EFFECT OF HYDROGENATION CONDITIONS ON RHEOLOGICAL AND MICRO-STRUCTURAL PROPERTIES OF FATS

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ALTUĞ BAŞKOÇAK

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
FOOD ENGINEERING

SEPTEMBER 2011

Approval of the thesis:

EFFECT OF HYDROGENATION CONDITIONS ON RHEOLOGICAL AND MICRO-STRUCTURAL PROPERTIES OF FATS

submitted by **ALTUĞ BAŞKOÇAK** in partial fulfillment of the requirements for the degree of **Master of Science in Food Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen _____________________
Dean, Graduate School of **Natural and Applied Sciences**

Prof. Dr. Alev Bayındırlı _____________________
Head of Department, **Food Engineering**

Assoc. Prof. Dr. Behiç Mert _____________________
Supervisor, **Food Engineering Dept., METU**

Examining Comitee Members:

Prof. Dr. Hami Alpas _____________________
Food Engineering Dept., METU

Assoc. Prof. Dr. Behiç Mert _____________________
Food Engineering Dept., METU

Prof. Dr. Aziz Tekin _____________________
Food Engineering Dept., Ankara University

Assist. Prof. Dr. İlkay Şensoy _____________________
Food Engineering Dept., METU

Assist. Prof. Dr. Aslı İşçi _____________________
Food Engineering Dept., Ankara University

Date: ______12.09.2011______

I hereby declare that, all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all materials and results that are not original to this work.

Name, Last Name : Altuğ Başkoçak

Signature :

ABSTRACT

EFFECT OF HYDROGENATION CONDITIONS ON RHEOLOGICAL AND MICRO-STRUCTURAL PROPERTIES OF FATS

BAŞKOÇAK, Altuğ
M.Sc., Department of Food Engineering
Supervisor : Assoc. Prof. Dr. Behiç MERT

September 2011, 87 pages

Hydrogenation is one of the most applied techniques in the fats and oils industry to produce wide range of hardened fats with different physical and chemical properties. Each different combination of hydrogenation conditions serves products of different rheological and micro-structural properties. Therefore, the purpose of this study is to examine the effect of different industrially available catalysts on rheological and micro-structural properties of hydrogenated fats.

Three different catalysts were used at two different concentrations to hydrogenate soybean oil. Two nickel based (Nysosel 222 and SP 10) and one palladium based (Pd/Al_2O_3) catalyst were employed. Each oil sample was hydrogenated for 20, 40, 60, 80 and 100 minutes of time intervals, under 165 ºC temperature, 2 bar H_2 pressure and 500 rpm stirring rate. Resulting hardened fat samples were analysed in terms of rheological and microstructural properties.

The outcomes of rheological and micro-structural analyses had a strong resemblence with the fatty acid distributions, solid fat contents, slip melting points and iodine values of the samples. The most selective catalyst was SP10, with the products of the highest trans fatty acid concent and more solid-like; where the least selective one was Pd/A with lowest trans fatty acid content and least solid-like. Crystal number and properties, the behaviours of storage and loss moduli were in correlation with trans fatty acid content of the samples. Also the moduli had a considerable parallelity with solid fat contents.

Key words : hydrogenation, rheology, microstructure, heterogeneous catalysts, soybean oil, nickel, palladium

ÖZ

HİDROJENLEME ŞARTLARININ YAĞLARIN REOLOJİK VE MİKRO-YAPISAL ÖZELLİKLERİNE ETKİSİ

BAŞKOÇAK, Altuğ
Yüksek Lisans, Gıda Mühendisliği
Tez Yöneticisi : Doç. Dr. Behiç MERT

Eylül 2011, 87 sayfa

Hidrojenasyon, yağ endüstrisinde farklı donma noktasına sahip birçok katı yağın üretilmesinde en çok kullanılan tekniklerden biridir. Birbirinden farklı hidrojenasyon koşulları, farklı reolojik ve mikro-yapısal özelliklerdeki ürünlere yol açar. Bu nedenle bu çalışmanın amacı, farklı endüstriyel katalizörlerin, hidrojene yağların reolojik ve mikro-yapısal özelliklerinin incelenmesi olarak belirlenmiştir.

Çalışma boyunca, soya yağının hidrojenlemesinde iki farklı derişimdeki üç farklı katalizör kullanılmıştır. İki nikel bazlı (Nysosel 222 ve SP10) ve bir paladyum bazlı (Pd/A) katalizör uygulanmıştır. Yağ örnekleri 20, 40, 60,80 ve 100 dakikalık sürelerle, 165 °C sıcaklık, 2 bar H2 basıncı ve 500 rpm karıştırma hızında hidrojene edilmiştir. Hidrojene ürünler reolojik ve mikro-yapısal özellikleri bakımından incelenmiştir.

Örneklerin reolojik ve mikro-yapısal analiz bulguları; yağ asidi dağılımı, katı yağ yüzdesi, kayma noktası ve iyot değerleri ile güçlü bir benzerlik göstermiştir. Kullanılan katalizörlerin en seçicisi olduğu gözlenen SP10 en yüksek trans yağ içerikli ve en katı-benzeri ürünlere yol açarken; en az seçicilikte olan Pd/A katalizörünün en düşük trans yağ içerikli ve en az katı-benzeri ürünler verdiği saptanmıştır. Kristal sayısı ve özelliklerinin; elastik ve viskoz modülüs davranışlarının örneklerin trans yağ içerikleriyle ilişkili oldukları gözlenmiştir. Örneklerin modülüs değerlerinin, katı yağ yüzdeleriyle de paralellik gösterdiği tespit edilmiştir.

Anahtar sözcükler : hidrojenasyon, reoloji, mikroyapı, heterojen katalizörler, soya yağı, nikel, paladyum

In precious memory of my dear friend Dr. İbrahim Erşan

ACKNOWLEDGEMENTS

I would like to express my deepest thanks and gratitude to my supervisor Assoc. Prof. Dr. Behiç Mert for his priceless guidance, cooperation and support all through my thesis period. Words are incapable to express my appreciation towards him, making me feel his encouragement and motivation during the completion of this study. Beside everything I learned from Dr. Mert, he made me reconstitute my definition of ideal lecturer.

I am also very grateful to Prof. Dr. Aziz Tekin for his kind donation of the fat samples used in the experiments, without which this study most probably could not have been issued.

Finally, I wish to extend my sincere appreciation to my dearest parents Nezihe and Yalçın Başkoçak, for their never ending support, encouragement and patience.

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

CHAPTER 1

INTRODUCTION

1.1 Fats

Fats of different physical and composition properties, have a widespread area of usage and are essential for human nutrition. The most important component of fats are fatty acids; the type, amount and distributions of which determine the nutritive and physical properties of products. Generally, saturated fatty acids give the fats and fat-containing products a solid character and cis-unsaturated fatty acids are in a liquid character; both of which should be intaken by definite amounts for a healthy nutrition.

1.1.1 Modification of Fats

Vegetable oils are not generally consumed raw. They are put on market rather in liquid after refining; or in solid after modification. (Narine & Humphrey, 2004) One of the most applied modification techniques, hydrogenation, is performed in order to cover the solid fat demands of consumers. It has complete, partial and selective methods of applications. In complete hydrogenation, all of the double bonds are saturated with hydrogen; where in the other techniques the reaction is carried out either selectively or partially to obtain a desired iodine number. Throughout the reaction, unsaturated fatty acids can undergo saturation, can pass to trans form and/or the double bond displacement can occur within the molecule. (A. P. B. Ribeiro et al., 2009) In the end, the final product can contain trans and local isomers of different types and amounts. These isomers not only affect the physical properties of the fat, they could also cause adverse health effects. Thus, for a healtier fat consumption, it became very important to determine and control the trans formation with respect to the reaction conditions. (Sowmya, Jeyarani, Jyotsna, & Indrani, 2009)

Despite hydrogenation forming a product of a high trans content is relatively low in cost; medical researchs show that trans fatty acids are not essential like cis isomers, moreover they cause coronary hearth diseases as well. Because of that, it is pretty crucial to monitor the conditions which give the desired selectivity and low isomer content throughout the process. (Cizmeci, 2007; Fernández, Piqueras, Tonetto, Crapiste, & Damiani, 2005)

1.1.2 Health Effects

Hydrogenation technology is found in order to satisfy the demand of fats giving the foods desired taste and texture characteristics by early 1900's, and still being used traditionally in food industry. (Cepeda & Calvo, 2008) The most important factor of hydrogenation getting so widespread applied, is that hydrogenated fats are relatively low in cost and can be produced with different physical properties by partial hydrogenation. However in 1980's the evidences showing that trans fatty acids cause coronary hearth diseases, made the relationship between hydrogenated fats, trans fatty acids and human health to be seriously reexamined. (Liu, Stephen Inbaraj, & Chen, 2007) Metabolic researches proove that trans fatty acids increase the LDL level while they are decreasing the HDL level in blood; besides this adverse effect is twice of the effect of saturated fats. Considering that 1/3 of the deaths are caused by coronary hearth diseases, the importance of trans fatty acids on nutrition could be understood beter. For this reason, experts advise that the intake of trans fatty acids should be decreased. Consequently, FDA obliged the trans content of a food product to be shown on the package by 01.01.2006.

The presence of a higher trans fatty acid content in the product leads to obtain desirable solid levels, owing to the higher melting point of the trans form, in comparison to the cis form. According to the researches; trans fatty acids not only raise LDL cholesterol level, but also lower HDL cholesterol level in blood which shows that they are more harmful than saturated fatty acids. Other studies showed that trans fatty acids increase the lipoprotein level as well. These two factors result in an increased risk of coronary heart diseases.(Mensink & Katan, 1990; A. P. B. Ribeiro, Grimaldi, Gioielli, & Gonçalves, 2009) The researches also claimed that saturated fatty acids raise the blood cholesterol levels, whereas mono- and poly-unsaturated fatty acids lower them. This is why a majority of consumers have changed their diet, prefering vegetable oils instead of animal fats. For this reason, hydrogenation of the vegetable oils to give them the desired physical characteristics has become widespread. (Enig, Pallansch, Sampugna, & Keeney, 1983; Ghotra, Dyal, & Narine, 2002; Karabulut, Kayahan, & Yaprak, 2003)

1.1.3 Trans Formation

The most important source of trans fatty acids are hydrogenation and modification of the process conditions is one of the primary methods to lower the trans content. Modification of the hydrogenation reaction in order to obtain fats containing lower trans content and desired iodine value, is performed by trying the combinations of different reaction conditions and catalysts. (Fernández, Sánchez M., Tonetto, & Damiani, 2009) However fats of lower trans contents have been obtained by the studies performed, the methods chosen are not commercially applicable. On the other hand, even in case different temperature, hydrogen pressure and stirring rate are used; production of fats having different fatty acid isomer distributions and melting properties could be possible. Therefore, the determination of the effects of different catalysts and reaction conditions on trans fatty acid production capacity and physical properties of the products, gain priority.

1.1.4 Rheology of Fats

Throughout the cooling, the rheology of the fats converts to a weak viscoelastic liquid from a weak viscoelastic solid system as they are being crystallized. (Rao, 2007) Which means that initially few large crystals were dominating their rheology, but after the shear applied liquid slip planes between solid crystals predominate the fluid behavior. (Zárubová, Filip, Kšandová, Šmidrkal, & Piska, 2010) Rate of this change is fastest for the one with a highest trans content, intermediate for the low trans blend and slowest for the commercial shortening. (Campos, Narine, & Marangoni, 2002; Pérez-Martínez, Alvarez-Salas, Charó-Alonso, Dibildox-Alvarado, & Toro-Vazquez, 2007) Change of the fluid behavior depends primarily on the fat composition (rate of crystallization, size and the number of spherulites formed). (Bell, Gordon, Jirasubkunakorn, & Smith, 2007; Fellows, 2000)

1.2 Soy Oil Production

In this study soybean oil is used in hydrogenation. Soybean oil is produced mostly by extraction, rather than by means of hydraulic presses which has a lower yield and higher cost. The production flowchart is basically like follows :

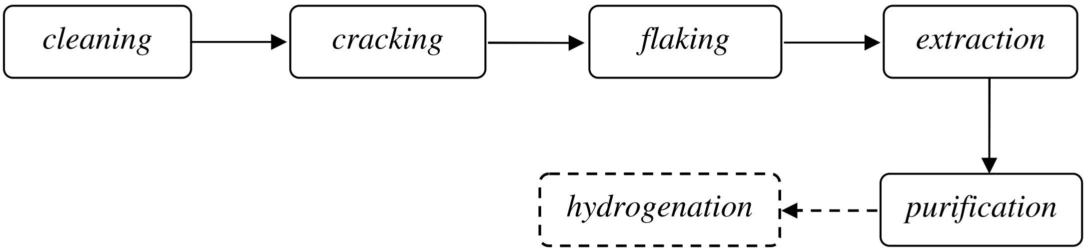

Figure 1.1 Soybean oil production flowchart.

