

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**AN INVESTIGATION ON THE RELATIONS BETWEEN PROCESS
PARAMETERS AND QUALITY CHARACTERISTICS OF PASTRY
MARGARINE**

M.Sc. THESIS

Emre Ömer NAS

Department of Food Engineering

Food Engineering Programme

JANUARY 2014

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**AN INVESTIGATION ON THE RELATIONS BETWEEN PROCESS
PARAMETERS AND QUALITY CHARACTERISTICS OF PASTRY
MARGARINE**

M.Sc. THESIS

Emre Ömer NAS
(506021415)

Department of Food Engineering

Food Engineering Programme

Thesis Advisor: Assistant Prof. Dr. Filiz ALTAY

JANUARY 2014

İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**PASTACILIK MARGARİN KALİTESİ VE ÜRETİM PROSES
PARAMETRELERİ ARASINDAKİ İLİŞKİLERİN ARAŞTIRILMASI**

YÜKSEK LİSANS TEZİ

**Emre Ömer NAS
(506021415)**

Gıda Mühendisliği Anabilim Dalı

Gıda Mühendisliği Programı

Tez Danışmanı: Assistant Prof. Dr. Filiz ALTAY (İTÜ)

OCAK 2014

Emre Ömer Nas, a M.Sc student of ITU Graduate School of Science Engineering and Technology student ID 506021415, successfully defended the thesis entitled “**An investigation on the relations between process parameters and quality characteristics of pastry margarine**”, which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assist. Prof. Dr. Filiz ALTAY**

İstanbul Technical University

Jury Members : **Assist. Prof. Dr. Funda K. GÜLER**

İstanbul Technical University

Dr. H. İmge O. BAŞEĞMEZ

TÜBİTAK

Date of submission : **6 January 2014**

Defence examination: **17 January 2014**

FOREWORD

The aim of the study was to determine correlations between process parameters and quality characteristics of pastry margarine.

The study revealed that there are correlations between baking product quality and process conditions. Main process parameters in this study were crystallisation unit temperature and solid fat content of emulsion. The outcomes of this study may help to developed pastry margarine with better baking quality.

January 2014

Emre Ömer Nas
(Food Engineer)

TABLE OF CONTENTS

	<u>Page</u>
FOREWORD	vii
TABLE OF CONTENTS	ix
ABBREVIATIONS	xi
LIST OF TABLES	xiii
LIST OF FIGURES	xv
SUMMARY	xvii
ÖZET	xix
1. INTRODUCTION	1
1.1 Purpose of Thesis	2
1.2 Literature Review	3
1.2.1 Shortening, margarine and puff pastry.....	3
1.2.2 Margarine production.....	4
1.2.2.1 Preparation of water and fat phases	5
1.2.2.2 Preparation of emulsion	6
1.2.2.3 Chilling, crystallization and kneading	7
1.2.2.4 Packing, filling and remelting.....	8
1.2.2.5 Storage.....	8
1.3 Affecting Parameters in Margarine Processing.....	9
1.4 Polymorphism and Crystallization	11
1.5 Quality Characteristics of Pastry Margarine	15
1.6 Hypothesis	18
2. MATERIAL AND METHOD	19
2.1 Materials	19
2.2 Methods	19
2.2.1 Production unit.....	19
3. RESULTS	23
4. CONCLUSION AND RECOMMENDATIONS	28
REFERENCES	31
CURRICULUM VITAE	35

ABBREVIATIONS

SFC	: Solid Fat Content
NMR	: Nuclear Magnetic Resonance
K1	: The temperature at the first crystallization tube
K2	: The temperature at the second crystallization tube
K3	: The temperature at the third crystallization tube
K4	: The temperature at the fourth crystallization tube

LIST OF TABLES

	<u>Page</u>
Table 1.1 : NBO Company Shares of Oils and Fats: % Value 2009-2013*	1
Table 1.2 : Sales of Oils and Fats by Category: Volume 2008-2013*	2
Table 2.1 : The formulations for emulsions used in this study	19
Table 2.2 : Sensory Test Table for Baking Performance	22
Table 3.1 : When solid fat content is same, cooling is different	24
Table 3.2 : Baking performance according to same cooling temperature and different solid fat content values	26

LIST OF FIGURES

	<u>Page</u>
Figure 1.1 : Model structures.	3
Figure 1.2 : Pastry dough during baking process.....	4
Figure 1.3 : Margarine production	5
Figure 1.4 : Hardness of margarine and percentage of solid fat content	11
Figure 2.1 : Boiling bottles at 20,30 and 35°C.....	20
Figure 2.2 : NMR measuring system.	21
Figure 2.3 : TA.XT Texture Analyzer.	21
Figure 2.4 : Sensory Analysis.	22
Figure 3.1 : Correlation between hardness and cooling temperature.....	23
Figure 3.2 : Correlation between solid fat content and hardnes.	25
Figure 3.3 : Hardness and Plasticity correlation.	27
Figure 3.4 : Plasticity and baking volume performans correlation.	27

AN INVESTIGATION ON THE RELATIONS BETWEEN PROCESS PARAMETERS AND QUALITY CHARACTERISTICS OF PASTRY MARGARINE

SUMMARY

Unilever, Ulker, Marsa and Turyağ meet % 90 of total margarin requirement of Turkey. All these plants have total almost 2500 workers. Pastry margarine consumption has been increased for ten years in Turkey however it has decreased at homes. Margarine consumption decreased %25 wherease pastry margarine consumption increased %9 industrially. Therefore producing high quality pastry margarine for industrial utilization is very important to stay in a competitive margarine market.

There are various affecting parameters for pastry margarine quality. In this study parameters which can affect quality of pastry margarine are defined. The parameters that can be easily controlled in a margarine process are temperature of crystallization and emulsion formulation especially solid fat content. Particularly plasticity and hardness of pastry margarine influence flavor, volume and performance of bakery. Therefore to obtain optimum plasticity and hardness of margarine is important by modifying solid fat content and controlling process parameters such as temperature and time in crystallization. Cooling temperature and emulsion content affect crystal formation. Crystal composition is important for margarine characteristic. The outcomes of this study may help to understand the relations between process parameters and quality characteristics of pastry margarine with better baking performance.

Pastry margarine is normally used for cakes and biscuits, generally needs to have a smooth consistency to facilitate mixing. This, could be achieved by ensuring that it solidifies in fine β crystals. A further requirement for bakery margarine is that it should not melt too quickly during baking, so that the air bubbles that have been incorporated into the batter during mixing until the cooking process has created structural materials from the other ingredients. Pastry margarine is characterized by a high degree of plasticity over a wide temperature range, sufficient plasticity for stretching and rolling in the dough preparation to ensure unbroken homogeneous thin layers of margarine in the dough, and the absence of softness or greasiness when

Puff pastry margarines have always been a challenge for the margarine industry to produce due to the many demands of the margarine such as a non-greasy surface so that the margarine is easy to work with both by hand and by extrusion process, very plastic, so that it can be folded without breaking, because breaks will lead to insufficient lift and flaky structure in the puff pastries, high functionality so that the best expansion can be obtained.

Puff pastry margarines are characterized by the plasticity, which allows the margarines to be worked with and folded and extruded without breaking and

becoming greasy. In order to obtain this margarine both the composition of the margarine, the processing and the tempering of the margarine are extremely important parameters.

PASTACILIK MARGARİN KALİTESİ VE ÜRETİM PROSES PARAMETRELERİ ARASINDAKİ İLİŞKİ İÇİN BİR ARAŞTIRMA

ÖZET

Unilever, Ulker, Marsa ve Turyağ margarine fabrikaları Türkiye pazarının % 90'nına hakimdir. Toplamda 2500 işçi çalıştırmaktadırlar. Türkiye'de son 10 yılda pastacılık ve endüstriyel yağların tüketimi artarken margarinlerin ev tüketimi azalmaktadır. Türkiye pazarında son on yılda margarinlerin ev tüketimi %25, yemeklik margarin tüketimi %60 azalırken, pastacılık ve endüstriyel yağ tüketimi %9 artmıştır. Bu nedenle yüksek kaliteli pastacılık margarinlerinin üretilmesi rekabetçi ve büyüyen pazar ortamında önem kazanmaktadır.

Üretim hatlarında pastacılık margarinlerinin kalitesini etkileyen bir çok parametre bulunmaktadır. Margarin üretim hatlarında kolayca kontrol edilebilen parametreler kristalizasyon sıcaklıkları ve emülsiyondaki katı madde miktarıdır. Pastacılık margarinin sertliği ve plastikliği, fırıncılık ürünlerinin hacimi ve performansı daha iyi hale getirek için ayarlanabilir. Margarinin fırıncılık ürünlerinde en iyi sonucu vermesi için plastiklik ve sertlik değerleri kristalizasyon sıcaklığı ve emülsiyon katı madde miktarı ile kontrol edilebilir. Kristalizasyon soğutma sıcaklığı ve emülsiyon içeriği kristal oluşumunu etkilemektedir. Kristal kompozisyonu margarinin karakteristiği açısından önemlidir. Bu çalışmanın sonunda elde edilen bulgular, pastacılık margarinlerinin fırıncılık ürünlerinde en iyi sonucu vermesi için kullanılabilir.

Pastacılık margarini bisküvi ve kek, pastahane ürünleri yapımında kullanılmaktadır. Genellikle hamur yapısının yumuşak ve pürüzsüz bir yapıda olması homojen bir karışımın sağlanması açısından önemlidir. Diğer önemli bir gereksinim ise pastacılık ürünlerinin pişmesi aşamasında margarinin hızlı bir şekilde erimemesidir. Bu şekilde karıştırma aşamasında hava kabarcıkları hamurun içinde kalmaktadır ve böylece daha homojen bir hamur elde edilmektedir. Şayet margarin hemen erirse yumuşak yapıda olacak hamur içinde hava kabarcıkları tutunamayıp dışarı kaçacaktır.

