous background and on the starch granule perfection due to prolonged hydrothermal effects.

In terms of pasting properties, low storage humidity increased peak viscosity (PV), initial hot-paste viscosity (V_{95i}) and final hot-paste viscosity (V_{95f}) at both low and high storage temperatures. This observation has been explained based on the starch granule perfection due to prolonged hydrothermal effects. Increasing storage temperature increased cold-paste viscosity (V_{50}), total setback (SB_t) and cold-paste:hot-paste viscosity ratio (C:H). At constant storage temperature, high storage humidity had higher SB_t and C:H than low storage humidity and this phenomenon was more pronounced at high storage temperature than at low storage temperature. The increase in the three retrodagradation parameters is due to the FFA-amylose complexation.

Storing the maize meal at higher temperature and for a long period increased the peak elastic modulus (G'_p) while decreased the peak viscous modulus (G''_p) of the isolated starch during heating.

The white maize meal exhibited shear-thinning behaviour during storage. The Herschel-Bulkley and Mizrahi-Berk models could be used to predict the flow behaviour for low temperature storage conditions during storage, while only for a limited storage period at high storage temperatures. The stress overshoot at low storage temperature conditions decreased during storage while it increased at high storage temperatures. This observation is due to formation of stronger gels at high storage temperatures than low storage temperatures due to the retrogradation effects observed during pasting. The flow behaviour indices and the yield stress decreased while the consistency indices increased at all conditions during storage. The changes in flow behaviour indices and consistency indices have also been attributed to formation of FFA-amylose complexes.

5.2. Significance of the research findings

In determining the stability of functional properties of white maize meal in Zambia, a developing nation, with all its attendant problems of data acquisitions and logistics, the researcher has added to the required knowledge of quality dynamics during storage of this staple food for many parts of Africa. The researcher has hope that this data may be valuable for decisions of quality related aspects of this staple food for Africa. Moisture sorption properties are important in the reactivity of other properties like browning of white maize meal during storage. The lowering of pH, increase in titratable acids and increase in lipid oxidation have the potential to affect the taste or flavor of the white maize meal. The browning colour encountered during storage is not only undesirable by the consumers but is also of nutritional concern as it further lowers the protein quality in white maize meal. Lipolysis is also of great concern as the abundant linoleic acid in its non-esterified form in maize meal has been associated with oesphagus cancer. Nonetheless, lipolysis has the potential of application to be used as a storage life marker of white maize meal. The increase in retrogradation properties during pasting and increase in consistency index for the flow behaviour due to storage conditions can have consequences for energy consumption during stirring, mixing or pumping of gelatinized maize meal pastes for the food industry. Manipulation of temperature, humidity and use of appropriate packaging material has the potential to control these phenomena. For instance, it clear from this study that for low temperature-high humidity

regions, the polyethyelene packaging would be recommended as it would retain the colour of maize meal for a longer period. On the other hand, for high temperature regions like the valleys, research into appropriate packaging would be required as the two packaging types studied here may not perform well in such regions.

5.3. Recommendations

While the influence of storage conditions on functional related properties have been established in this research, probably one would also say more questions have been raised especially for a product that has not been researched by many researchers yet. To better understand this product and to fully utilize it, the recommendations for further work in the area of white maize meal types in Africa cannot be avoided:

i. Almost all the research in literature on partially degermed maize meal does not report the extraction rates of the maize meal used. It seems that the extraction rates of the partially degermed maize meals could have a great influence on the quality properties of maize meals. It is therefore, recommended that the moisture sorption behaviour be determined for the different extraction rates in the African maize meal types

ii. It also appears that the enzymes might be playing a big role during storage of maize meal. To better understand there role or effects on quality properties there is need to study the role of enzymes like lipoxygenase, lipases, amylases and proteases. This should incorporate the study on susceptibility of maize varieties to lipid oxidation because we suspect that different maize varieties will have different amounts and activities of enzymes

iii. In our study we have not reported on the influence of different storage conditions on the packaging. Although not reported, our preliminary observations showed that storage conditions created physical changes in the appearance of the packaging material used, particularly, polypropylene

iv. In our study, apart from the sunlight exposure experiment, the rest of the experiments were based on fixing constant storage conditions (temperature and relative humidity).

There is need to study the maize stability under cyclic storage conditions as this will be closer to real storage conditions which fluctuate even within one given day

v. Although we have not adequately reported on the microbiological stability of the maize meal, it is evident from the data given in this research that this aspect plays a significant role in the stability of maize meal. Particularly, it will be important to study the role of yeast and moulds in contributing to exogenous amylases, proteases, lipoxygenases and lipases which are significant in accelerating the deterioration of maize meal in storage.