Before hydrogenation, the fatty acid distribution of the produced soybean oil is as in Table 1.1.

Table 1.1 Fatty acid distribution of soybean oil. (Cizmeci, Musavi, Tekin, & Kayahan, 2006)

Fatty Acid	**% Contribution**
$C_{18:2}$ (linoleic acid)	49.0 - 51.5
$C_{18:1}$ (oleic acid)	23.5 - 30.8
C_{16} (palmitic acid)	2.3 - 10.6
$C_{18:3}$ (α-linolenic acid)	2.0 - 10.5
C_{18} (stearic acid)	2.4 - 6.0
C_{20} (arachidic acid)	<0.5
C_{14} (myristic acid)	<0.4
$C_{16:1}$ (palmitoleic acid)	<0.2
C_{12} (lauric acid)	<0.2

1.3 Hydrogenation

One of the most applied fat modification techniques, hydrogenation, alters the physical and chemical properties of an oil to a great extent. (Li, Zhang, Lee, & Zhong, 2009) Chemically, the basis of the process involves catalytic addition reactions in which the double bonds of the unsaturated fatty acids are saturated by hydrogen, giving a product of a desired iodine number. (Liu et al., 2007) Especially the edible modified fats are hardly considered healthy; because the remaining unsaturated portions of the partially hydrogenated fat, generally exist in trans form. However, by means of the novel methods which result to zero trans fat products, it is getting possible to benefit hydrogenation without causing any harm. (Pernetti, van Malssen, Flöter, & Bot, 2007)

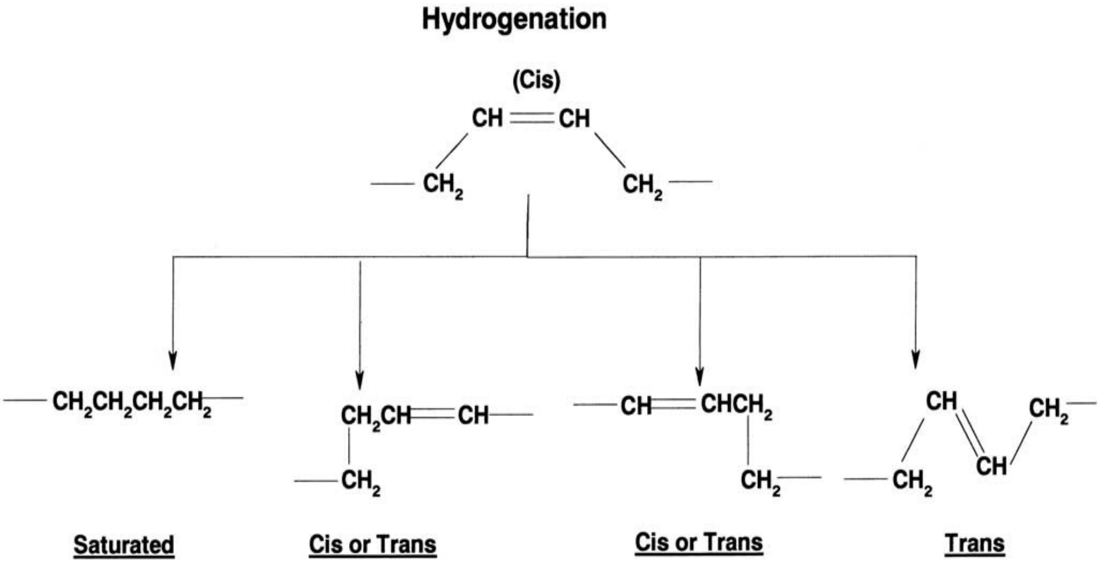

Figure 1.2 Four possible courses of a hydrogenation reaction (Ghotra et al., 2002)

In catalytic hydrogenation of fats, π-bonds of fatty acids are saturated with hydrogen, in the presence of a catalyst surface. The mechanism of this reductive catalytic hydrogenation reaction causes the relative unsaturation of oils to reduce and causes geometric and positional isomerization. Trans isomers have higher melting points and greater stability compared to cis isomers. Thus their formation alters the physical and chemical properties of the final products. (Cizmeci, Musavi, Kayahan, & Tekin, 2005)

Hydrogenation reduces the number of double bonds while a vast proportion or the remaining double bonds are isomerized through cis/trans conversion or positionally shifted in the fatty acid chain. This process improves the consistency, increases the melting point and resistance to oxidation. (Fernández et al., 2009; Karabulut & Kayahan, 1999; Karabulut et al., 2003)

1.3.1 History of Hydrogenation

In 1869, a French chemist Mege Mouries produced the first margarine alike butter substitute from beef tallow and skimmed milk. Mouries' work was then followed, modified and patented by several inventors. In 1873, Roudebush developed another substitute for lard, in the USA. He used tallow and skimmed milk softened by cottonseed oil as well. In 1903, a liquid phase hydrogenation process was patented by Norman. (Fernández et al., 2009; Ghotra et al., 2002)

Commercial hydrogenation of oils constantly increased by 1960's as modified vegetable oils took the part of animal fats in the diets of many countries. The initial motivation towards hydrogenation was because of its low cost; and later margarine was claimed to be more beneficial than butter for health. (Erickson, 1995) It was also providing the same texture characteristics and an extended shelf life to the products. Consumption continued rising in the 1980's until the public accepted its connection with heart disease. After 1980's, hydrogenated fats are losing their credit in the consumer choice, because of the trans content. (Cizmeci et al., 2005)

1.3.2 Aim of Hydrogenation

The main aim of hydrogenating the unsaturated fatty acids of a vegetable oil is to alter its stability, to increase its shelf life and to give it desirable melting properties. (Mondal & Lalvani, 2008) Hydrogenated fats don't provide a preferable medium for microorganisms, as a result they don't get spoiled as easily as natural unsaturated oils. Their relatively higher melting points and good textural properties make them popular in frying and pastries. (M. Izadifar & Jahromi, 2007)

A baked product without shortening has a hard and tough sense upon chewing. This feel arises because of the adhering of gluten and starch particles. When shortening is present, the fat breaks the continuity and doesn't allow the protein and starch structure to remain. So that the gluten particles get lubricated and more spongy and tender bakery products are produced. (Ghotra et al., 2002) Products with shortenings are altered as well in;

- tenderness and texture,
- mouth feel,
- structural integrity,
- lubrication,

- incorporation of air,
- heat transfer and
- shelf life. (Ghotra et al., 2002; Jacob & Leelavathi, 2007)

1.3.3 Types of Hydrogenation

The process is performed either complete, partial or selective. Among these application techniques, complete hydrogenation, involves the saturation of all the double bonds of the fat to be modified. In the other two techniques, hydrogenation is performed partially of selectively, in order to obtain a product having a definite iodine number. (Fernández, Tonetto, Crapiste, & Damiani, 2007) Complete hydrogenation of some oils, give products which have melting points above the body temperature.

Table 1.2 Melting points and digestion ratios of some naturally hydrogenated lipids. (Kayahan, 2002)

Oil type	Melting point (°C)	Digestion ratio (%)
Cottonseed oil	-	98
Olive oil	0 - 9	98
Palmseed oil	25 - 29	98
Sheep fat	27 - 42	88
Pork fat	26 - 39	97
Hydrogenated cottonseed oil	35	97
Hydrogenated cottonseed oil	50	92
Hydrogenated cottonseed oil	52	79

This refers to the partial digestion after their intake. So in order the oils to have a suitable melting point for the body physiology, they need to be hydrogenated by maintaining or slightly changing some particular characteristics of them. At this point, hydrogenation is applied up to a particular iodine number. (Ojijo et al., 2004) The approach of nutrition physiology today, is to partially saturate the polyunsaturated fatty acids up to monounsaturated structure. (Jovanović, Čupić, Stanković, Rožić, & Marković, 2000) On the other hand, by means of changing the process parameters, complete saturation of mono unsaturated fatty acids are monitored and forbidden to increase a significant amount. (Kayahan, 2002)

1.3.4 Factors Affecting Hydrogenation

Hydrogenation of fats involves several physical formations, and consequent and concurrent reactions. Different process parameters are effective on these reactions and determine their courses. Hydrogenation conditions involve temperature, hydrogen pressure, stirring rate, catalyst type and concentration. (Erickson, 1995)

Table 1.3 Influence of process conditions during hydrogenation (Ghotra et al., 2002)

	Parameter affected	
Increase in	**Degree of selectivity**	**Trans isomer formation**
H_2 pressure	Decreases	Decreases
Temperature	Increases	Increases
Stirring rate	Decreases	Decreases

In edible fat industry, supported nickel catalysts are generally used. In such cases, temperature is held between 140-200ºC and hydrogen pressure is held between 1-3 bar. (Cepeda & Calvo, 2008) By changing process parameters, fatty acid profiles, slip melting points, and solid fat contents change as well. For the final product to possess the desired properties, all of these factors should be carefully chosen.(Wright, Mihele, & Diosady, 2003)

Selectivity is also a crucial term for a hydrogenation reaction. It refers to the ratio of reaction rates of the individual steps throughout the reaction. The saturation process of a polyenic fatty acid can be decribed as follows (Kayahan, 2002) :

$$\text{Triene} \xrightarrow{k_3} \text{Diene} \xrightarrow{k_2} \text{Monoene} \xrightarrow{k_1} \text{Saturated fatty acid}$$

Referring to the definition, the selectivities of the steps can be expressed as :

$$S_{32} = k_3/k_2 \qquad S_{21} = k_2/k_1 \qquad S_{31} = k_3/k_1$$

Altering the fatty acid distribution of the final product to a great extent, selectivity, also has a great role in its melting profile. High temperature and catalyst concentration favor greater selectivity with large amounts of trans fatty acid formation. (Fernández, Tonetto, Crapiste, Ferreira, & Damiani, 2005)

Table 1.4 Conditions affecting selectivity of hydrogenation (Ghotra et al., 2002)

Reaction parameter	Selective hydrogenation	Non-selective hydrogenation
Temperature	High	Low
H_2 pressure	Low	High
Stirring rate	Low	High
Catalyst concentration	High	Low
Trans isomer formation	More	Less

In general less selective conditions are selected for hydrogenation. These less selective conditions refer to lower temperatures and higher H_2 pressures which make the product a more gentle SFC profile, compared to one produced by more selective conditions. (Ghotra et al., 2002)

1.3.5 Hydrogenation Mechanism

The saturation reaction of π-bonds also include the formation of geometric and positional isomers of fatty acids. (M. Izadifar, 2005) The reaction proceeds according to Horiuti-Polanyi mechanism. According to this mechanism, diatomic hydrogen molecules are dissociated on the catalyst surface and saturation occurs within an unstable half-hydrogenated intermediate complex. After it is formed, either desaturation and/or isomerization occurs or the saturation goes towards completion. (A. Musavi, Cizmeci, Tekin, & Kayahan, 2008; Santana, Larrayoz, Ramírez, Nistal, & Recasens, 2007)

Half-hydrogenated complex is formed by the following steps:

- Hydrogen molecules are adsorbed on the metal surface of the catalyst and become highly active hydrogen radicals,
- Double bonds of the fatty acids interact with d-orbitals of the metals,
- Hydrogen binds to one of the carbon atoms of the double bond to form the half-hydrogenated complex. (A. Musavi, 2006)

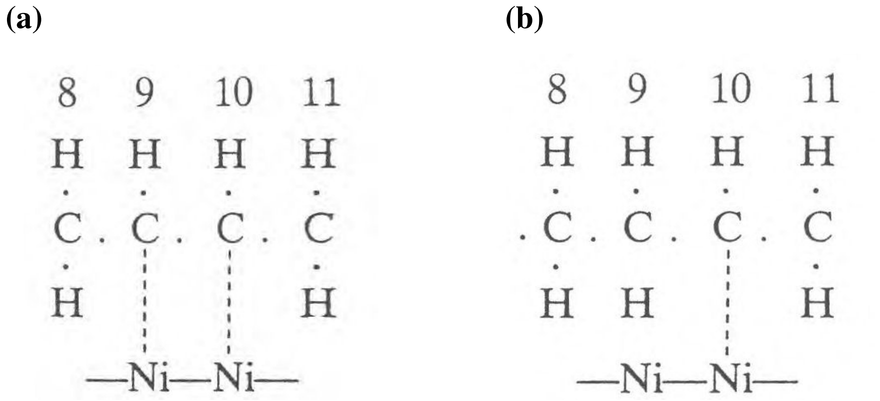

Figure 1.3 a) Adsorbtion of the fatty acid on the nickel surface. b) Formation of the half-hydrogenated complex. (Cizmeci, 2007)

After the formation of half-hydrogenated complex, reaction may either proceed to completion or dehydrogenation, depending on the amount of hydrogen on the catalyst surface. (Santana et al., 2007)

In order to define the physical and chemical principles of hydrogenation reactions, it should be taken into account that these reactions proceed in a triple phase system of solid, liquid and gas. Considering, that mechanical mass transport steps and chemical reaction steps are the determining factors of the mechanism of hydrogenation reactions, rate differences between these steps should be well known. (Kayahan, 2002)