Pastacılık margarini için plastik yapı önemli bir özelliktir. Çünkü bu özelliği ile hamurun karıştırma işlemi daha kolay ve etkin bir şekilde yapılabilecektir. Şayet margarinin plastik özelliği az ise hamurda homojen olmayan bir yapı ve tanecikli bir yapı gözlemlenmektedir. Bu yapı ile üretilen hamur ürünlerinin hacmi ve kalitesi düşmektedir ki bu durum müşteriler tarafından istenmemektedir. Hamura plastik yapısını β' kristalleri vermektedir. Dolayısıyla bu kristallerin daha fazla üretilmesi pastacılık margarin kalitesi açısından önemlidir. Bu kristal yapısının oluşturulması üretim proses şartlarının doğru bir şekilde sağlanması ile mümkün olabilmektedir. Ancak hangi üretim şartlarında istenen kristal kompozisyonun üretileceğini bilmek gerekmektedir. Bunun için üretim sisteminin iyi tanınması ve hangi proses

parametrelerinin değiştirilerek hangi tür kristal oluşturulacağını bilmek gerekmektedir.

Yüksek maliyetlerle kurulan ve yüksek basınç altında çalışan margarin üretim sistemlerinde istenen şartların tespit edilmesi ancak yapılacak bir dizi çalışmalarla mümkün olabilmektedir. Yapılan deneme üretimi çalışmaları, müşterinin istediği ürün özelliklerinin yakalanabileceği ürünler üretilmektedir.

Üretim şartlarının belirlenmesinde müşteri ihtiyacının doğru bir şekilde anlaşılması önemlidir. Dünyada birçok pastacılık ürünü bulunmaktadır. O nedenle öncelikle pastacılık ürünün özelliğinin net bir şekilde tanımlanması ve buna uygun margarinin tespit edilmesi ihtiyacı karşılanması açısından önemlidir. Müşterilerin istediği pastacılık ürünlerinin hazırlanış tarifinin bilinmesi üretilen margarin ürünlerinin denenmesi ve sonuçlarının etkisinin görülmesi için gereklidir. Pastacılık ürünün özelliklerinin doğru bir şekilde anlaşılması ve üretim prosesinin net bir şekilde öğrenilmesinden sonra, istenen yapının nasıl bir pastacılık margarinini ile sağlanacağını tespit etmek kolaylaşmaktadır. Pastacılık margarinin sertlik ve plastiklik özellikleri değiştirilerek pastacılık ürünü üzerinde denenerak sonuçların duysal test ile gözlenmesi ve sonuçların kayıt edilerek istenen sertlik ve plastiklik özelliğinin ne oranda olması gerektiği tespit edilmelidir.

Nasıl bir pastacılık margarinine ihtiyacı olduğunu tespit ettikten sonra bu özellikteki margarinin nasıl üretileceğini belirlemek gerekmektedir. Bunun için bu tezde deneme üretimleri yapıp sonuçlar değerlendirilerek hangi üretim parametrelerinin değiştirilerek nasıl bir sonuç alındığı tespit edilmiştir. Hangi parametreler arasında ne ilişki olduğu tespit edilmiştir. Bu tespitler göstermiştir ki pastacılık yağlarının sertlik ve plastikliği ile son ürün performansı arasında bir ilişki vardır. İstenen sertlik ve plastiklik özelliği üretim parametrelerinin değiştirilmesi ile elde edilebilmektedir.

Üretim hatlarının belli bir basınç üstünde çalışmaması ve istenildiği kadar soğutmanın yapılamaması gibi sınırların olması istenen margarin özelliklerinin yakalanması için optimum şartların tespitini gerektirmektedir. Örneğin daha sert ürün üretildiğinde daha yüksek basınç oluşabilmekte ve sisteminin kendini durdurması gerekebilmekte ve üretimin yapılamamasına sebep olabilmektedir. O nedenle sistemin dayanabileceği sınır değerlerinin olması yapılan işi zorlaştırmaktadır. İstenen sonuç ancak bir kaç parametrenin değiştirilmesi ile elde edilmektedir ki bir sonuca ulaşmak için birkaç üretim parametresini değiştirmek değişken sayısını arttırmaktadır. Ancak hangi üretim parametreleri ile hangi margarin özellikleri arasında ne gibi ilişki olduğu sistemler için belirlenirse proses kontrol kolaylaşmakta istenen ürünler üretilmektedir.

Birbirinden farklı yapıda olan margarin üretim sistemlerinde bir sistem için geçerli bir doğru diğer sistem için geçerli olmayabilir. O nedenle mutlaka her sistem için deneme üretimleri yapılmalı ve istenen margarin özellikleri ile proses parametreleri arasındaki ilişki net bir şekilde tanımlanmalıdır.

Bu tezde yapılan çalışmada sanayi boyutunda bir üretim tesisinde çalışma tamamlanmıştır. Çalışma aşamasında öncelikle müşterinin istediği pastacılık ürünün hacim ve görünüm yapısı belirlenmiştir. Pastacılık ürününde istenen yapının sağlanması için margarinde sertlik ve plastiklik özelliği formül ve üretim şartları değiştirilerek elde edilmeye çalışılmıştır. Formül değiştirilerek daha değişik sertliklerde emülsiyonlar üretilmiş ve sonucunun pastacılık ürünü üzerindeki etkisi duysal analiz ile tespit edilmiştir. Margarinin sertliği ve belli sıcaklıktaki katı madde miktarı gerekli ölçüm ekipmanları ile ölçülmüştür. Yapılan her bir ölçüme

karşılık pastacılık ürünü üzerinde denenmiş ve sertlik, plastiklik özelliğinin değişmesi ile arasındaki değişimin etkisi grafikler üzerinde incelenmiştir.

Çalışma sonunda gerek ölçüm ekipmanlarından elde edilen veriler ile gerekse son ürün üzerindeki ölçümlenen veriler arasında ilişkiler tespit edilebilmiştir. Margarinin yapısı ile pastacılık ürünü yapısı arasında önemli bir ilişki olduğu tespit edilmiştir. Bu şekilde istenen pastacılık ürünün üretilebilmesi için hangi özellikte pastacılık yağının kullanılması gerektiği belirlenmiştir.

Elde edilen sonuç ile başka margarin üretim tesislerinde de benzer çalışmalar yapılarak ilişkinin o tesisler içinde yapılması müşteri memnuniyeti ve istenen özellikte pastacılık margarinin üretilmesini sağlayacaktır.

1. INTRODUCTION

Since margarine was invented by Me`ge Mourie`s in 1896 as the substitute of butter, the continuing increased margarine production and per capita consumption around the World confirms the importance of margarine as a significant food item (Liu et al., 2010)

The national brand owners (NBO) company shares of oils and fats in Turkey are presented in Table 1.1 (Url-1). According to this table, the first three biggest shares belong to BIM Birleşik Mağazacılık A.Ş., Yudum Gıda San. ve Tic. A.Ş and Yıldız holding A.Ş, respectively.

Table 1.1: NBO Company Shares of Oils and Fats: % Value 2009-2013*.

% retail value rsp	2009	2010	2011	2012	2013
BIM Birlesik Magazacilik AS	11.46	12.92	14.49	15.06	15.59
Yudum Gida Sanayi ve Tic AS	8.15	8.51	9.99	12.58	13.32
Yildiz Holding AS	10.23	9.96	12.70	12.55	12.35
Ana Gida ihtiyaç Maddeleri San AS	11.20	11.90	13.19	11.23	12.16
Trakya Yagli Tohumlar Tarim Satis Birligi	4.77	5.24	6.10	6.43	7.22
Unilever Sanayii ve Ticaret Türk AS	8.41	7.88	7.05	6.53	6.13
Orkide AS	3.77	3.84	4.17	4.87	5.07
Taris Zeytin ve Zeytinyagi Birligi	3.38	3.23	2.90	2.80	2.50
Sütas AS	0.68	0.72	0.85	0.83	0.83
Kristal Tic ve San Kontuvari AS	1.88	1.78	1.58	1.28	0.71
Toros Ltd	0.97	1.02	0.88	0.77	0.66
Pinar Süt Mamülleri San ve Tic AS	0.56	0.59	0.64	0.64	0.61
Edirne Yag Sanayi AS	0.80	0.84	0.70	0.58	0.46
Turyag Turkiye Yag ve Mamulleri AS	0.53	0.47	0.40	0.33	0.27
Verde Yag Besin Mad San ve Ticaret AS	0.28	0.29	0.20	0.32	0.24
Tat Konserve Sanayii AS	0.15	0.17	0.20	0.18	0.18
Rekor Gida AS	0.14	0.11	0.07	0.06	0.04
Lio Yag San ve Tic AS	0.04	0.04	0.03	0.02	0.01
Teksut Mamulleri Sanayii ve Ticaret AS	0.20	0.21	0.22	0.00	0.00
Paksoy Ticaret ve Sanayii AS	0.69	0.66	0.44	0.30	-
Marsan Gida San ve Tic AS	5.49	4.29	-	-	-
Aytac Gida AS	0.03	0.01	-	-	-
Trakya Ciftligi	-	-	-	-	-
Türk Henkel Kimya San ve Tic AS	-	-	-	-	-
Others	26.18	25.34	23.20	22.63	21.65
Total	100.00	100.00	100.00	100.00	100.00

*Source: Euromonitor International from official statistics, trade associations, trade press, company research, store checks, trade interviews, trade sources

In Table 1.2, the sales numbers of total fats and oil market in Turkey from 2008 to 2013. If we look the sales of margarine and spreadable oils and fats, it looks confusing. Due to health concerns of consumers margarine sales seem to decrease by 26.8% in five years whereas spreadable oils and fats, which pastry margarines included that commodity, appear to increase by 6.46% (Table 1.2) (Url-1).

Table 1.2: Sales of Oils and Fats by Category: Volume 2008-2013*.

'000 tonnes	2008	2009	2010	2011	2012	2013
Butter	17.62	18.56	20.75	27.71	24.43	25.26
Margarine	35.07	36.13	36.63	28.15	26.97	25.67
Olive Oil	65.66	74.20	85.03	97.87	112.84	123.00
Spreadable Oils and Fats	140.40	140.42	139.91	142.59	146.01	149.47
Vegetable and Seed Oil	662.16	670.77	709.24	706.80	734.37	782.83
Oils and Fats	920.92	940.07	991.55	1,003.13	1,044.62	1,106.24

*Source: Euromonitor International from official statistics, trade associations, trade press, company research, store checks, trade interviews, trade sources

Taking this increase in spreadable oils and fats market into account, producing high quality pastry margarine is very important to stay in competitive market.