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NOMENCLATURE

Nomenclature

ANOVA	Analysis of Variances
A_w	Water activity
BD	Breakdown index (Pa.s)
BET	Brunauer-Emmett-Teller
C:H	Cold-paste: Hot-paste viscosity ratio
CIMMYT	International Maize and Wheat Improvement Centre
db	Dry basis
δ	Phase angle (^{o})
ΔG	Free energy at T_β (kJ/mol)
Δh_d	Net isosteric heat of sorption, or net differential enthalpy (kJ/mol)
$\left(\overline{\Delta h}_d\right)$	Average enthalpy (kJ/mol)
ΔH	Gelatinization enthalpy change (J/g)
ΔS_d	Differential entropy of sorption (kJ mol^{-1} K^{-1})
$\left(\overline{\Delta S}_d\right)$	Average entropy (kJ mol^{-1} K^{-1})
DSC	Differential Scanning Calorimetry
E_{ci}	Model predicted values
E_{ei}	Experimental values
EDTA	Ethylenediamine tetraacetic acid
EMC	Equilibrium moisture content (g H_2O/g, dry basis)
ERH	Equilibrium relative humidity
FA	Fatty acids
FFA	Free fatty acids
G*	Complex modulus (Pa)
G′	Elastic modulus (Pa)
G'_p	Peak elastic modulus (Pa)
G″	Viscous modulus (Pa)
G''_p	Peak viscous modulus (Pa)
GAB	Guggenheim-Andersen-de Boer
GMO	Genetically modified organisms
HMF	Hydroxyl-methylfurfural

K	Consistency index (Pa.s^n)
m	Number of $(\Delta h_d, \Delta S_d)$ data pairs
M_{gm}	Monolayer moisture content (g H_2O/g, dry basis)
MOST	The USAID Micronutrient program
Max	Maximum
MR	Maillard reaction
MRE	Mean relative error
N	Number of experimental data
n	Flow behaviour index
NEB	Non-enzymatic browning
NMR	Nuclear Magnetic Resonance
NSTL	Non-starch total lipids
PE	Polyethylene
PP	Polypropylene
PV	Peak viscosity (Pa.s)
R	Universal gas constant 0.008314 (kJ mol^{-1} K^{-1})
RH	Relative humidity (%)
r^2	Determination coefficient
T	Temperature (K)
T_β	Isokinetic temperature (K)
T_{hm}	Harmonic mean temperature (K)
RH	Relative humidity
SANS	Small Angle Neutron Scattering
SAXS	Small Angle X-ray Scattering
SB	Setback (Pa.s)
SB_t	Total setback (Pa.s)
SEM	Scanning electron microscopy
SR	Swelling rate (Pa.s/min)
T_E	Gelatinization end temperature (^oC)
TEM	Transmission electron microscopy
T_o	Gelatinization onset temperature (^oC)
T_p	Gelatinization peak temperature (^oC)

USAID	United States Agency for International Development
V_{50}	Cold-paste viscosity (Pa.s)
V_{95f}	Final Hot-paste viscosity (Pa.s)
V_{95i}	Initial Hot-paste viscosity (Pa.s)
WAXS	Wide Angle X-ray Scattering
WVTR	Water Vapor Transmission Rate (g $m^{-2}day^{-1}$) at specified temperature and relative humidity)
Wb	Wet basis

Curriculum vitae

John Shindano was born on 24.08.1970 in Solwezi, Zambia. He obtained a Bachelor of Science Degree in Chemistry (with merit) in 1994 from the University of Zambia, Lusaka, Zambia. He then worked from 1994 to 1996 for National Milling Company of Zambia as a Quality Assurance Officer in charge of quality control of the milled maize and stockfeed products. Between 1994 and 1996, he also worked on part-time as a Laboratory demonstrator with the Department of Chemistry at the University.

In 1996 he obtained a BADC scholarship to pursue an ICP programme from which he obtained a Masters of Science Degree in Food Science and Technology in 1998 from the University of Gent, Belgium. He was awarded a great distinction in Complimentary studies and a distinction in advanced studies. The MSc thesis was on 'isolation and separation of peptides from dry fermented sausage' under the promotership of Prof. D. Demeyer and Dr. Ir. R. Ramaekers at the Laboratory of meat science, Melle.

He then joined the University of Zambia in 1999 where he works up to now as a Lecturer for the recently introduced undergraduate Degree programme in Food Science and Technology in the Department of Food Science and Technology. He was seconded to work as a research trainee since 2001 within the VLIR-UNZA-IUC programme (Food Science and Technology Component) after which the same work led to his registration for the Ph.D programme in 2005 at the University of Gent, Belgium. The following are some of the publications in his research career:

Kabwit Nguz, **John Shindano**, Simbarashe Samapundo, Andre Huyghebaert (2005) Microbiological evaluation of fresh-cut organic vegetables produced in Zambia, Food Control, 16, 623 – 628

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