In order the saturation reactions to proceed, both the hydrogen dissolved in oil, and the unsaturated compounds in the reaction medium to be tranferred to the catalyst surface, also the products after saturation to be given back to the liquid phase; are crucial for a continuous reaction. These steps take place according to diffusion laws. (Kayahan, 2002)

According to the reaction mechanism, isomerization reactions differ in rate. The rate depends on the temperature of the medium, hydrogen pressure, stirring rate, catalyst type and its concentration, reaction time, type of the oil and also the agitator design of reactor. Among these parameters, catalyst type and its concentration are the most important ones when choosing the hydrogenation conditions. (Cizmeci et al., 2005) Simultaneous detection of the products of catalytic hydrogenation reactions are not possible today. They are rather monitored indirectly, by kinetic measurements of their conformations and compositions. (Kayahan, 2002; Santana, Fernández, Larrayoz, & Recasens, 2008) The reaction progress can be monitored simultaneously by determining the reaction rate, isomer formation rate, selectivity, solid fat content, and melting point, throughout the reaction. (Cizmeci et al., 2005)

1.4 Catalysts

Except a few number of reactions, no reaction between elemental hydrogen and organic compounds occurs under 480 °C, without any catalysis. The reaction between them is only possible in the presence of a catalyst surface which allows the adsorbtion of both and enables their contact. (Hudlicky, 1996)

In hydrogenation reactions; both the overall reaction rate and the courses of parallel and consequent side reactions, primarily vary upon the type, structure and concentration of the catalyst used. Referring to the widespread opinion, the properties of the catalyst play the main role in the course of the hydrogenation reactions. On the other hand, despite the knowledge on the variable effects of the surface activity between lipid and catalyst is unsufficient so far; the gathered information from the studies with homogeneous catalysts, show that this unsufficiency will be eliminated in the near future. (Kayahan, 2002)

Table 1.5 Effect of catalyst concentration on high pressure hydrogenation (Temperature 70°C, pressure 750 psi, %5 Pd/Al_2O_3) (Hsu, Diosady, & Rubin, 1989)

Catalyst Concentration	**Iodine Number**	**Total Trans (%)**	**S_{32}**	**S_{21}**	**kx1000 (min^{-1})**
5 ppm	107,6	6,1	1,3	1,1	1,79
25 ppm	72,5	14,2	1,6	1,7	10,50
50 ppm	70,5	14,6	1,4	1,7	22,00
100 ppm	72,2	14,1	1,2	1,6	60,70

Table 1.6 Effect of different hydrogen pressure and catalyst concentration combinations on reaction rate, iodine number and trans acid formation (A. Musavi, 2006)

Hydrogen Pressure	**Catalyst Concentration (%)**	**Reaction Rate**	**Iodine number**	**Total Trans (%)**
5 psi	0,1	0,17	67,6	50,5
5 psi	0,55	0,28	57,2	51,2

Table 1.6 (continued)

5 psi	1	0,91	67,7	57,9
27,5 psi	0,1	0,61	78,6	43,0
27,5 psi	0,55	0,79	67,2	54,7
27,5 psi	1	0,97	78,3	43,3
50 psi	0,1	0,89	67,8	48,6
50 psi	0,55	1,06	59,6	50,8

1.4.1 Catalysis Mechanism

Obtainability and consumability of the hydrogen gas are two crucial factors affecting the course of hydrogenation. (Larsson, 1983; A. Musavi, 2006) Besides, for the continuity of the reaction, mass transfer in the reaction medium becomes more of an issue. Researchs show that this transfer occurs completely depending on diffusion laws; and stepwise :

- Hydrogen gas of a definite purity, temperature and pressure, is enriched on the oil surface in until the dissolving conditions are fulfilled,
- Dissolved hydrogen passes through the thin oil layer which is less mobile,
- Dissolved hydrogen passes through the oil layer surrounding the catalyst surface,
- Hydrogen molecule reaches the catalyst pore,
- Inside the pore, molecule approaches the catalyst surface,
- Adsorbtion occurs on the catalyst surface. (Cizmeci, 2007)

In order the triglyceride molecule forming the liquid phase to react, it has to reach the catalyst surface inside the pores as well.

After the reaction, the constituents bound to the catalyst surface should,

- get desorbed from the catalyst surface to the medium,
- reach back to the pore exit,
- get back to the medium by passing through the oil film surrounding the catalyst particle. (A. Musavi, 2006)

Binding of a fatty acid to the metal occurs via two-point adsorption during hydrogenation. For the two-point adsorption to take place, the ideal interatomic distance is 2.73 Å which is satisfacted by the interatomic distance of the catalytic active metals. (Cizmeci, 2007)

1.4.2 Types of Catalysts

Catalysis of edible oil hydrogenation is either performed by homogeneous or heterogeneous catalysts.

Heterogeneous catalysts are widely used in oil industry and they have a great importance on the process mechanism, by constituting a different physical phase in the system. (Fernández et al., 2005) Type of the catalyst is the primary factor on the consumability of hydrogen; because both the reactants and the products should be transferred through the layer covering the catalyst surface. The mass transfer rate throughout this layer depends on the surface area and the number of active sites on the surface. (Cizmeci, 2007)

Heterogeneous catalysts are also referred as solid supported contact catalysts, and they contain mostly the VIB, VIIB, VIIIB group elements of the periodic table. These elements constitute the active site of the catalyst, either by their metallic form or by their compounds with the VIA group elements. Also they are commonly used as homogeneously imbued onto a proper inorganic support material. (Kayahan, 2002)

Coordinate covalent compounds of transition metal hydrides which contain tertiary phosphine ligands, are used in homogeneous catalysis. They tend to form π-complexes with the unsaturated organic compounds and provide their hydrogenation. Studies show that, homogeneous catalysis barely differ from heterogeneous catalysis in terms of the reaction steps and isomers formed. (Kayahan, 2002)

1.4.3 Catalyst Metals

Edible oil hydrogenation technique has barely changed since it was first performed. However homogeneous catalysts are also being used, heterogeneous catalysis of hydrogenation is more commonly performed. (Wright, Wong, & Diosady, 2003) This trend can be explained by the higher activity, ease of filterability, reusability of heterogeneous catalysts. Metals that can be used as catalysts are divided into four groups based on the electron configurations of their valence orbitals:

1) Molybdenum and Wolfram;
2) Titanium, Ruthenium, Rhodium, Rhenium, Osmium and Iridium;
3) Iron, Cobalt, Nickel, Copper, Palladium, Silver and Platinum;
4) Zinc, Gallium, Germanium, Cadmium, Indium, Tin and Lead.

Metals of the third group posess free d-orbitals to accept electron pairs of the double bond of the unsaturated fat; thus the third group can be considered the most convenient group of metal catalysts. (Cizmeci, 2007; Gray & Russell, 1979)

Table 1.7 Electron configurations of some metals used in hydrogenation

Co:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^7$
Ni:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$
Cu:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^9$
Fe:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^6\ 4s^2$
Pd:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^8$
Ag:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5s^1$
Pt:	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^8$

Considering its low cost, ease of filtration, proper selectivity and high activity, Nickel, is mostly preferred in industry. (Gabrovska, Krstić, Edreva-Kardjieva, Stanković, & Jovanović, 2006; Wright, Wong et al., 2003) Besides metallic nickel, it can be used in subsulfide form or with the sulfides of wolfram or molybdenum for special purposes. Also metallic copper and copper-nickel powder are used for special purposes. As support materials, heat stable oxide compounds such as kieselguhr, SiO_2 or Al_2O_3 are being used. (Kayahan, 2002)

Piqueras showed that the selectivities to the trans, monounsaturated and saturated fatty acids are sensitive to the catalyst metal particle diameter. Larger metal particles favor the unsaturated and trans fatty acid formation, where small particles favor the saturated and low trans content. Researchers explain this by the adsorbtion strenght of the high-unsaturated fatty acids, which is determined by the particle size. Small particles favor direct hydrogenation from linoleic acid to saturated products. (Piqueras, Bottini, & Damiani, 2006)

1.4.4 Catalytic Activity

In view of the researches, depending on the activity of saturating the double bonds, metals can be ordered : Pd>Rh>Pt>>Ir>Ru>Os; where a great difference of activity is observed between the first and the second three metals. On the other hand, when the order is selectivity based : Pd>Rh>Pt>Ru>Ir; and when it is trans-formation based : Pd>Rh>Ru>Ir>Pt are obtained. (Rylander, 1970; Zajcew, 1960)

Table 1.8 Effects of different Pd catalysts with different hydrogenation temperatures (Cizmeci, 2007; Riesz & Weber, 1964)

Catalyst Type	Temperature (ºC)	Reaction Rate (mmol/min)	Total Trans (%)
5% Pd/C	35	0.36	5.7
5% Pd/C	100	0.97	13.8
5% Pd/$BaSO_4$	35	0.50	6.4
5% Pd/$BaSO_4$	100	1.46	6.2
1% Pd/SiO_2	80	0.055	4.0
1% Pd/SiO_2	100	0.55	7.8
0.5% Pd/Al_2O_3	35	0.27	5.4

Table 1.8 (continued)

0.5% Pd/Al_2O_3	100	1.20	11.4
0.2% Pd/C	35	0.11	3.8
0.2% Pd/C	80	0.48	8.6
0.2% Pd/C	150	1.54	15.4

A heterogeneous catalyst is formed of an active-metal-containing complex fixed on a support material and shows a porous structure. Catalyst quality is dependent on particle size, pore number and size; besides the type of the active metal and the support material used. Increasing pore number, pore size and surface area cause an increase in catalyst activity and rate of hydrogenation.

1.4.5 Support Materials

Surface structure of the catalyst is highly important for a higher catalyst activity. Holding all other factors constant; a catalyst with a support material having a higher number of smaller particles and more porous structure, has a higher activity. Moreover, support material decreases the risk of aggregation on the surface and poisoning of the catalyst. (Gabrovska et al., 2006)

In the edible oil industry, nickel catalysts were being supported by diatomaceous earth until 1980's. Beside its cost efficiency, diatomaceous earth shows a high performance. On the other hand, containing many various metals, it causes fluctuations on the product quality. Researchs show that catalysts in which SiO_2-Al_2O_3 blend is used as a support material, have higher activities compared to the ones with diatomaceous earth. (Cizmeci, 2007)

Table 1.9 Effect of supported Ni catalysts on hydrogen consumption rate with different temperatures (Cizmeci, 2007; Riesz & Weber, 1964)

Catalyst Type	**Temperature (ºC)**	**Hydrogen Consumption Rate (mmol/min)**
25% Ni / 10% Kieselguhr	150	0.59
14% Ni / SiO_2-Al_2O_3	150	1.59
59% Ni / Kieselguhr	80	0.26
14% Ni / SiO_2-Al_2O_3	80	0.50

1.5 Objective of The Study

This study aims to analyse and compare the effects of different industrially available catalysts on rheological and microstructural properties of hydrogenated fats. To serve this purpose, Two nickel based (Nysosel 222 and SP 10) and one palladium based (Pd/Al_2O_3) catalyst were used at three different concentrations to hydrogenate soybean oil. The oil samples were hydrogenated for 20, 40, 60, 80 and 100 minutes and resulting hardened fat samples were analyzed in terms of rheological and microstructural properties.

CHAPTER 2

MATERIALS AND METHODS

2.1 Materials

Neutral soy oil containing 46.44% linoleic, 30.70% oleic, 10.20% palmitic, 8.46% linolenic and 3.77% stearic acid was obtained from MARSA. The catalysts; 10% Pd/Al_2O_3 was purchased from Aldrich (Germany), Nysosel 222 (22% Ni/SiO_2) and SP10 -the nickel of which is in subsulfide (Ni_3S_2) form- (21% Ni/Al_2O_3) was purchased from Engelhard (NJ, USA). Supelco 37, blend of fatty acid methyl esters (methly ester of cis-vaccenic acid and methyl ester mix of linoleic acid isomers), was obtained from Supelco (Bellefonte, PA, USA). Methyl esters of vaccenic and cis-12-octadecanoic acid, blend of conjugated linoleic acid methyl esters and methyl esters of cis-trans isomer mix of linolenic acid was purchased from Sigma-Aldrich (St. Louis, MO, USA). Sunflower oil was obtained from Yudum Gıda.

2.2 Sample Preparation

After the preliminary tests performed; optimum hydrogenation conditions enabling a better detection of the differences between catalysts, were determined as 165±0.5 ºC temperature, 2±0.03 bar Hydrogen pressure and 500±3 rpm stirring rate. Hydrogenation of the soy oil in the presence of different catalysts, was performed in a 4-L, 316SS stainless steel, Snap-Tite reactor which was purchased from Autoclave Engineers (PA, USA). This reactor enables the control of temperature, pressure and stirring rate throughout the process.