Fats and lipids affect the quality of baked products including air incorporation, lubrication, heat transfer, tenderness, moisture, mouth feel, flavor, structure, and shelf life. The physicochemical qualities of lipids affect its baking performance. In pastry bakery products, the compositions of lipid crystals play a predominant role in determining structure. This affects the volume and texture of the finished bakery products (Zhong et al., 2013).

1.1 Purpose of Thesis

For best quality of baked products, hardness and plasticity of pastry of margarine should be optimized during margarine production. There is strong correlation between production parameters and margarine quality, which leads baking performance of baked products. The purpose of this study was to investigate correlations between temperatures of crystallization units in the processing line and solid fat contents as affecting parameters and hardness as a quality characteristic of pastry margarine. In order to do that, each parameter were changed at three different levels and the hardness of the final product was measured by using a texture analyzer (TA) for pastry margarine in a plant.

1.2 Literature Review

1.2.1 Shortening, margarine and puff pastry

Margarine is a water-in-oil emulsion and consists of at least 80% fat phase and at most 16% aqueous phase. The fat phase consists of both liquid oil and crystalline fat. The solid structure is achieved by a matrix of fat crystal aggregates in which tiny water droplets are entrapped (Bongers and Almeida-Rivera, 2011).

According to the FDA (Food and Drug Administration), margarine (or oleomargarine) is defined as the food in plastic form or liquid emulsion, containing not less than 80 percent fat (Url-2). Shortening is a term described as the function performed by naturally occurring solid fats such as lard and butter in baked products (O'Brien, 2008). Shortenings actually shorten or tenderize baked products. Being insoluble in water, fat prevents the cohesion of gluten strands during mixing, thus literally shortening them and making the product tender. Shortening is often used interchangeably with the term “fat” (Anonymous, 2011). Puff pastry is characterized by its laminated structure of baked layers of dough separated by thin layers of pastry margarine. During the lamination process, one layer of margarine will separate each layer of dough (Anonymous, 2011). After preparation of the dough, the layers can be illustrated as in Figure 1.1, and 1.2 (Anonymous, 2011).

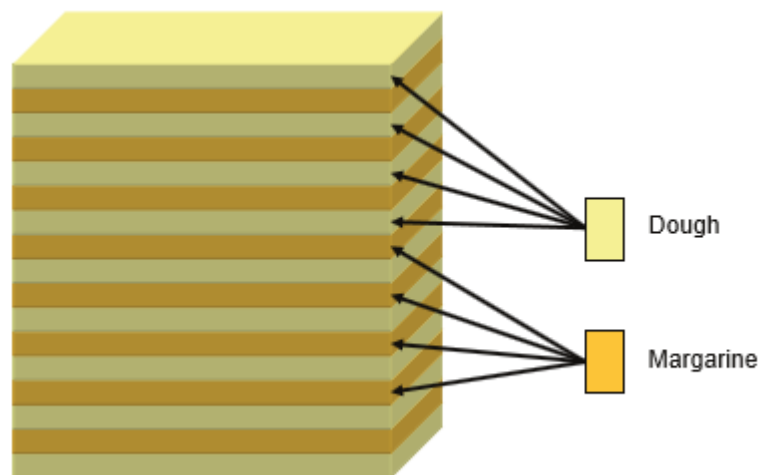


Figure 1.1 : Pastry dough with layers of dough and margarine (Anonymous, 2011).

After baking this lamination of the dough will result with a nice lamination and volume (expressed as height and expansion) (Anonymous, 2011).

The dough layers should not absorb margarine; the fat film has to remain continuous during the rolling process. Therefore, the quality of baked products depends strongly on the quality of the shortening margarine (Anonymous, 2011).

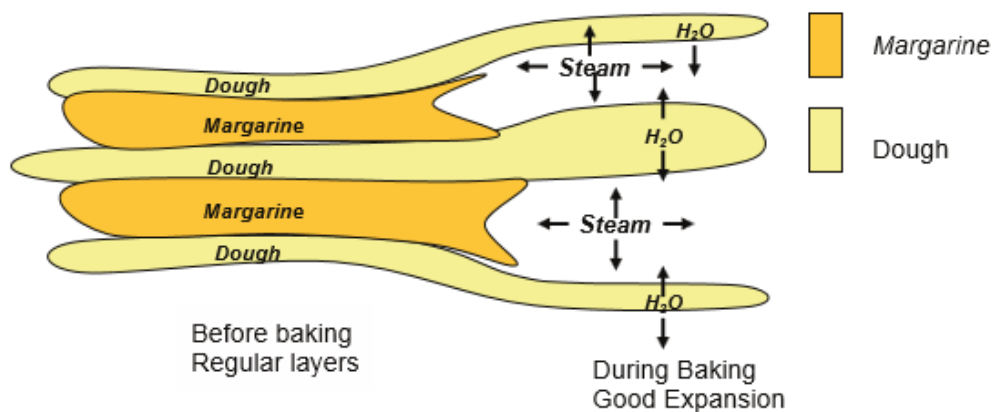


Figure 1.2 : Pastry dough during baking process (Anonymous, 2011).

1.2.2 Margarine production

Margarine, like butter, can be characterized as water in oil emulsion, i.e. the water phase is dispersed as droplets in the continuous fat phase.

Minor ingredients such as emulsifiers, salt, preservatives, color, flavor, antioxidants and vitamins are dispersed in the phases according to solubility. In addition, the extents to which additives may be used in food as well as the maximum dosage permitted often vary from country to country (Url-3).

The manufacturing process can generally be divided into the following sub-processes (Figure 1.3) (Url-3).

- 1) Preparation of water phase
- 2) Preparation of emulsion
- 3) Chilling, crystallization and kneading
- 4) Packing and remelting
- 5) Storage

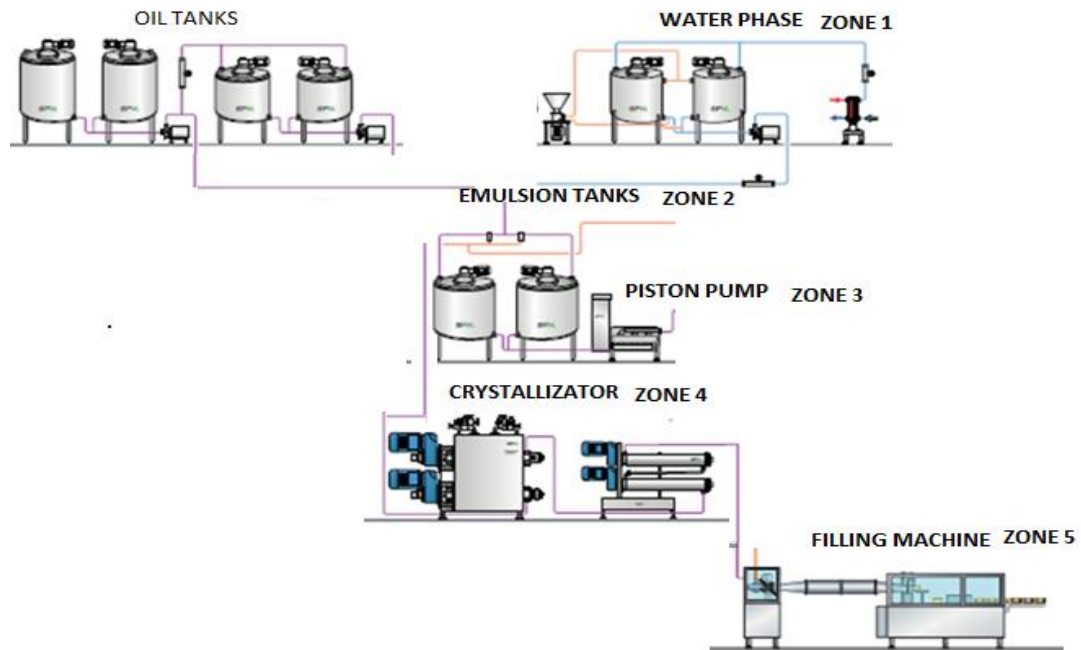


Figure 1.3: Margarine production (Url-3).

In Figure 1.3, zone 1 represents the preparation of water phase, zone 2 represents preparation of emulsions. The zone 3 shows the pumping of emulsion to the crystallizator from the emulsion tanks (Fig 1.3). The zone 4 represents crystallizator in which chilling, crystallization and kneading occur while the zone 5 shows the packaging of the product (Fig 1.3) (Url-3).

In the following section, the margarine manufacturing steps will be explained.

1.2.2.1 Preparation of water and fat phases

The water phase is often prepared batch-wise in the water phase tank. The water should be of good drinking quality (Url-3).

The major ingredients in the fat phase, the fat blend, normally consist of a blend of different fats and oils. In order to achieve margarine with the desired characteristics and functionalities, the ratio of fats and oils in the fat blend is decisive for the performance of the final product (Url-3).

1.2.2.2 Preparation of emulsion

The emulsion is prepared by transferring various oils and fats or fat blends to the emulsion tank. Usually, the high melting fats or fat blends are added first followed by the lower melting fats and the liquid oil. To complete the preparation of the fat phase, the emulsifier and other oil-soluble minor ingredients are added to the fat blend. When all the ingredients for the fat phase have been properly mixed, the water phase is added and the emulsion is created under intensive but controlled mixing (Url-3).

The main component for the manufacture of margarines is the fat blend. In the simplest case, the fat blend consists of structured fat and liquid oil. From the structure point of view, margarine consists of a continuous liquid fat phase with fat globules, crystalline fats and aqueous phase dispersed in it (Piska et al., 2005).

Different systems can be used for metering the various ingredients for the emulsion of which two are working batch-wise:

1. Flow meter system
2. Weighing tank system

A continuous in-line emulsification system is a less preferred but used solution in high capacity lines where limited space for emulsion tanks is available. This system is using dosing pumps and mass flow meters to control the ratio of the added phases into a small emulsion tank (Url-3).

Margarine emulsions can be made by either a batch or continuous system. The batch system has been used for many years and comprises an agitated, temperature-controlled mixing tank to receive the water and oil phases. After the batch has been mixed to form a stable emulsion at the required temperature, the emulsion is then pumped to a scraped-surface heat exchanger for supercooling. The batch system is usually used for operations required to produce many different types of margarines with production runs of relatively short duration (Carr and Vaisey-Genser, 1993).

Typically, a two-tank system is used for preparing the emulsion in order to be able to run the crystallization line continuously. Each tank works as a preparation and buffer tank (emulsion tank), thus the crystallization line will be fed from one tank while a new batch will be prepared in the other and vice versa. This is called as the flip-flop system (Url-3).

1.2.2.3 Chilling, crystallization and kneading

The scraped-surface heat exchanger (A unit) is the centerpiece of equipment of the margarine processing line, where initial cooling, super cooling, and subsequent induced nucleation and crystallization take place (Haighton, 1976; Rajah et al., 1992; Joyner, 1953). The A unit has to have a high degree of flexibility with regard to variation of process conditions for different product types and formulations (Rajah, 1992).

Reducing the residence time in the processing equipment increases the cooling rate. It has been shown that a reduced residence time is associated with formation of smaller emulsion droplets due to a stronger degree of super cooling. As smaller droplets are formed, the system is more likely to coalesce (Rønholt et al., 2014).

The emulsion is pumped to the crystallization line by means of a high pressure piston pump. The crystallization line for the production of margarine and related products typically consists of a high pressure crystallizer cylinder which is cooled by ammonia or Freon type cooling media. Pin rotor machine(s) and/or intermediate crystallizers are often included in the line in order to add extra kneading intensity and time for the production of plastic products. A resting tube is the final step of the crystallization line and is only included if the product is packed (Url-3)

When margarine emulsion passes through the space between the shaft and cylinder wall, a thin crystallized product film is constantly and very rapidly scraped off the cylinder wall and remixed with warmer product because of the scraping action of the blades and the shaft's high rotation speed. This causes rapid crystal nucleation, further emulsification of the product, very high overall heat transfer coefficients, and a homogeneous cooling of the margarine emulsion under precise temperature control of the product being crystallized (Rajah, 1992; Joyner, 1953).

The emulsion is efficiently scraped off by the rotating scrapers, thus the emulsion is chilled and kneaded simultaneously. When the fat in the emulsion crystallizes, the fat crystals form a three-dimensional network entrapping the water droplets and the liquid oil, resulting in products with properties of plastic semi-solid nature (Url-3).

Depending on the type of product to be manufactured and the type of fats used for the particular product, the configuration of the crystallization line (i.e. the order of the

chilling tubes and the pin rotor machines) can be adjusted to provide the optimum configuration for the particular product (Url-3).

The crystallization process, the processing conditions and the processing parameters have a great influence on the characteristics of the final margarine and spread products. When designing a crystallization line, it is important to identify the characteristics of the products planned to be manufactured on the line. To secure the investment for the future, flexibility of the line as well as individually controllable processing parameters are necessary, since the range of products of interest might change with time as well as raw materials (Url-3).

When producing margarine for stick or block wrapping, a resting tube is normally connected directly to a packaging machine to allow the product sufficient time to attain a hardness that is suitable for wrapping (Haighton, 1976; Rajah, 1992; Joyner, 1953).

1.2.2.4 Packing, filling and remelting

The consistency of the product is very different if it is produced to be packed or filled. It is obvious that a packed product must exhibit a firmer texture than a filled product and if this texture is not optimal the product will be diverted to the remelting system, melted and added to the buffer tank for re-processing (Url-3).

1.2.2.5 Storage

In some cases where the shortening oil blend includes very slowly crystallizing oils especially in case of palm oil. It can be necessary to store the produced product in a storage room with a temperature of approx. 25°C for a period of max. 48 hours. The tempering is necessary to ensure the stability of the β' crystal structure. The stability is achieved by holding the processed shortening in the quiescent state at a temperature just below the melting point of the lowest melting crystals (Url-3).

Careful consideration should be given to the storage stability of margarine. During storage, changes may occur to physicochemical, textural and viscoelastic properties of the margarine. This is mainly due to changes in the crystals and crystal network of margarine. Changes in the crystals and crystal network often lead to deterioration of margarine quality such as oiling-off and development of a sandy taste (Cheong et al., 2009).

1.3 Affecting Parameters in Margarine Processing

For most consumers, the textural (hardness) attributes of margarines is a key factor influencing its performance in the final products (Liu et. al, 2010).

Margarines designed for such applications have to possess specific properties in order to make the final product satisfying: to be very firm and to have a good plasticity without being oily. Predetermined plasticity, hardness and solid fat content profile are the main requested properties. They allow the margarine to perform essential functions in the shortening margarine preparation, which are mainly to separate the dough layers and to trap water that evaporates in the oven, which leads to an expanded final product. The dough layers cannot absorb margarine; the fat film has to remain continuous during the rolling process. Consequently, the quality of baked products depends strongly on the quality of the shortening margarine (Lefebure et al., 2012).

The puff pastry fat must have certain specific structural characteristics, such as predetermined plasticity, firmness and solid fat content (SFC) profile. The plasticity of puff pastry fats can be attained in a number of ways, one of which is the partial hydrogenation of vegetable oils. The use of partially hydrogenated oils, however, leads to the presence of trans fat, now a widely recognise contributor to cardiovascular disease (Simovic et al., 2009).

Puff pastry margarine is subjected to a high degree of shear when stretching and thinning the dough, certain product characteristics are essential. The product needs to be plastic and not sticky. Moreover, b'-crystals are preferred over a and b, as they are associated with an increased firmness and a less grainy macroscopic structure (Rønholt et al., 2014).

Several studies show that formulation is a key factor affecting the final product quality, and the process conditions are critical factors (Lefebure et al., 2012).

For optimum baking performance, bakery margarine should contain a minimum of 10% solid fat content (SFC) at 20°C to prevent oil exudation or oiling off. In addition, it should also contain a minimum of 8% SFC at working temperature (25°C) to withstand dough making. In addition, it should have a high consistency or firmness without the need for refrigeration. Another important characteristic of bakery margarine is the crystallization in the form of b' in order to produce cookies with a crispier and better snap texture (Cheong et al., 2009).

SFC is one of the physical parameters associated with the quality of margarine including general appearance, oil exudation, organoleptic properties, and spreadability (Saadi et al., 2011).

There are a couple of different characteristics of shortening margarine, which can be classified as structure, hardness, plasticity, and spreadability (Wiedermann, 1972). These end product properties are related to a number of different parameters. The most important two main parameters are formulation of emulsion (the amount of solid triglycerides or solid fat index) and processing conditions during shortening margarine production (Haighton, 1976). Formulation or choice of oil blend allows control of the solid content, which, for identical processing conditions, is directly related to the consistency and type of crystalline structure formed (Haighton, 1976; Thomas, 1978). Processing conditions (rate and degree of cooling, mechanical working, final product temperature, etc.) regulate the type of crystals formed and the morphology and extent of intertwining of the solid structure that holds the liquid oil (Rivarola et al., 1987).

There is a relationship between the solid fat content of emulsion and its hardness. When solid content of emulsion decreases, that is mean margarine loses some of plastic properties, the hardness of margarine is also goes down sharply (deMan, 1964). There is a strong correlation between the hardness of margarine and solid content under same process production conditions can be seen in figure 1.4 (Haighton, 1976; Haighton, 1959).

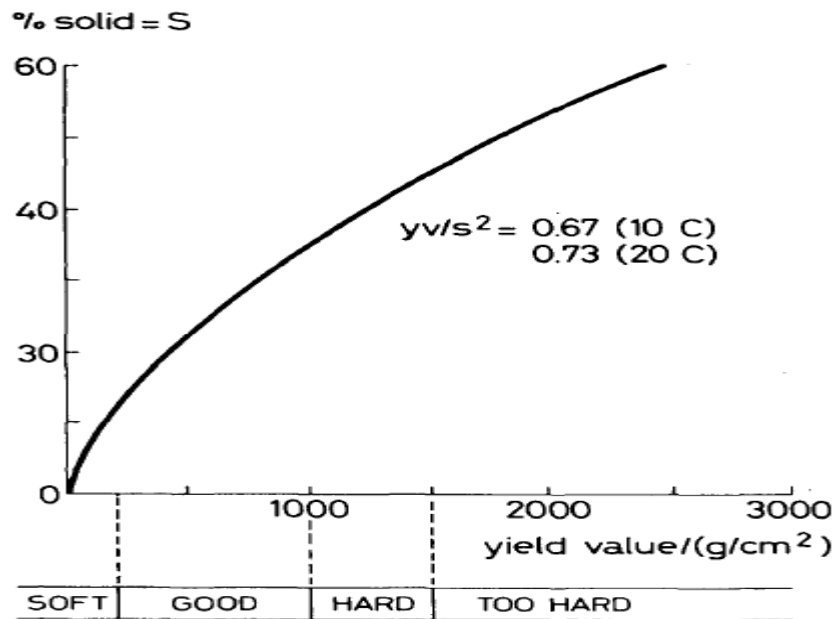


Figure 1.4: Hardness of margarine and percentage of solid fat content (Vereecken et al., 2007).

All of the structure levels that lead to good technological functionality, a factor that is determined by the macroscopic properties of the fats. The formulation (amount of solids), the polymorphism of the solid state (the microstructure of the network of crystalline particles) play a role in the development of the macroscopic properties, and all of these factors are influenced by processing conditions (Vereecken et al., 2007).

The physical properties of the product is the result of the complex interactions of a range of factors including the polymorphism, formulation (solid fat content, composition) margarines related to process conditions (Liu et al., 2010).

1.4 Polymorphism and Crystallization

Fats tend to crystallize in various forms having different melting points. Each of these crystalline forms with their respective melting point are called polymorphs and the phenomenon is called polymorphism (Url-3).

The triglycerides exhibit, with some exceptions, three basic crystalline forms designated alpha (α), beta prime (β'), and beta (β).