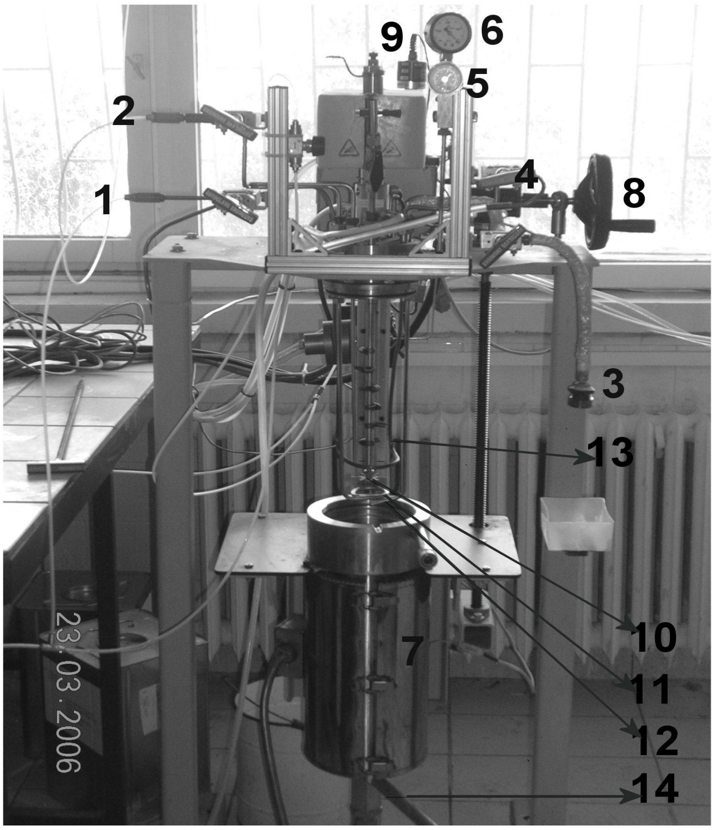

Figure 2.1 Hydrogenation reactor (Cizmeci, 2007)

1) Gas inlet, 2) Gas outlet, 3) Filtration device, 4) Vacuum valve, 5)Manometer, 6) Vacuum gauge, 7) Coat heater, 8) Lid stoper turncock, 9) Pressure transducer, 10) Stirrer, 11) Gas nozzles, 12) Sampling pipe, 13) Cooling loop, 14) Oil discharge pipe

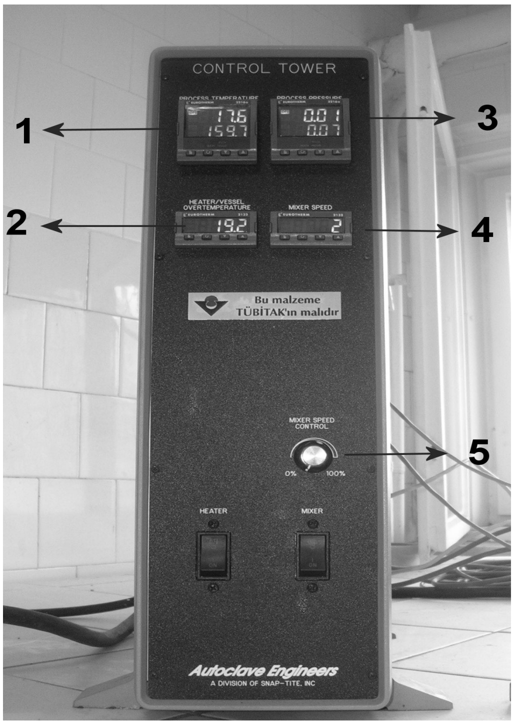

Figure 2.2 Control unit (Cizmeci, 2007)
1) Coat heater adjuster/monitor, 2) Internal temperature monitor, 3) Pressure adjuster/monitor, 4) Stirring rate monitor, 5) Stirrer control button

Reactor containing 2300 g soy oil and a corresponding amount of catalyst (Table 2.1) were dried under nitrogen, in order to prevent the oxidation possibility. This oil/catalyst blend was then heated while stirring and nitrogen was passing through. After the whole mix inside the reactor was reached to 165ºC, nitrogen gas was replaced with hydrogen. At this point, reaction was assumed to be initiated. Samples were taken by 10 minutes of intervals through the filtration system which was appended to the reactor outlet, retreated with nitrogen and stored at -10ºC until being analysed. The samples used in this study, are only the ones hydrogenated for 20, 40, 60, 80 and 100 minutes.

Table 2.1 Catalyst types and their concentrations applied in the hydrogenation

Catalyst Type	Applied concentration (ppm)
Nysosel 222	200, 300
SP 10	1000, 2000
Pd/Al_2O_3	25, 50

2.3 Rheological Measurements

Isothermal time sweep and dynamic frequency sweep tests were performed by AR2000ex model rheometer (TA Instruments, USA). All measurements were carried out at 10 ºC, with 20 mm paralel plate geometry, at a gap distance of 2 mm.

After the conditioning of each oil sample at 80 ºC for 5 minutes, isothermal time sweep tests were done at 10 ºC, under a constant strain of 0.05 % and an angular frequency of 6.283 rad/s; to determine the behaviors of storage and loss moduli over time.

Time sweep tests were followed by dynamic frequency sweep tests, to obtain the behaviors of storage and loss moduli over the angular frequency range of 6.283 to 62.83 rad/s. Time sweep tests were also performed by applying a constant strain of 0.05 % and 10 ºC.

2.4 Optical Microscopy

5 µL of each specimen was diluted by 5 µL sunflover oil and stored for 2 days at 20 ºC. The crystals formed are then photographed under 4x magnification, using a Leica DM3000 model optical microscope and a Leica DFC320 model PC connected camera (Leica Microsystems, Germany).

Samples prepared by the same manner, were used to record the crystal formation upon cooling as well. Each sample were initially subjected to 70 ºC for 5 minutes to fully remove the crystals; then cooled with a rate of 2 °C/min up to 10 °C. Crystal formations were observed and recorded under 4x magnification, beginning from the time at which crystallization starts. From the crystallization movies, snapshots were captured by 30 second of intervals by ImageGrab 5.0.6En software. Number of crystallized particles were then counted by Image-Pro Plus 6.0 and plotted on graph.

2.5 Analysis of Fatty Acids and Isomers

Determination of fatty acids and isomers were performed according to IUPAC method 2.301. Samples are esterified prior to the fatty acid analysis, then 1 µL from each sample is injected to the Thermo Quest gas chromatography. Fatty acid composition results are given in terms of percent methyl esters. (Cizmeci, 2007)

Gas Chromatography : Thermo Quest 2000
Detector : FID
Column : Supelco SP2560 Fused Silica Capillary Column
100 m x 0.25 nm x 0.20 µm film thickness
Carrier Gas : He (0.7 mL/min)
Split Ratio : 1:100
Temperatures
  Injection Block : 230 °C
  Column : 175 °C
  Detector : 240 °C

2.6 Solid Fat Content Analysis

Solid fat contents of the fats were determined according to AOCS official method Cd-16b-93. In the analyses, Maran SFC (Resonance Instrument Ltd., Witney, UK) model NMR device was used at 0, 10, 21.1, 33.3 and 40.6 °C, with a constant frequency of 20 MHz. (Cizmeci, 2007)

2.7 Slip Melting Point Analysis

Slip melting points of the fats were determined according to AOCS official method Cc 3-25. (Cizmeci, 2007)

2.8 Iodine Number Analysis

Iodine numbers of the fats were determined according to AOCS official method Cd 1c-85. (Cizmeci, 2007)

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Composition of soy oil

Fatty acid distribution and the iodine number of neutral soy oil used in the hydrogenation is given in Table 3.1 Fatty acid composition and iodine number of the soy oil used in the hydrogenation

Table 3.1 Fatty acid composition and iodine number of the soy oil used in the hydrogenation

Fatty acid	Composition (%)
14:0	0.07
16:0	10.20
16:1	0.08
18:0	3.77
18:1 trans	0.00
18:1 cis	30.70
18:1 total	30.70
18:2 trans	0.00
18:2 cis	46.40
18:2 total	46.40
Conjugated linoleic	0.00
18:3 trans	0.00
18:3 cis	8.46
18:3 total	8.46
20:0	0.32
Total saturated	14.36
Total unsaturated	85.64
Iodine number	130.1

As can be seen in Table 3.1; neutral soy oil to be hydrogenated has the iodine number of 130.1 and is composed of 14.36% saturated and 85.64% unsaturated fatty acids. The material without any conjugated linoleic acid and trans content, contains 10.20% palmitic acid, 3.77% stearic acid, 0.32% arachidic acid and 0.07% myristic acid as saturated; 46.4% linoleic acid, 30.7% oleic acid, 8.46% linolenic acid and 0.08% palmitoleic acid as unsaturated.

3.2 Hydrogenations with N222 catalyst

Hydrogenations with N222 catalyst are performed in the presence of 200 and 300 ppm active nickel in the oil to be processed.

3.2.1 Hydrogenation with 200 ppm active nickel

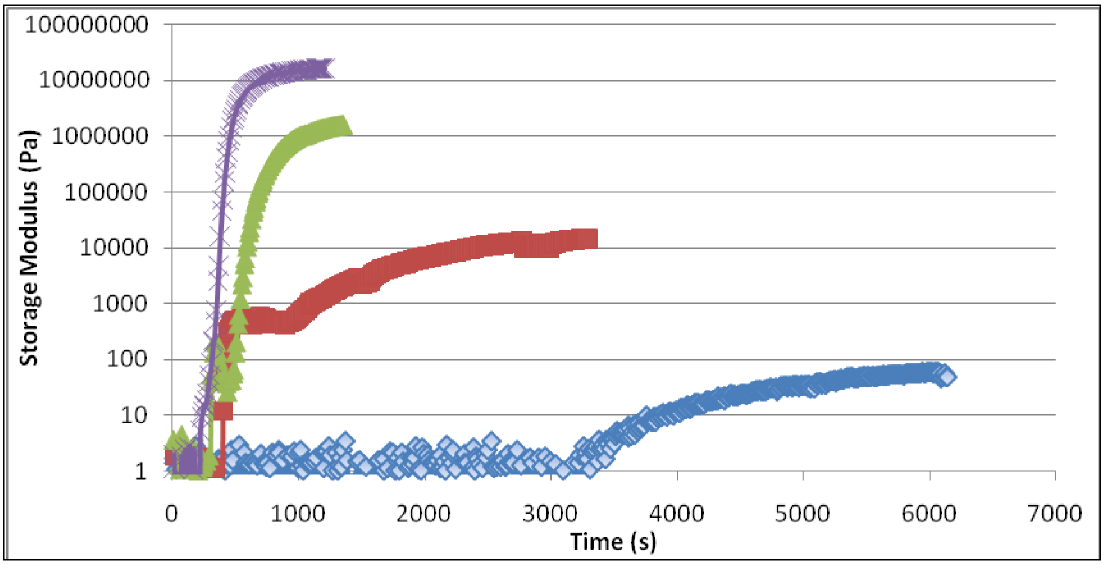

Figure 3.1 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 200 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.1 presents that the plateau values of the storage moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 47.36, 14620, 1620000 and 16520000 Pa respectively. Samples hydrogenated for 60, 80 and 100 minutes show a narrow plastic range and the one for 40 minutes shows a broad plastic range. Also the sample hydrogenated for 20 minutes didn’t have a regular and stable storage modulus behaviour.

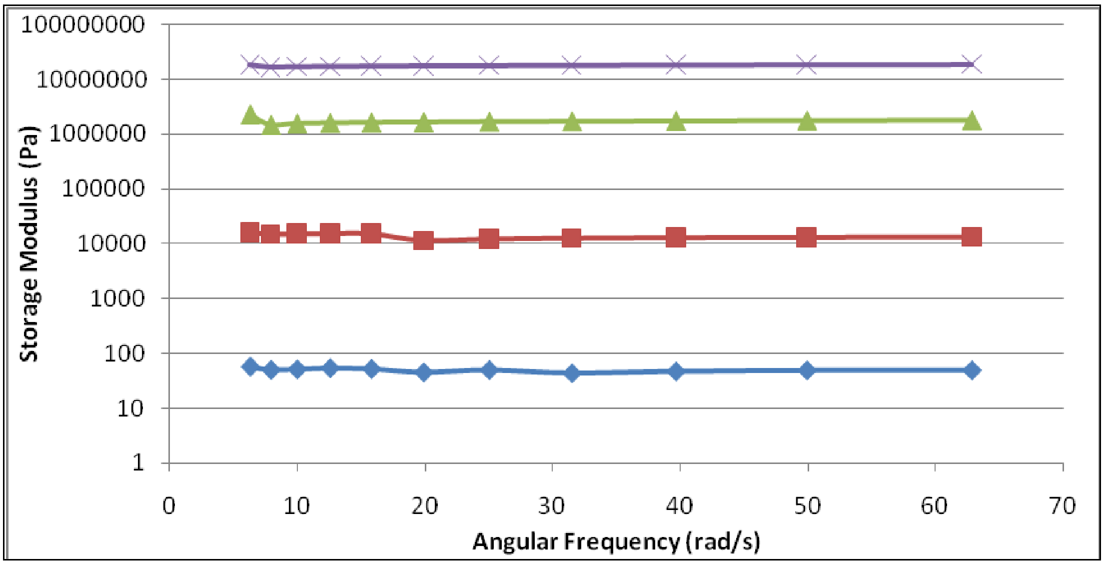

Figure 3.2 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.2 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 50.02, 13370, 1821000 and 18920000 Pa respectively. Also the sample hydrogenated for 20 minutes didn’t have a measurable storage modulus.