In general, transformations take place in the order: $\alpha > \beta' > \beta$

When cooling the melt, α crystals are generally formed, but this form is never stable in triglycerides and transforms to β' form. In most cases, β' crystals are relatively slowly transformed to the stable β form. The time of transformation from one crystal form to another depend on the composition of the triglycerides and the presence of diglycerides in the fat blend. However, some fats possess both β' and β forms, others only either stable β' form with no further transition or stable β form (Url-3).

Apart from a few types of shortening the β' crystals are the most desirable. They are relatively small and can incorporate a larger amount of liquid oil in the crystal network. β' crystals result in a glossy surface and a smooth texture (Url-3).

The transition from the α -form to the β' -form takes place in the crystallization equipment. All fats tend to crystallize in the β' -form when crystallization takes place in a plant. Fats that are not stable in the β' -form due to its triglyceride composition will during storage transform into the β -form. The rate of this transition is increased by temperature fluctuations (Url-3).

Crystal sizes are essential for final product consistency and acceptability, with smaller crystals leading to firmer products, whereas larger size crystals ranging between 30 and 140 micrometers are reported to produce a sandy mouth feel. Crystal aggregates become visible to the naked eye and can be perceived in the mouth. Stability of β' -form polymorphs, smaller crystal sizes and sparser spatial distributions of mass within the fat crystal networks could resist temperature fluctuations (Zong et al., 2010).

The main demands to puff pastry margarine are therefore plasticity and firmness, since soft and oily margarines tend to be absorbed by the dough and hard and brittle margarines are difficult to spread between the two dough layers during the rolling procedure. In both cases the baking performances may be affected negatively. Puff pastry margarine is by the professional baker evaluated by a subjective method called finger evaluation of plasticity, which include a thumb test and a kneading test. The thumb test is performed by pressing the thumb several times in adjacent areas in a slice of margarine. This gives an indication if the margarine is firm and homogeneous without lumps (Url-3).

There are two crystallization steps, one is nucleation forming, and the other is crystal growth. In order to form crystal nuclei, the fat system should stay in super-cooling or as a supersaturated system. Once the nucleation forms, they continue to grow and form

crystals. Fat crystal generally experiences a fat-free period, nucleation form, rapid crystal accumulation period and endgame of crystallization with slowing down of speed and reaching the maximum. The shape of crystal solid fat content vs. time can give important clues for the crystallization mechanism of a particular substance (Zang et al., 2007).

Nucleation is the development of small solid particles exceeding the critical size. Below this size, clusters of molecules re-dissolve rather than grow, while above this size, they will grow further. From a minor component perspective, nucleation can be influenced by providing heterogeneous nucleation sites, stabilizing the developing nuclei, or affecting the driving force, e.g. by changing the solubility of the other components, reducing the surface tension etc. They may also increase secondary nucleation by adsorbing at growth sites, leading to crystal defects and weaker crystals that may break at that point. Where the nucleation rate is reduced, this may be due to shielding of the heterogeneous nuclei present by the minor component or additive, rendering them less suitable as initiators of crystallization (Kevin et al., 2011).

Different isothermal crystallization curves signify different crystallization mechanisms. Temperature changing not only affected the solid fat content of products but also affected the crystallization behavior of the product. Thus, it would affect the nature of the products. In order to describe the crystallization behavior in more detail, the Avrami crystallization theory has been used, the Avrami equation fitted with the percentage of crystallinity, as a function of time by linear regression. The equation fitted the data very well over the entire range of fractional crystallization values. Correlation coefficients obtained were always higher than 0.96 for the linear regression of $\log[-\ln(1-X)]$ on $\log(t)$. The Avrami exponent (n), Avrami constant (K), and the half-times of crystallization ($t_{1/2}$). The avrami equation is given below (Zang et al., 2007):

$$\ln(-\ln(1-X)) = n \ln t + \ln K \quad (1.1)$$

Triglycerides exhibit three main crystal types alpha; β' , and β with increasing degrees of stability and melting point (deMan, 1964).

According to widely used nomenclature to date, three major fat polymorphs occur in margarines: alpha form shows a single line near 4.15 A° , β' form exhibits two strong lines near 4.20 and 3.88 A° or three strong lines near 4.27 , 3.97 , and 3.71 A° , and β form shows a very strong line at 4.60 A° (Liu et al., 2010).

Crystals of the alpha is approximately 5 microns in size, which is in form of fragile, and transparent. They are extremely transitory and require quite low temperatures to exist. β' crystals are very tiny and the length is generally less than 1 micrometer. β crystals are larger than β' crystals and approximately its size 25–50 microns and can grow to over 100 microns during extended periods of product storage. The β form is responsible for product quality failure in “sandy” and “grainy” margarines (Hoerr, 1960).

The plasticity is evaluated by means of two subjective tests. The first was based on the test of the thumb test. The thumb test is performed by pressing the thumb several times in adjacent areas in a slice of margarine. This gives an indication if the margarine is firm and homogeneous without lumps. The bending test is the second subjective method showing whether a slice of margarine can be bent without cracking. If the margarine can be bent, the margarine is evaluated to be plastic (Cavillot et al., 2009).

Generally, β' polymorphic form is desirable for margarines, which gives product a smooth consistency and spreadability. But according some studies, the β' crystal polymorph occurs in single, needle shaped crystals about 5–7 micrometers in length, whereas the β crystal polymorph is about 20–30 micrometers. The smaller the crystal size is, the smoother the product is, and thus the more β crystals in margarine make the product harder (Liu et al., 2010).

In the manufacture of margarine, the emulsion is processed in a scraped-surface heat exchanger that must super cool the melted fat quickly in order to form as many crystal nuclei as possible. The fat is believed to first crystallize in the alpha form, which is transformed more or less rapidly to the β' form depending on the crystal habit of the fat, rate of cooling, and the amount of mechanical work applied (Hoerr, 1960). β' is the crystal form desired in margarines as it promotes plasticity (Wiedermann, 1978; Thomas, 1978). The β' crystal form tends to structure as a fine three-dimensional network capable of immobilizing a large amount of liquid oil (Rivarola et al., 1987). Large β crystals do not tend to give a three-dimensional structure. Both Wiedermann, 1978 and Thomas 1978 have grouped various oils and fats according to their crystal habits. As an example, soybean, sunflower seed, corn, coconut, and peanut oils show a β tendency. Cottonseed oil, palm oil, tallow, and butter oil have a β' tendency. Oil blend formulation has a significant influence on the crystal form attained by a margarine or shortening. The suitability of a fat or oil for margarine formulation is very much dependent on the crystal size present, amount, and habit of these crystals (Riiner, 1971). Incorporation of a higher

melting β' tending oil to a basestock can induce the crystallization of the entire fat into a stable β' form (Thomas, 1978).

In margarine with a good consistency, the fat crystals have formed a three-dimensional network consisting of primary and secondary bonds. The crystals may vary in shape and appearance in the form of small needles or platelets with lengths ranging from less than 0.1 to 20 microns or more (Haighton, 1976 and Rivarola et al., 1987). They do not behave as individual particles and can grow together, forming a strong network (primary bonds). They may also show a tendency to agglomerate, forming tiny porous crystal clusters with considerable fewer contact points (secondary bonds) (Haighton, 1976). As a result of this and depending on the resulting crystal form obtained, branched and intertwining long chains are formed (Rivarola et al., 1987). These chains are responsible for forming the three-dimensional network. The primary bonds are strong and are not readily reestablished when broken by mechanical work. Secondary bonds are weak and readily reestablished when broken by application of mechanical work. Processing conditions involving fast cooling rates and application of a certain amount of mechanical work tend to produce margarines with a better stability and consistency. It is generally accepted that a larger amount of primary bonds are established if margarine is allowed to crystallize without sufficient degree of mechanical work. This results in a product exhibiting excessive post hardening and a hard and brittle texture. Due to this, it is advantageous to crystallize the product as much as possible in the scraped-surface heat exchanger to achieve the desired spreadability or consistency (Calvelo, 1986).

The most important aspect of the physical properties of oils and fats is related to their melting and crystallization behavior. If crystallization conditions changed, crystal habit, crystal size and crystal numbers would be influenced. These changes are eventually be reflected in the product performance (Zhang et al., 2007).

1.5 Quality Characteristics of Pastry Margarine

In margarine or shortening formulations, the measurement of solids over a certain range of temperatures is utilized by the industry to evaluate the plastic temperature interval of fats and oils. The solids content should be defined at a number of temperatures, typically from 5 to 40⁰C, covering the range of practical use (Liu et al., 2010).

For margarines and shortenings containing high fat contents, although solid fat content (solid fat content) is always thought to have strong influences on the mechanical behavior of fats and taken as evaluating indicator in industry, many studies also found that solid fat content alone is unreliable to predict hardness of fats. As early as in 1965, Haighton suggested that the permanent tridimensional fat crystal networks contribute to 60–80% of the total hardness. Relationship of fat crystal networks to their macroscopic rheological properties and conclude that the plastic properties (sensory hardness) of fat crystal networks depend integrally on the nature of the microstructure. Polymorphism and lipid composition of the network, whilst important, cannot yet provide an adequate prediction of the mechanical strength of the network. In a word, the physical properties of the product is the result of the complex interactions of a range of factors including the lipid composition, solid fat content, the polymorphism of the solid fat, and the microstructure of the network of crystalline fat, etc. Thus, an understanding of the relationship between lipid composition, crystallization behavior, microstructure, and mechanical properties of fats is required for improvement of texture of, e.g., palm oil-based margarine (Liu et al., 2010).

The solid fat content is not the sole parameter that influences the ultimate strength of fat crystal network. The hardness of fat had no linear correlation with the solid fat content, and other important factors that characterize crystal habits also have significant influences. Various crystal types and/or network structures that are formed upon crystallization of hard fats can result in variability in hardness. The mechanical properties of fats can be influenced by a series of other factors in addition to the solid fat content. These factors may include lipid composition, polymorphism, crystallization behavior and microstructure of margarines (Liu et al., 2010).

The fatty acid composition has an important influence on the crystallization process (Zhang et al., 2007).

Soybean, sunflower seed, corn, coconut, and peanut oils show a β tendency. Cottonseed oil, palm oil, tallow, and butter oil have a β' tendency. Oil blend formulation has a significant influence on the crystal form attained by a margarine or shortening. The suitability of a fat or oil for margarine formulation is very much dependent on the crystal size present, amount, and habit of these crystals (Riiner, 1971).

In certain margarines formulated mainly on hydrogenated oils, such as sunflower seed oil and canola oil, with very strong β tendency, the problem of sandiness can be pronounced. Addition of crystal-modifying agents or crystal inhibitors to such margarines can retard the development of sandiness by delaying the transformation from the unstable α form to the stable β form. The addition of sorbitan esters stabilizes the intermediate β' form and helps prevent the formation of the β form (Garti et al., 1982).

Palm oil is extracted from the mesocarp of the fruit of the oil palm *Elaeis guineensis*. It is semi-solid and high in saturated fat at room temperature, with a natural melting point of about 306 K. Palm oil exhibits several excellent properties such as high productivity, low price, ease of the formation of β -prime type crystal, high thermal oxidative stability and plasticity at room temperature conditions (Zhang et al., 2007).

Palm oil fractions originated from different dry fractionation operation conditions exhibit different composition and physical properties, moreover, crystallization behaviors of palm oil fractionations will also affect the physicochemical properties of the end products such as margarine and shortening, therefore it is of great significance to explore the crystallization behavior of the palm oil fractions (Zhang et al., 2007).

Among numerous vegetable oils, palm oil has been widely applied in margarines and shortenings due to its several advantageous properties, such as (a) high productivity, (b) low price, (c) high thermal and oxidative stability, and (d) plasticity at room temperature (Liu et al., 2010).

Nuclear Magnetic Resonance (NMR) has demonstrated to be very useful in determining the composition in acyl groups of vegetable oils and other oil components that are usually present in much lower concentrations than triglycerides, such as mono- and di-glycerides, free fatty acids or antioxidant compounds such as phytosterols. The usefulness of NMR is reinforced by the simplicity of the sample preparation, the speed of the analysis and the great deal of information that is obtained in a very few minutes. All these advantages make NMR a very valuable tool, not only for investigation purposes, but also for quality control (Sopelana et al., 2013).

The traditional quality control tool for estimating plasticity has been the solid fat content (SFC). Solid margarine converts to liquid when equilibrated at three temperatures: 10, 20, and 30⁰C. Nuclear magnetic resonance (NMR), which depends on differences in the magnetic environment of protons in the solid and liquid phases, is being used to solid fat

content. The solid fat content (SFC) values from NMR evaluations are considered as an indication of hardness and plasticity (Vaisey-Genser, 2013).

1.6 Hypothesis

Margarine characteristics should meet the quality such as higher volume etc. for baked products. If plasticity of margarine is higher and not very soft the dough layers should not absorb margarine then, the fat film has to remain continuous during the rolling process. Therefore, the quality of baked products depends strongly on the quality of the shortening margarine.

Optimum β and β' composition should be obtained for margarine with the best quality depending on solid fat content and process parameters in the crystallization. β crystals give hardness and β' crystal give plasticity. If relations between process conditions during processing and quality parameters of the product can be established, then production can be adjusted according to these parameters for best baking performance.

2. MATERIAL AND METHOD

2.1 Materials

Table 2.1: The formulations for emulsions used in this study.

Sample no	Palm oil (%)	Palm stearin (%)	Cotton oil (%)
1	60	25	15
2	57	28	15
3	54	31	15
4	52	33	15
5	63	22	15

2.2 Methods

2.2.1 Production unit

In order to study the process parameters affecting margarine quality, 40 different batches were processed in a margarine plant, which has a capacity of 4 metric tonnes per hour. Each batch was 30 metric tonnes. During processing all parameters were recorded. There are two emulsion tanks for continuous production. One cooling combinatory consists of four tube type cooling cylinders. The cooling tubes were coded as K1, K2, K3 and K4, respectively. The temperature at each tube was measured with electronic thermometers automatically in the system. The cooling for the crystallization tubes were provided by ammonia at -22°C. Margarine was pumped by piston pump with a ten metric tons of capacity. One filling machine, which can fill 10 kg of margarine into cartoon boxes, has been used for the study.

2.2.2 Solid fat content measurement

- 10-ml pipette,
- Stirrer with heater,
- Magnetic fish,
- NMR tubes,
- Haake DC3 ± K15 or K10 water bath Haake DC30 ± / acceptance criteria: ± 1.5,
- NMR spectrophotometer (Minispec, Bruker, USA).

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is a research technique that exploits the magnetic properties of certain atomic nuclei. It determines the physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of molecules. The intramolecular magnetic field around an atom in a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule (Url-4).

Most frequently, NMR spectroscopy is used by chemists and biochemists to investigate the properties of organic molecules, although it is applicable to any kind of sample that contains nuclei possessing spin. Suitable samples range from small compounds analyzed with 1-dimensional proton or carbon-13 NMR spectroscopy to large proteins or nucleic acids using 3 or 4-dimensional techniques. The impact of NMR spectroscopy on the sciences has been substantial because of the range of information and the diversity of samples. Impurity and moisture free samples placed on a stirrer heater was thoroughly mixed to ensure homogeneity by using magnetic fish sample. The four NMR tubes from each sample were filled to the level of 4 cm by using a 10 mL-pipette. The tubes with sample were being conditioned in a water bath (Figure 2.1). The conditioning process was conducted as follows:

- The tubes were kept in a water bath at 60 °C for 30 min
- Then, the tubes were taken from the water bath at 60°C to 0°C and left there for 30 min
- The each tube from the four were put in water baths at 20, 25, 30 and 35°C for 30 min.



Figure 2.1: Boiling bottles at 20,30 and 35°C.

The NMR instrument was set by the standards. Sample tubes were placed into the chamber of the instruments. The % solid fat content were obtained from the NMR (Figure 2.2).



Figure 2.2: NMR measuring system.

2.2.3 Hardness measurement

The hardness of the samples was determined using the penetration test by a texture analyzer (TA-XT Plus 12976, TTC, Hamilton, USA) (Figure 2.3). The conic shaped SMS P/5 was used as a sensor. The return distance, the return speed and contact force were 45 mm, 10 mm/sec and 10 g, respectively.

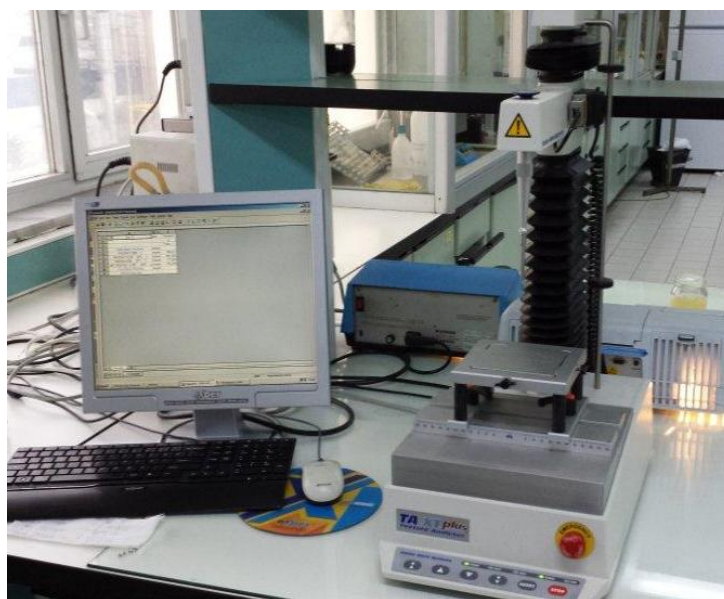


Figure 2.3: TA.XT Texture Analyzer.

2.2.4 Sensory analysis

When conducting a taste panel, puff pastry is uniformly prepared and presented to three panelists in isolated booths including the test form (Table 2.2). Judges record evaluations of the product on a sensory evaluation sheet that is decoded and analyzed as below table for baking performance. Maximum score in the table are defined according to customer requirements.

Each panelists are free from the following defects: a) taste perception disorders b) odor perception disorders c) color blindness d) denture defects.

Plasticity and baking performance have been measured with sensory tests by cake chief, two engineers in kitchen is shown in Figure 2.4. These two values are measured from 1 point to 10 ten points according to experience and eye looking. 1 point is the worst and 10 points are the best pointed for measuring plasticity and baking performance. For example, if cakes volume is perfect and big volume this is pointed with ten points or if Plasticity is perfect and margarine is very plastic and not breakable this product is pointed with ten points. Sensory measured values collected from two replications with 1 = disliked very much and 10 = liked very much.

Table 2.2: Sensory test form for baking performance.

Attributes	Max-Score	Sample 1	Sample 2
Appearance	3		
Texture	3		
Size	4		
Total Score	10		

As the same way, plasticity also has been measured by sensory test with same panelist. Each panelist has given points for each margarine plasticity. Maksimum point has given to the best plastic margarine ranged 0 to 10 points.



Figure 2.4: Sensory analysis room.

3.RESULTS

In Table 3.1, the results for sample 1 at different cooling temperatures of K1, K2, K3 and K4.