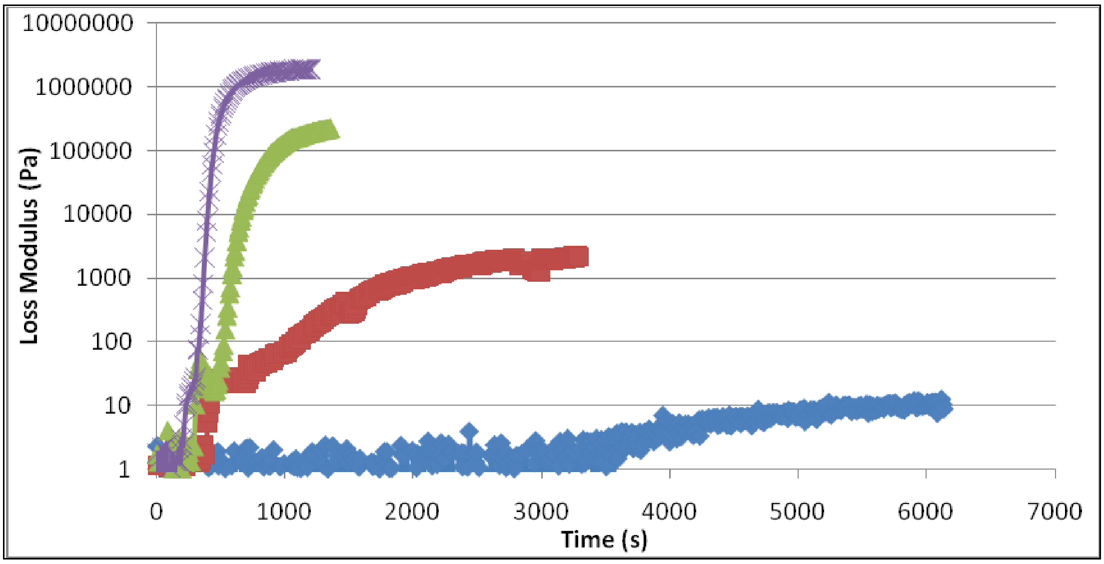

Figure 3.3 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.3 presents that the plateau values of the loss moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 8.803, 2158, 225400 and 1892000 Pa respectively. Samples hydrogenated for 80 and 100 minutes show a narrow plastic range and the ones for 40 and 60 minutes show a broad plastic range. Also the sample hydrogenated for 20 minutes didn’t have a regular and stable loss modulus behaviour.

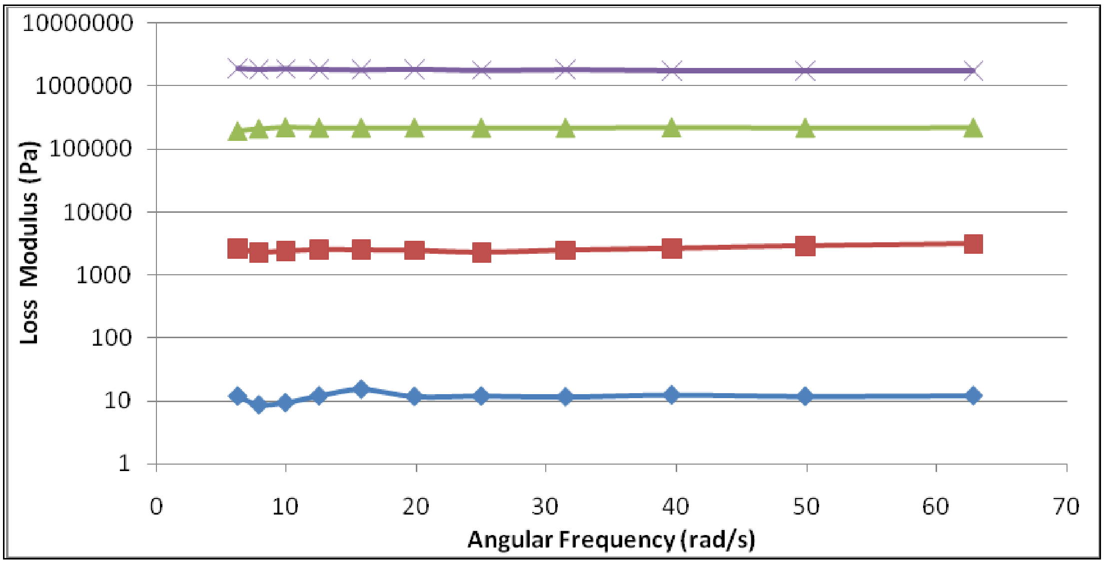

Figure 3.4 Frequency sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.4 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 12.11, 3115, 221300 and 1771000 Pa respectively. Also the sample hydrogenated for 20 minutes didn't have a measurable loss modulus.

Fatty acid contents and iodine value of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.2.

Table 3.2 Change in the fatty acid distributions of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration

Time (min)	**0**	**40**	**60**	**80**	**100**
Iodine number	130.1	114.4	99.6	83.4	70.6
18:0	3.77	4.88	5.94	8.93	13.59

Table 3.2 (continued)

18:1 trans	0.00	5.94	13.63	22.57	30.42
18:1 cis	30.70	36.69	41.35	43.19	39.97
18:2 trans	0.00	2.17	4.28	5.09	3.77
18:2 cis	46.40	34.53	21.43	8.63	1.30
18:3 trans	0.00	0.35	0.42	0.21	0.00
18:3 cis	8.46	4.59	2.12	0.60	0.23
Total trans	0.00	8.59	18.43	27.93	34.19
Conjugated linoleic	0.00	0.13	0.10	0.06	0.00

As can be seen from Table 3.2, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Melting points of both acids are fair above the room temperature, thus their percents are strongly effective on the rheological behaviour of the sample. Stearic acid reaches to 13.59% and trans 18:1 acid increases up to 30.42% where total trans fatty acids are at 34.19% at 100. minute. Cis 18:1 and trans 18:2 acids are increased until 80. minute and decreased to 39.97% and 3.77% respectively at the end of the reaction. Cis 18:2 acids continuously decreased during the reaction down to 1.30%. Cis and trans forms of 18:3 acid are fairly decreased until 100. minute and cis form reaches to 0.23%, where trans form is completely eliminated. Moreover, conjugated 18:2 acids are also decreased to 0.00% and the iodine number decreased up to 70,6 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.3.

Table 3.3 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration

Time (min)	SMP (°C)	Solid fat content (%)				
		$N_{0°C}$	$N_{10°C}$	$N_{21.1\ °C}$	$N_{33.3\ °C}$	$N_{40.6\ °C}$
40	<15	5.3	3.0	0.5	0.0	0.0
60	21.6	22.8	13.9	4.7	0.0	0.0
80	27.6	47.2	35.0	15.9	1.9	0.0
100	37.6	69.0	60.5	36.0	9.8	2.4

Solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are plotted in Figure 3.5.

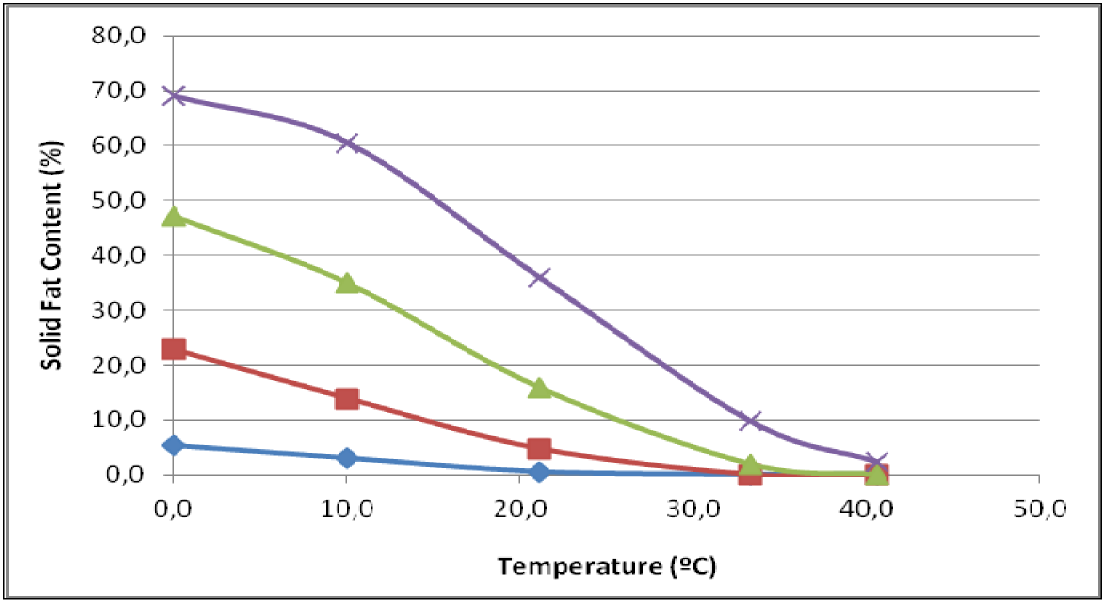

Figure 3.5 Change in solid fat contents of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Table 3.3 and Figure 3.5 show that, slip melting point of the sample exceeded 20 ºC after 60 minutes of hydrogenation and reached to 37,6 ºC at the end of 100. minute. Until 60. minute all the samples taken at 33.3 ºC are liquid; whereas at 100. minute, solid fat contents of the samples are 69.0% at 0 ºC, 60.5% at 10.0 ºC, 36.0% at 21.1 ºC, 9.8% at 33.3 ºC and 2.4% at 40.6 ºC.

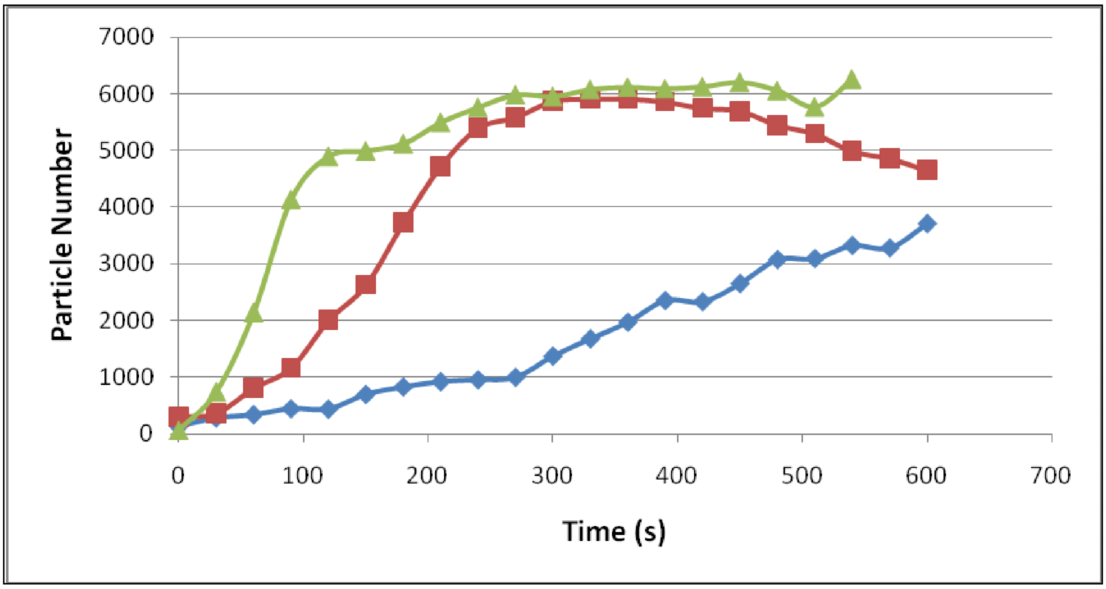

Figure 3.6 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 200 ppm active nickel concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3.6; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn’t show a significant crystal formation, which is also proven by the light microscope photos.