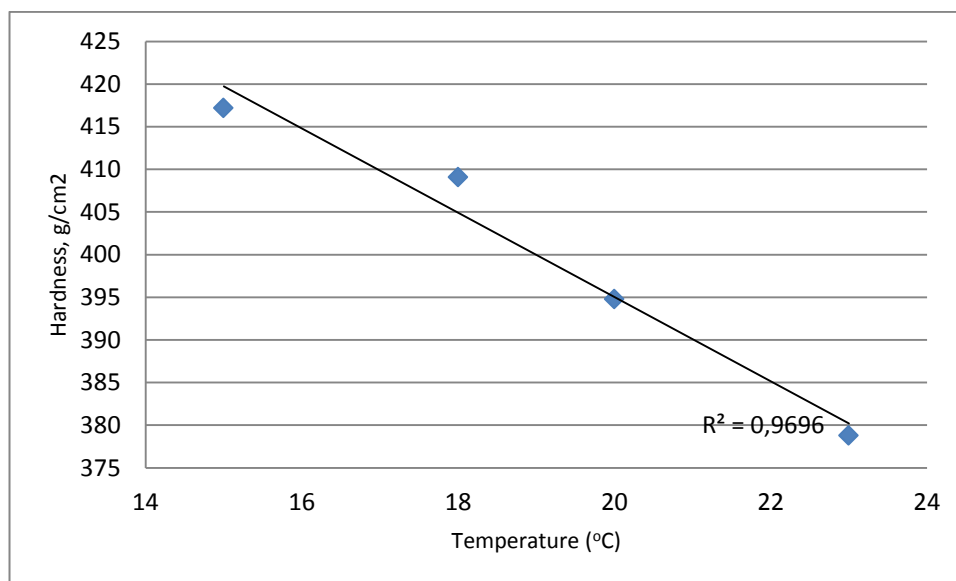


Figure 3.1: Correlation between hardness and cooling temperature (K4) (Data were taken from Table 3.1).

Table 3.1 and figure 3.1 showed that as cooling unit temperatures at K4 decreased the margarine became harder for same solid fat content (for same emulsion). This was due to fact that cooling at lower temperature produces more β crystals which are harder than β' crystals.

Table 3.1: Results for the sample 1 at different cooling at K1, K2, K3 and K4.

Sample no	Pump capacity (%)	K1 (°C)	K2 (°C)	K3 (°C)	K4 (°C)	Rework temperature (°C)	End product temperature (°C)	Solid fat content at 20°C (%)	Solid fat content at 30°C (%)	Solid fat content at 35°C (%)	TA Hardness at 24°C (g/cm ²)	Plasticity (10-best,1-worst)	Baking Performance (10-best ,1-worst)
1	55	33	30	25	23	60	31.4±0.1	49.9±0.2	30.3±0.6	21.7±0.3	378.8±2.2	6.5±0.7	6.0±0.0
1	55	30	27	22	20	60	31.6±0.1	50.1±0.3	30.4±0.1	21.5±0.4	394.8±4.8	6.5±0.7	6.0±0.0
1	55	27	24	21	18	60	31.7±0.2	49.6±0.9	31.0±0.4	21.6±0.3	409.1±5.0	6.0±0.0	6.5±0.7
1	55	23	21	18	15	60	31.3±0.3	49.3±0.2	30.5±0.4	21.5±0.6	417.2±3.1	6.5±0.7	6.5±0.7

When solid fat content of emulsion increased, the hardness of margarine was also increased.

Figure 3.2 shows that the correlation between solid fat content of the emulsion and their hardness. It appears that when solid fat content in the emulsion was higher, hardness of pastry margarine increased.

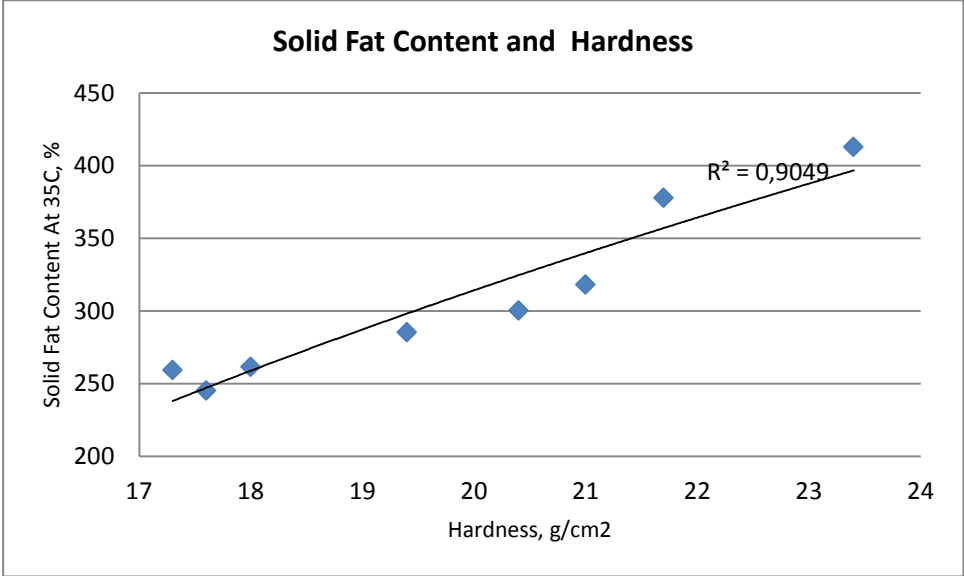


Figure 3.2: Correlation between solid fat content and hardness (Data were taken from Table 3.2).

Table 3.2: Results for samples with different solid fat contents at the same cooling temperature at K1, K2, K3 and K4.

Sample no	Pump Capacity	K1	K2	K3	K4	Rework temperature	End Product Temperature	Solid Fat content (20°C) %	Solid Fat content (30°C) %	Solid Fat content (35°C) %	TA Hardness (g/cm ²) at 24°C	Plasticity	Baking Performance (10-best, 1-worst)
1	55	33	30	25	23	59.0±1.4	29.7±2.4	49.7±0.3	30.2±0.7	21.7±0.2	377.8±3.5	6.5±0.7	6.0±0.0
2	55	33	30	25	23	58.0±2.8	28.5±0.7	48.8±0.1	28.6±0.9	19.4±0.1	285.3±7.0	8.0±1.4	8.0±1.4
3	55	33	30	25	23	57.5±3.5	28.7±0.3	45.5±4.1	26.1±2.4	18.0±0.1	261.4±9.8	9.0±0.0	9.0±0.0
1	55	33	30	25	22.5	58.0±0.0	28.0±0.0	49.6±0.4	28.2±1.8	21.0±0.2	318.2±11.2	7.0±0.0	6.5±0.7
4	55	33	30	25	23	59.5±3.5	28.0±1.4	43.5±0.4	24.6±0.2	17.3±0.1	259.3±0.8	9.0±0.0	10.0±0.0
5	55	33	30	25	23	57.5±0.7	29.9±1.9	51.2±0.4	31.8±0.2	23.4±0.1	412.9±3.7	6.0±0.0	7.0±0.7
4	55	32.5	30	25	23	57.0±5.7	28.0±0.0	46.0±2.8	25.4±0.4	17.6±0.1	245.1±0.6	9.5±0.7	9.5±0.7
2	55	33	30	25	23	57.0±2.8	28.6±0.1	48.6±0.5	28.1±0.8	20.4±0.8	300.3±1.4	8.5±0.7	8.5±0.7

Table 3.1 and 3.2 show that when cooling temperature are fixed and solid fat content values are changed, baking performance and hardness are also changed. When solid fat content values are increased margarine becomes harder, plasticity becomes lower.

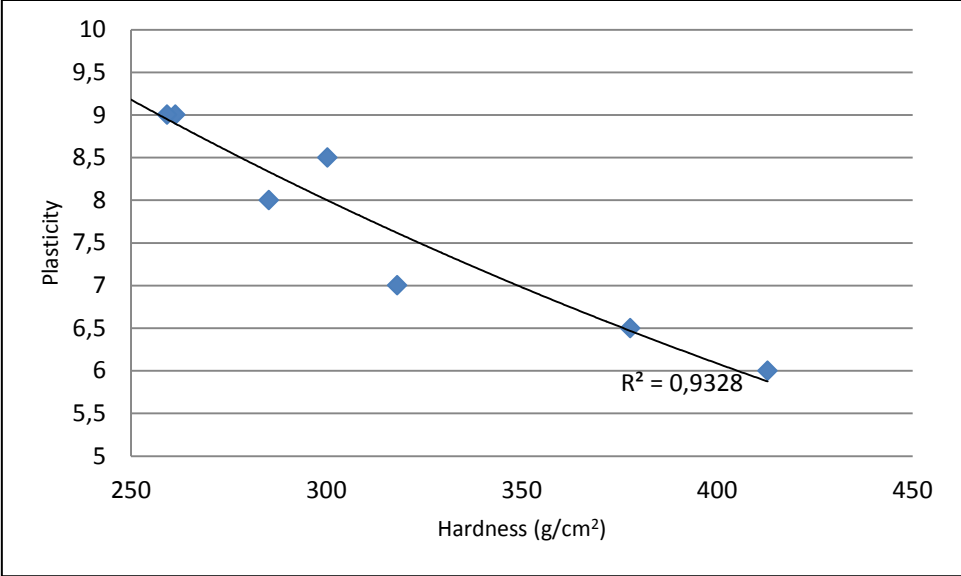


Figure 3.3: The correlation between hardness and plasticity for samples (Data were taken from Table 3.2).

In Figure 3.3 shows that there is an opposite correlation between hardness and plasticity of pastry margarine. When hardness increased, plasticity becomes decreased.

Figure 3.4 shows that there is a correlation between baking performance and plasticity for pastry margarine. It appears that baking performance increased with plasticity.

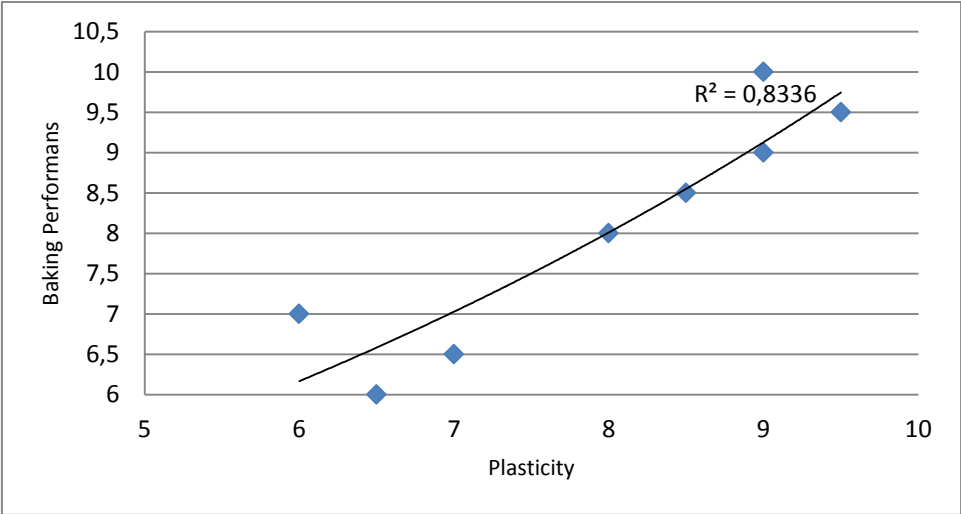


Figure 3.4: The correlation between plasticity and baking volume performance (Data were taken from table 3.2).