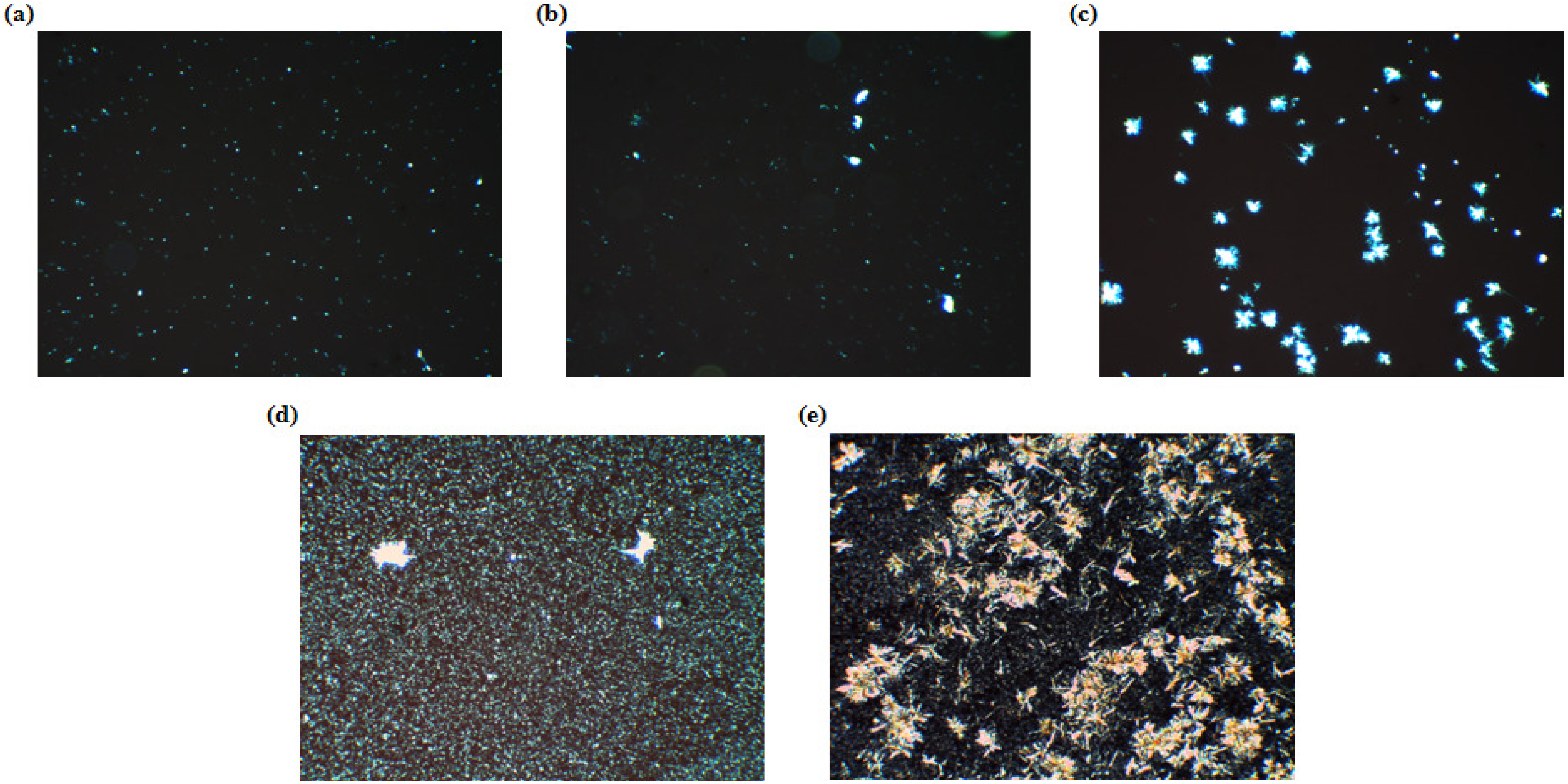

Figure 3.7 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 200 ppm active nickel concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times, stored at 20 ºC for 2 days.

The photos in the Figure 3.7 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 60, 80 and 100 minutes. The ones hydrogenated for 20 and 40 minutes didn't show a considerable crystal formation.

3.2.2 Hydrogenation with 300 ppm active nickel

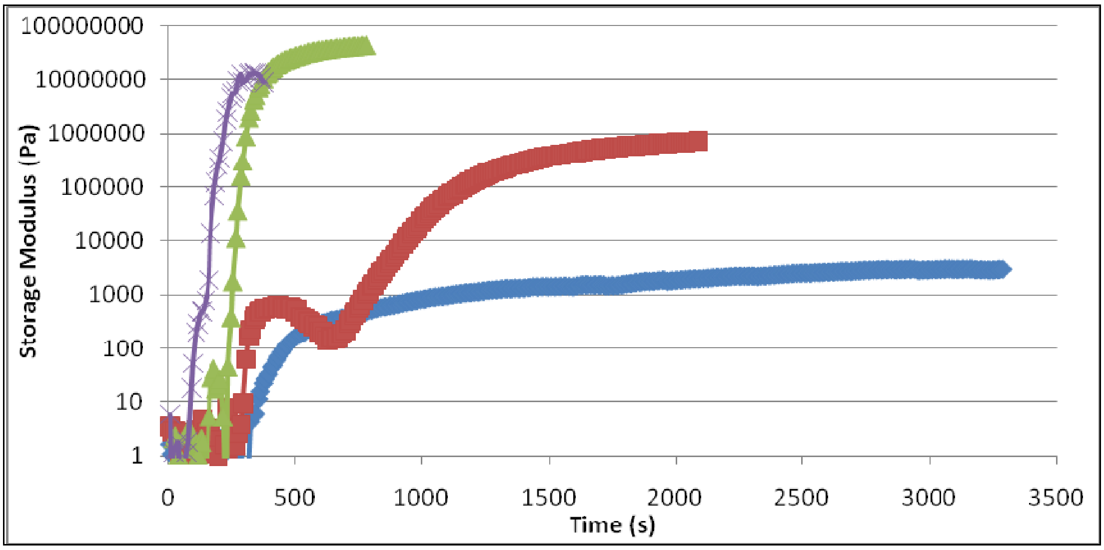

Figure 3.8 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.8 presents that the plateau values of the storage moduli for the samples hydrogenated for 40, 60 and 80 minutes are 3010, 719700 and 43880000 Pa respectively. Samples hydrogenated for 80 and 100 minutes show a narrow plastic range and the ones for 40 and 60 minutes show a broad plastic range. Also the sample hydrogenated for 20 minutes didn't have a regular and stable storage modulus behaviour, where the one for 100 minutes lost contact with the upper plate of the rheometer before reaching a plateau.

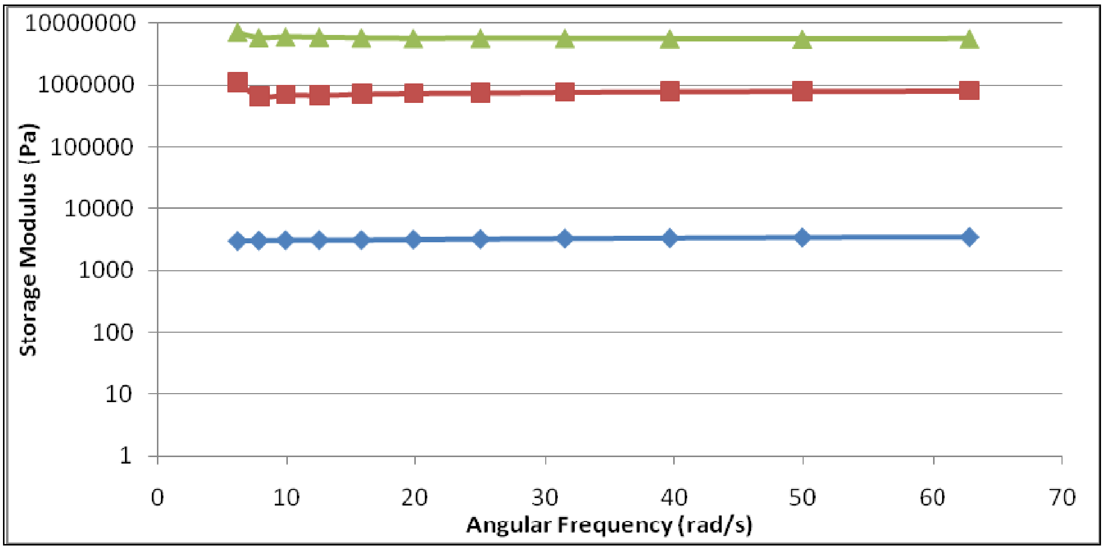

Figure 3.9 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■) and 80 minutes (▲) of hydrogenation times

Figure 3.9 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 40, 60 and 80 minutes are 3434, 821300 and 50390000 Pa respectively. Also the sample hydrogenated for 20 minutes didn’t have a measurable storage modulus, where the modulus of one for 100 minutes was out of the measurable range of the rheometer.

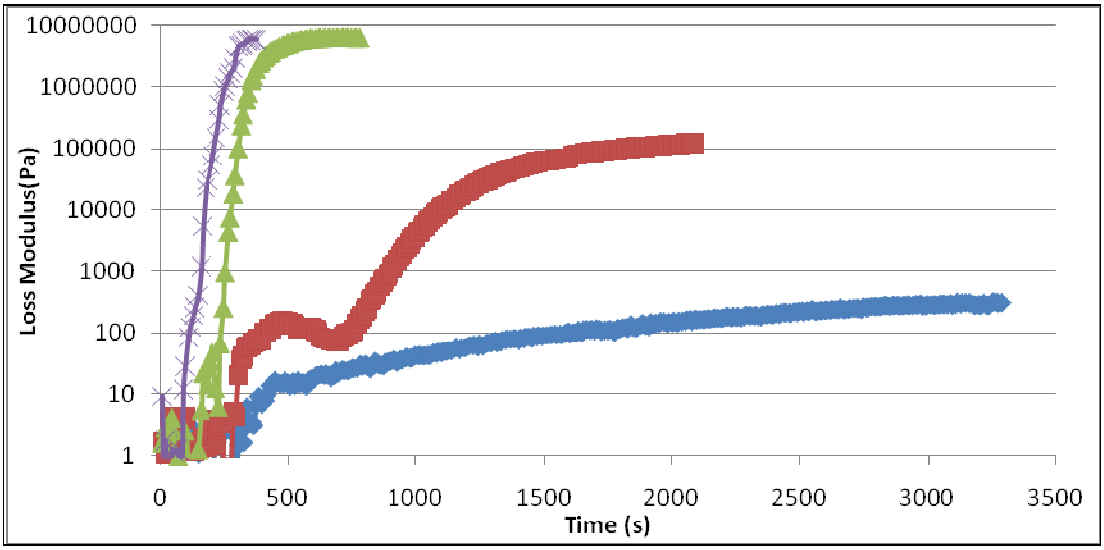

Figure 3.10 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.10 presents that the plateau values of the loss moduli for the samples hydrogenated for 40, 60 and 80 minutes are 309.3, 123200 and 6269000 Pa respectively. Samples hydrogenated for 80 and 100 minutes show a narrow plastic range and the ones for 40 and 60 minutes show a broad plastic range. Also the sample hydrogenated for 20 minutes didn’t have a regular and stable loss modulus behaviour, where the one for 100 minutes lost contact with the upper plate of the rheometer before reaching a plateau.

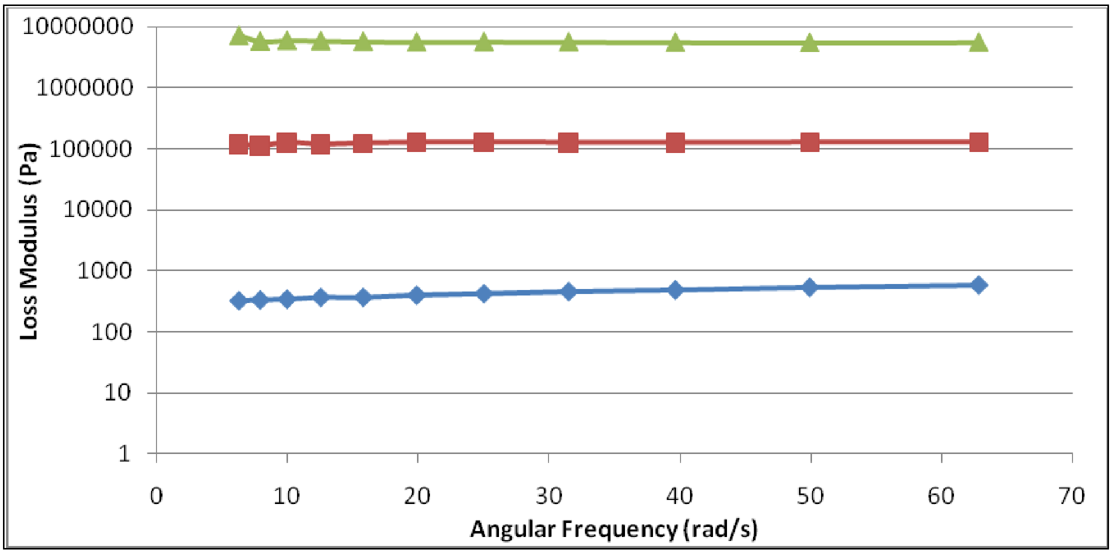

Figure 3.11 Frequency sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■) and 80 minutes (▲) of hydrogenation times

Figure 3.11 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 40, 60 and 80 minutes are 587.5, 128100 and 5592000 Pa respectively. Also the sample hydrogenated for 20 minutes didn’t have a measurable loss modulus, where the modulus of one for 100 minutes was out of the measurable range of the rheometer.

Fatty acid contents and iodine values of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.4.

Table 3.4 Change in the fatty acid distributions of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration

Time (min)	**0**	**40**	**60**	**80**	**100**
Iodine number	130.1	102.5	81.2	64.4	50.9
18:0	3.77	5.36	8.16	17.48	30.92
18:1 trans	0.00	11.42	24.05	35.95	43.05
18:1 cis	30.70	41.45	45.37	33.73	15.08
18:2 trans	0.00	3.96	4.21	1.79	0.23
18:2 cis	46.40	24.30	6.96	0.17	0.00
18:3 trans	0.00	0.37	0.00	0.00	0.00
18:3 cis	8.46	2.22	0.44	0.15	0.00
Total trans	0.00	15.94	28.34	37.74	43.28
Conjugated linoleic	0.00	0.19	0.08	0.00	0.00

As can be seen from Table 3.4, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Stearic acid reaches to 30.92% and trans 18:1 acid increases up to 43.05% where total trans fatty acids are at 43.28% at 100. minute. Cis 18:1 and cis 18:2 acids decreased until 100. minute down to 15.08% and 0.23% respectively. Trans 18:2 acids increased at the first 60 minutes and then decreased until 0.23 at 100. minute. Cis and trans forms of 18:3 acid fairly decreased and completely eliminated at 100. minute. Moreover, conjugated 18:2 acids also decreased to 0.00% already at 80. minute and the iodine number decreased up to 50.9 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.5.

Table 3.5 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration

Time (min)	SMP (ºC)	Solid fat content (%)				
		$N_{0°C}$	$N_{10°C}$	$N_{21.1\ °C}$	$N_{33.3\ °C}$	$N_{40.6\ °C}$
40	19.5	16.6	9.5	2.4	0.0	0.0
60	28.8	48.9	36.7	15.2	1.2	0.0
80	40.4	84.3	80.0	57.4	20.1	6.0
100	48.3	94.9	92.8	77.1	46.6	31.9

Solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are plotted in Figure 3.12.

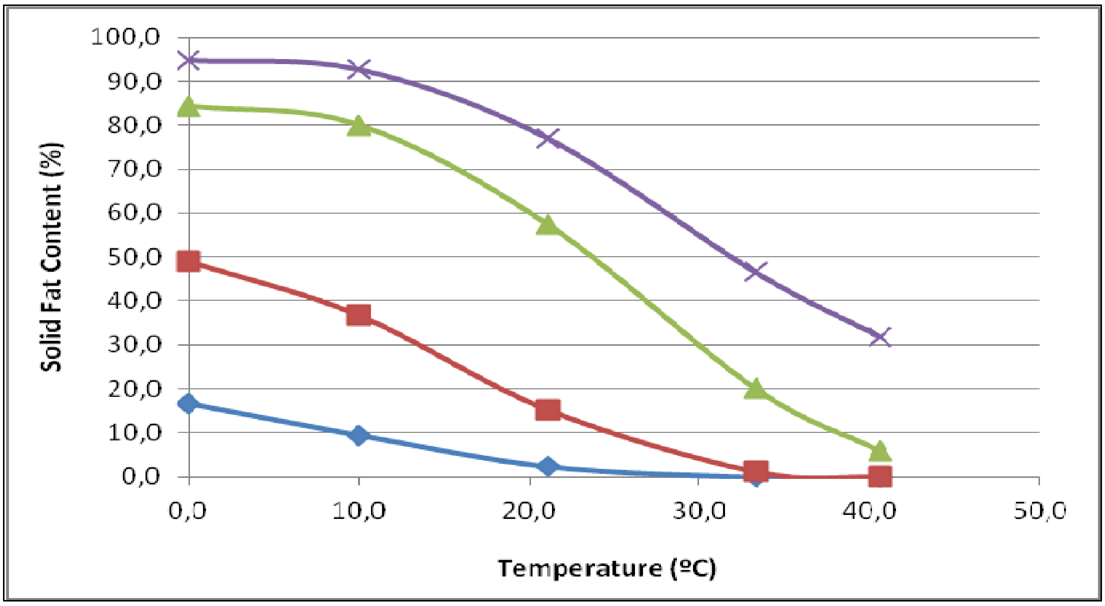

Figure 3.12 Change in solid fat contents of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Table 3.5 and Figure 3.12 show that, slip melting point of the sample exceeded 20 ºC after 60 minutes of hydrogenation and reached to 48.3 ºC at the end of 100. minute. Until 40. minute all the samples taken at 33.3 ºC are liquid; whereas at 100. minute, solid fat contents of the samples are 94.9% at 0 ºC, 92.8% at 10.0 ºC, 77.1% at 21.1 ºC, 46.6% at 33.3 ºC and 31.9% at 40.6 ºC.

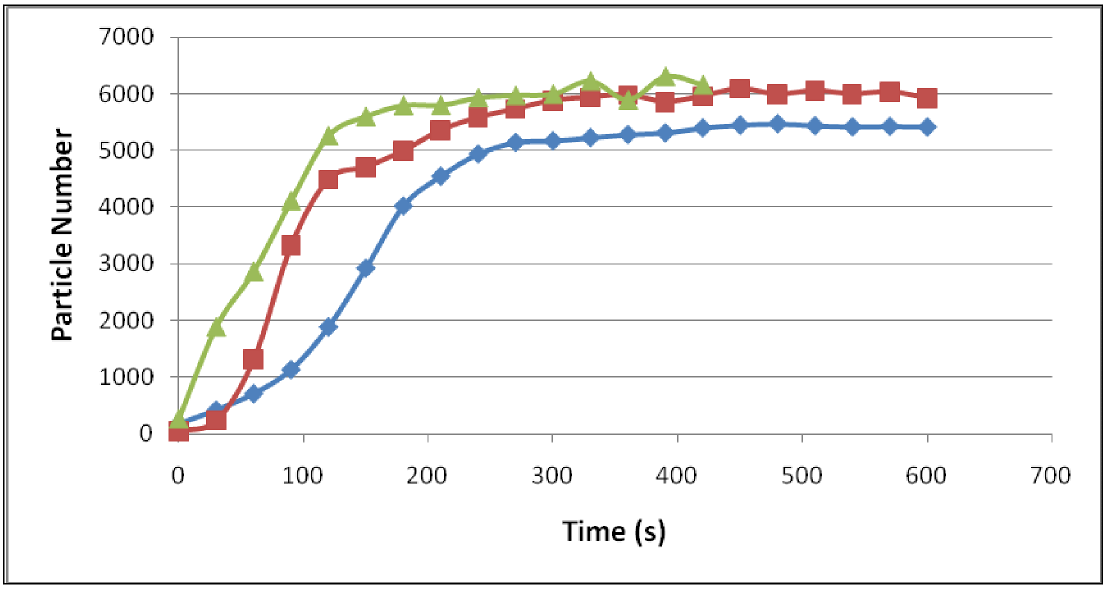

Figure 3.13 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 300 ppm active nickel concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3.13; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn't show a significant crystal formation, which is also proven by the light microscope photos.

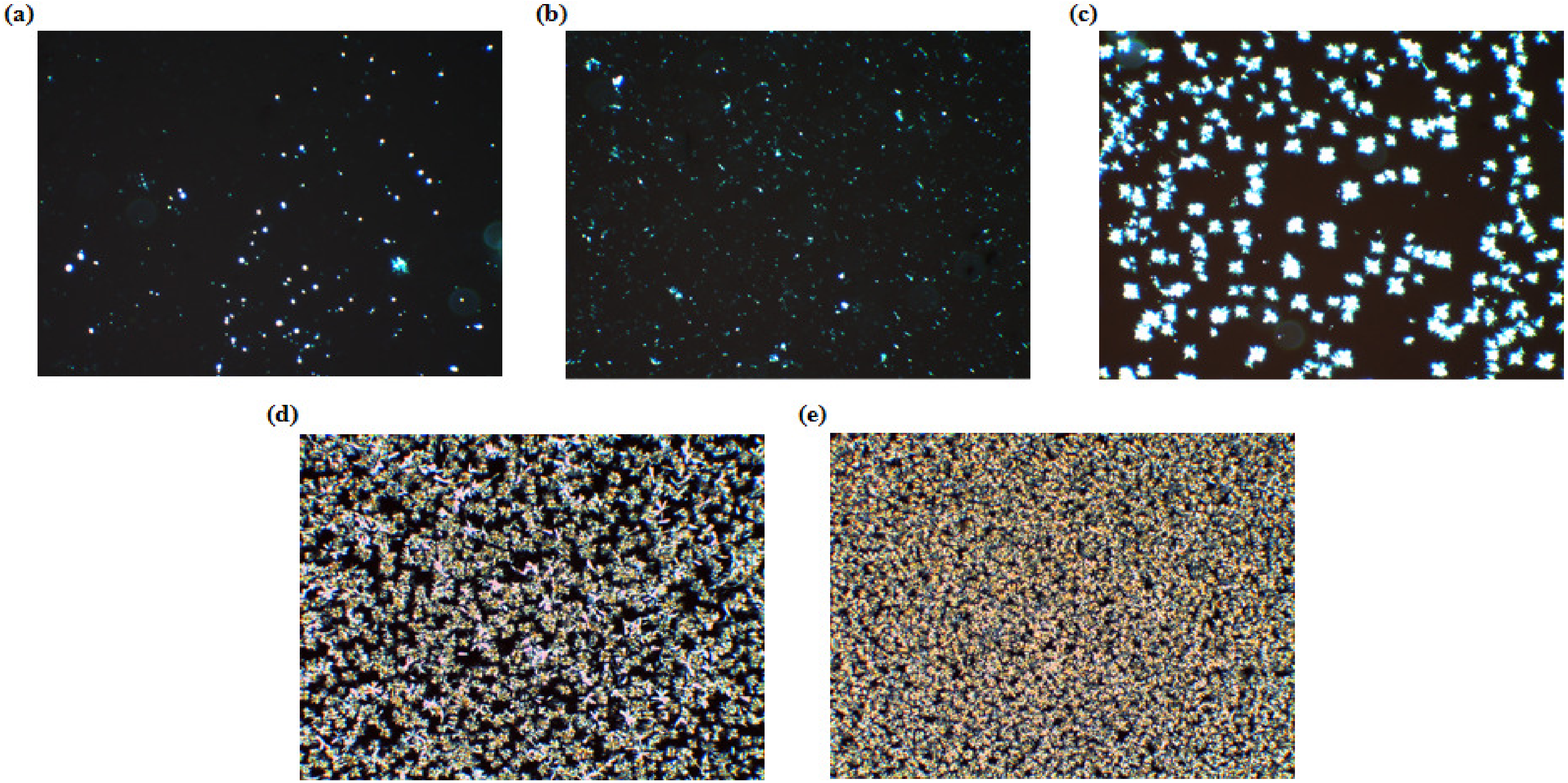

Figure 3.14 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 300 ppm active nickel concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times stored at 20 ºC for 2 days.

The photos in the Figure 3.14 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 60, 80 and 100 minutes. The ones hydrogenated for 20 and 40 minutes didn't show a considerable crystal formation.

3.3 Hydrogenations with SP10 catalyst

Hydrogenations with SP10 catalyst are performed in the presence of 1000 and 2000 ppm active nickel in the oil to be processed.

3.3.1 Hydrogenation with 1000 ppm active nickel

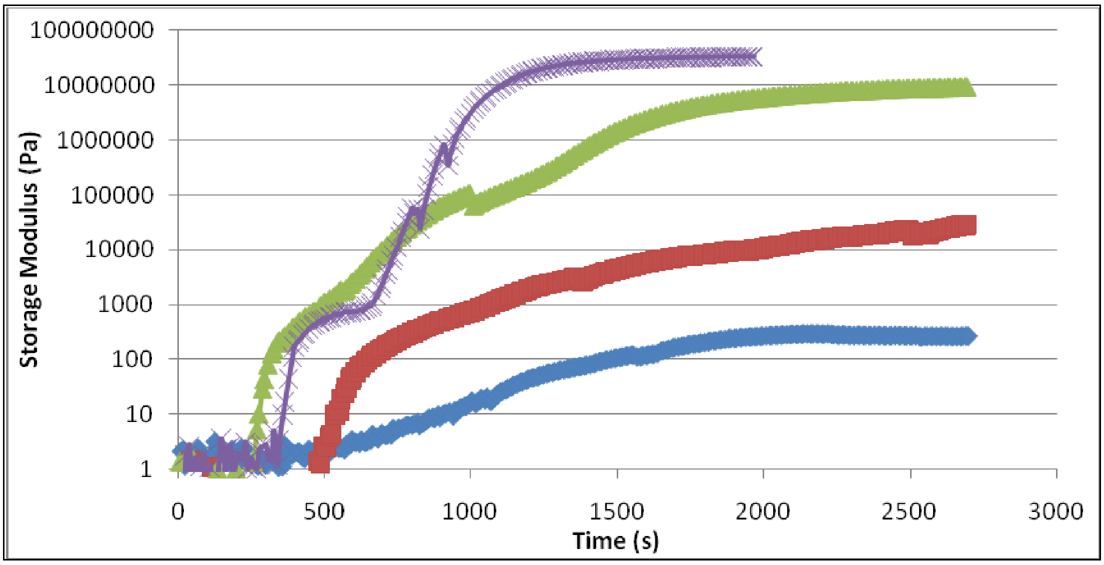

Figure 3.15 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.15 presents that the plateau values of the storage moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 63.4, 28540, 9592000 and

33190000 Pa respectively. All of the samples hydrogenated for 40, 60, 80 and 100 minutes show a broad plastic range. Also the sample hydrogenated for 20 minutes didn’t have a regular and stable storage modulus behaviour.