4. CONCLUSION AND RECOMMENDATIONS

At the end of this study 40 different production have been completed. It is clearly shown that there is a strong correlation between plasticity, hardness, cooling temperature and solid fat content of margarine. When margarine plasticity is higher dough layers separated in oven perfectly. Its mean more plastic margarine is required. More plastic margarine can be produced in two ways. One of them is increasing crystallisation temperature and another way using emulsion with less solid fat content. But when we increase crystallisation temperature, filling in filling machine can not be processed due to the very soft and wet margarine. The cubic margarine shape can not be supplied. Therefore we can not increase crystallisation temperature as much as we want. At the same way decreasing solid fat content of emulsion too much can cause softy margarine surface and can not be shaped in filling machine. Therefore optimum solid fat content for emulsion and optimum temperature should be found for good shaped filling and baking performance. Hardness and solid fat content can be defined for this system as following equation:

$$\text{Hardness} = -0,0002(\text{solidfatcontent})^2 \pm 0,1797(\text{solidfatcontent}) - 25,139, \quad r = 0,98$$

If hardness values are kept between 185-220 g/cm², best bakery performance results may be obtained for the system studied. If equation is used for these values best solid fat content nmr values can be calculated and palm stearin quantity in the emulsion can be regulated according to this result.

As Liu et al. (2010) mentioned that the textural (hardness) attributes of margarines is a key factor influencing its performance in the final products. As Lefebure et al. (2012) mentioned that margarines designed for such applications have to possess specific properties in order to make the final product satisfying: to be very firm and to have a good plasticity without being oily. Predetermined plasticity, hardness and solid fat content profile are the main requested properties. They allow the margarine to perform essential functions in the shortening margarine preparation, which are mainly to separate the dough layers and to trap water that evaporates in the oven,

which leads to an expanded final product. The dough layers cannot absorb margarine; the fat film has to remain continuous during the rolling process. Consequently, the quality of baked products depends strongly on the quality of the shortening margarine.

REFERENCES

- Anonymous**, (2011), Puff pastry margarine focusing on functionality and fat reductions, *Palsgaard Technical Paper*.
- Bongersa, P., and Almeida-Rivera, C.** (2011), Dynamic modelling of the margarine production process, *European Symposium on Computer Aided Process Engineering*. (pp 1301-1310), Elsevier B. V., Netherlands.
- Carr, R.A., and Vaisey-Genser, M.** (1993), Method of Manufacture, *Encyclopaedia of Food Science, Food Technology and Nutrition.*, (pp 2280 – 2884), Academic Press, London.
- Cavillot, V., Pierart, C., De Meerendré, M.K., Vincent, M., Paquot, M., Wouters, J., Deroanne, C., and Danthine, S.** (2009), Physicochemical Properties Of European Bakery Margarines With And Without Trans Fatty Acids, *Journal of Food Lipids* 16, 273–286.
- Cheong, L., Tan, C., Long, K., Yusoff, M.S.A., and Lai, O.** (2009), Physicochemical, Textural and Viscoelastic Properties of Palm Diacylglycerol Bakery Margarine During Storage, *Journal of the American Oil Chemist's Society* 86, 723–731.
- deMan, J.M.** (1964), Physical Properties of Milk Fat, *J. Dairy Sci.*, **47**, 1194.
- Garti, N., Wellner, E., and Sarig, S.** (1981), Effect of Food Emulsifiers on Crystal Structure and Habit of Stearic Acid, *Journal of the American Oil Chemists' Society*, 58, 12, 1058-1060.
- Garti, N., Wellner, E., and Sarig, S.** (1982), Crystal structure modifications of tristearin by food emulsifiers, *Journal of the American Oil Chemists' Society*, 59, 4, 181-185.
- Haighton, A.J.** (1959), The Measurement of the Hardness of Margarine and Fats with Cone Penetrometers, *Journal of the American Oil Chemists' Society*, 36, 8, 345-348.
- Haighton, A.J.** (1976), Blending, Chilling, and Tempering of Margarines and Shortenings, *Journal of the American Oil Chemists' Society*, 53, 6, 397-399.
- Hoerr, C.W.** (1960), Morphology of Fats, Oils, and Shortenings, *Journal of the American Oil Chemists' Society*, 37, 10, 539-546.
- Joyner, N.T.** (1953), The plasticizing of edible fats, *Journal of the American Oil Chemists' Society*, 30, 11, 526-535.
- Lefébure, E., Ronkart, S., Brostaux, Y., Béra, F., Blecker, C., and Danthine, S.** (2012). Investigation of the influence of processing parameters on physicochemical properties of puff pastry margarines using surface

response methodology. *LWT - Food Science and Technology*, 51, 225-232.

- Liu, Y., Meng, Z., Zhang, F., Shan, L., and Wang, X.** (2010) Influence of lipid composition, crystallization behavior and microstructure on hardness of palm oil-based margarines, *Euro Food Res Technology*, 230, 759–767.
- Meng, Z., Liu, Y., Shan, L., Jin, Q., Wang, X.** (2010), Reduction of Graininess Formation in Beef Tallow-Based Plastic Fats by Chemical Interesterification of Beef Tallow and Canola Oil, *J American Oil Chem Soc*, 87, 1435–1442.
- O'Brien, R.D.** (2008). Shortenings Types (Chapter 5), in *Fats and Oils Formulating and Processing for Applications* (Third Ed.) (pp 347-360), CRC Press, Boca Raton, FL.
- Piska, I., Rubova, M.Z., Ecky, T.L., Karami, H., and Filip, V.** (2005), Properties and crystallization of fat blends, *Journal of Food Engineering* 77, 433–438.
- Rajah, K.K.** (1992), Oils and Fats in the Nineties, *International Food Science Centre A/S* (V. K. S. Shukla and F. D. Gunstone, eds.), (pp 254–282), Denmark.
- Riiner, U.** (1971), Investigation of the polymorphism of fats and oils by temperature programmed x-ray diffraction, *LWT - Food Science and Technology*, 4, 6, 175.
- Rivarola, G., Segura, J.A., and Anon, M.C.** (1987), Crystallization of Hydrogenated Sunflower-Cottonseed Oil, *Journal of the American Oil Chemists' Society*, 64, 11, 1537-1543.
- Rønholt, S., Kirkensgaard, J.K., Høyer, K.F., Mortensen, K., Knudsen, J.C.** (2014), The Effect of Capacity, Rotational Speed and Storage on Crystallization and Rheological Properties of Puff Pastry Butter, *J American Oil Chem Soc* 91, 29–38.
- Saadi, S., Ariffin, A.A., Ghazali, H.M., Miskandar, M.S., Abdulkarim, S.M., and Boo, H.C.** (2011), Effect of Blending and Emulsification on Thermal Behavior, Solid Fat Content, and Microstructure Properties of Palm Oil-Based Margarine Fats, *Journal of Food Science*, 76, 1.
- Simovic, D.S., Pajin, B., Seres, Z., and Filipovic, N.** (2009), Effect of low-trans margarine on physicochemical and sensory properties of puff pastry, *International Journal of Food Science and Technology*, 44 , 1235–1244.
- Smith, K.W., Bhaggan, K., and Talbot, G.** (2011), Crystallization of Fats: Influence of Minor Components and additives, *Journal of the American Oil Chemists' Society*, 88, 1085–1101.
- Sopelana, P., Arizabaleta, I., Ibargoitia, M.L., and Guillén, M.D.** (2013), Characterisation of the lipidic components of margarines by H Nuclear Magnetic Resonance, *Food Chemistry*, 4, 141, 3357-64.

- Thomas, A.E.** (1978), Shortening Formulation and Control, *Journal of the American Oil Chemists' Society.*, 55, 11, 830-833.
- Vaisey-Genser, M.** (2013), Types and Properties Methods of Manufacture Composition and Analysis Dietary Importance, *Elsevier Science*, (pp 3704 – 3709), London.
- Zhang, X., Li, L., Xie, H., Liang, Z., Su, J., Liu, G. and Li, B.** (2013), Comparative Analysis of Thermal Behavior, Isothermal Crystallization Kinetics and Polymorphism of Palm Oil Fractions, *Molecules*, 18, 1036-1052.
- Zhong, H., Allen, K., Martini, S.** (2013), Effect of lipid physical characteristics on the quality of baked products, *Food Research International*, 55, 239 – 246.
- Wiedermann, L.H.** (1972), Margarine and Margarine Oils: Finished product quality, *Journal of the Oil Chemists' Society*, 49, 8, 478-480.
- Wiedermann, L.H.** (1978), Margarine and Margarine Oil, Formulation and Control, *Journal of the American Oil Chemists' Society*, 55, 11, 823-829.
- Url-1,** <<http://www.portal.euromonitor.com/Portal/Pages/Statistics/Statistics.aspx>>, data retrived 05.03.2014.
- Url2,**<<http://www.accessdata.fda.gov/scripts/cdrh/cfdoc/cfcfr/CFRSearch.cfm?fr=166.110>>, data retrived 05.03.2014.
- Url-3,** < <http://www.spx.com/en/gerstenberg-schroder/>>, date retrieved 10.10.2013.
- Url-4,** < <http://www.bruker.com/>>, date retrieved 10.10.2013.

CURRICULUM VITAE



Name Surname: Emre Ömer Nas

Place and Date of Birth: Kadıköy and 26.05.1979

Address: Dr. Sıtkı Özferendeci sok. Ilgazcan apt. No11/8 Üsküdar

E-Mail: nasemreomer@hotmail.com

Universities and Colleges attended: Istanbul Technical University and Food Engineer