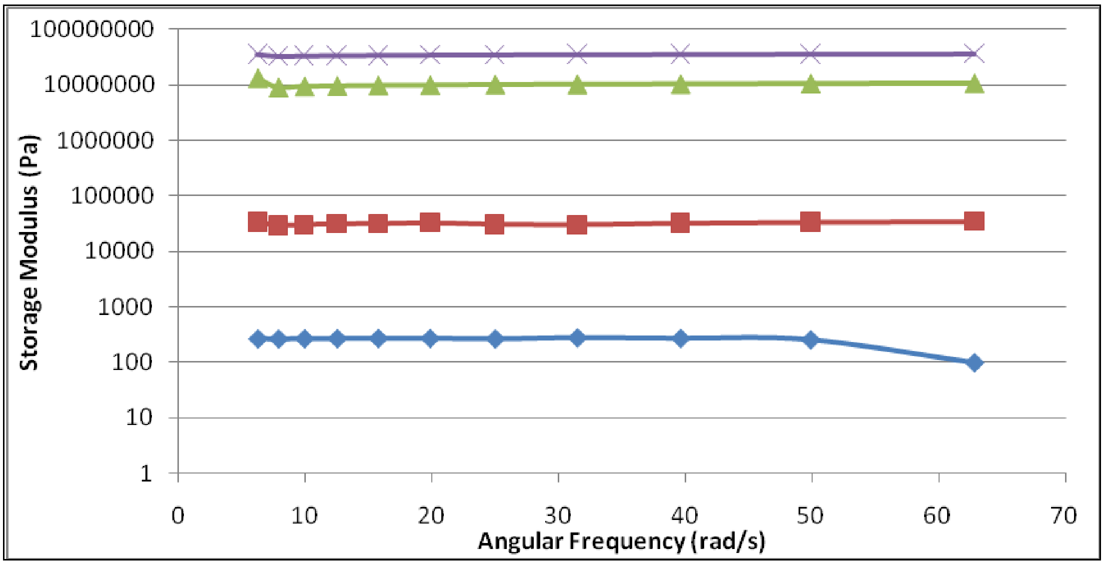

Figure 3.16 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.16 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 99.05, 35260, 10880000 and 37170000 Pa respectively. Also the sample hydrogenated for 20 minutes didn’t have a measurable storage modulus.

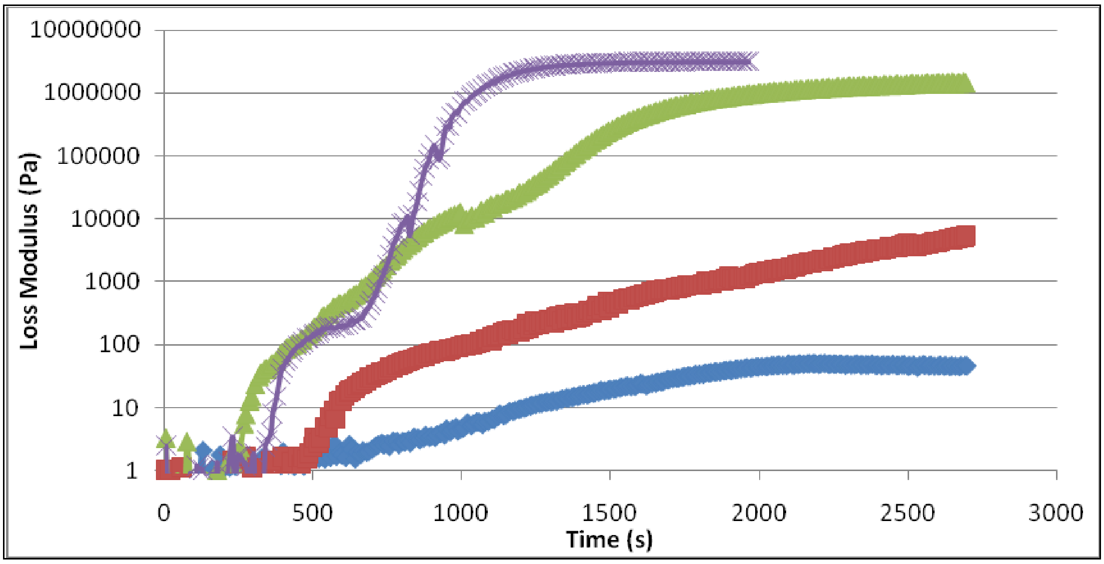

Figure 3.17 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.17 presents that the plateau values of the loss moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 46.72, 5348, 1429000 and 3185000 Pa respectively. All of the samples hydrogenated for 40, 60, 80 and 100 minutes show a broad plastic range. Also the sample hydrogenated for 20 minutes didn't have a regular and stable loss modulus behaviour.

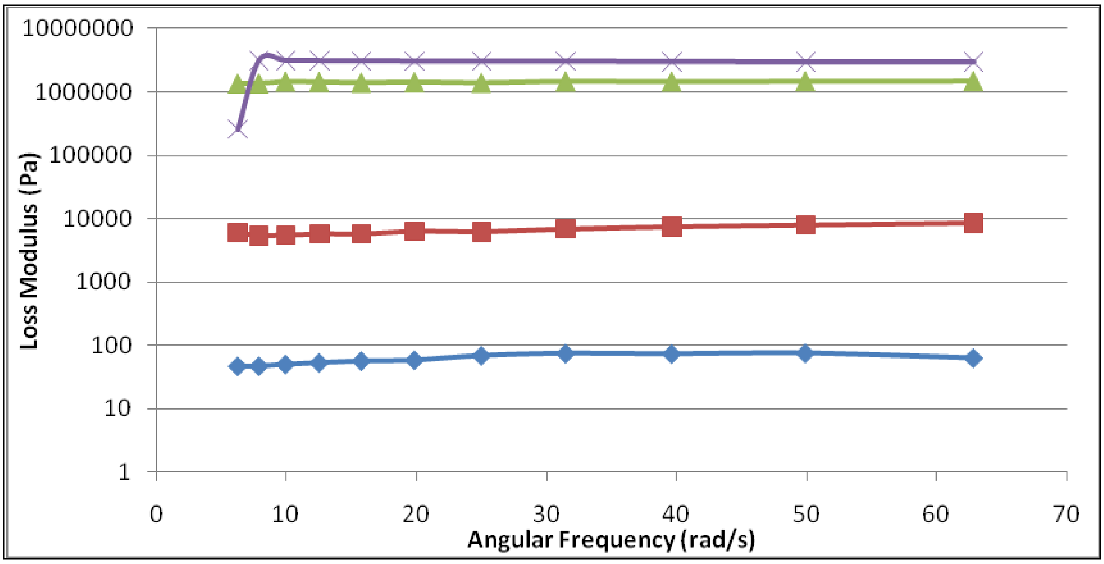

Figure 3.18 Frequency sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Figure 3.18 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 40, 60, 80 and 100 minutes are 62.75, 8580, 1469000 and 2966000 Pa respectively. Also the sample hydrogenated for 20 minutes didn't have a measurable loss modulus.

Fatty acid contents and iodine values of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.6.

Table 3.6 Change in the fatty acid distributions of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration

Time (min)	**0**	**40**	**60**	**80**	**100**
Iodine number	130.1	106.8	95.4	84.8	77.2
18:0	3.77	4.45	4.91	5.39	6.82

Table 3.6 (continued)

18:1 trans	0.00	15.20	28.56	42.68	52.48
18:1 cis	30.70	33.91	31.44	27.82	23.73
18:2 trans	0.00	21.00	19.99	12.98	6.27
18:2 cis	46.40	11.21	2.43	0.00	0.00
18:3 trans	0.00	1.36	0.55	0.13	0.00
18:3 cis	8.46	0.50	0.20	0.00	0.00
Total trans	0.00	39.24	50.31	56.07	58.75
Conjugated linoleic	0.00	1.68	1.21	0.28	0.00

As can be seen from Table 3.6, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Stearic acid reaches to 6.82% and trans 18:1 acid increases up to 52.48% where total trans fatty acids are at 58.75% at 100. minute. Cis 18:1 and trans 18:2 acids both decreased and are present 39.97% and 3.77% respectively at the end of the reaction. Cis 18:2 acids are already eliminated at 80. minute. Cis and trans forms of 18:3 acid and conjugated 18:2 acid as well are completely eliminated until the end of the reaction. The iodine number decreased up to 77.2 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are given in Table 3.7.

Table 3.7 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 40, 60, 80 and 100 minutes, under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration

Time (min)	**SMP (°C)**	**Solid fat content (%)**				
		$N_{0°C}$	**$N_{10°C}$**	**$N_{21.1\,°C}$**	**$N_{33.3\,°C}$**	**$N_{40.6\,°C}$**
40	<15	18.4	8.3	1.5	0.0	0.0
60	21.0	45.1	29.0	7.0	0.0	0.0
80	28.3	70.5	58.6	24.3	0.0	0.0
100	28.8	84.0	76.8	44.1	1.3	0.0

Solid fat contents of the samples hydrogenated for 40, 60, 80 and 100 minutes, are plotted in Figure 3.19.

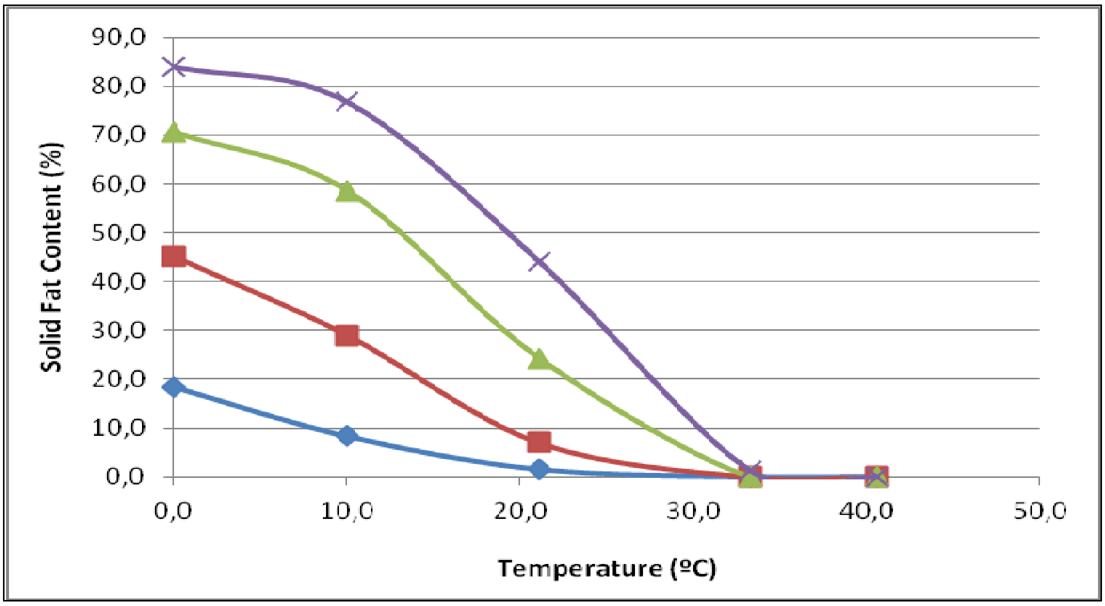

Figure 3.19 Change in solid fat contents of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 40 minutes (♦), 60 minutes (■), 80 minutes (▲) and 100 minutes (×) of hydrogenation times

Table 3.7 and Figure 3.19 show that, slip melting point of the sample exceeded 20 ºC after 60 minutes of hydrogenation and reached to 28.8 ºC at the end of 100. minute. All the samples taken throughout the reaction at 40.6 ºC are liquid; whereas at 100. minute, solid fat contents of the samples are 84.0% at 0 ºC, 76.8% at 10.0 ºC, 44.1% at 21.1 ºC, 1.3% at 33.3 ºC and 0.0% at 40.6 ºC.

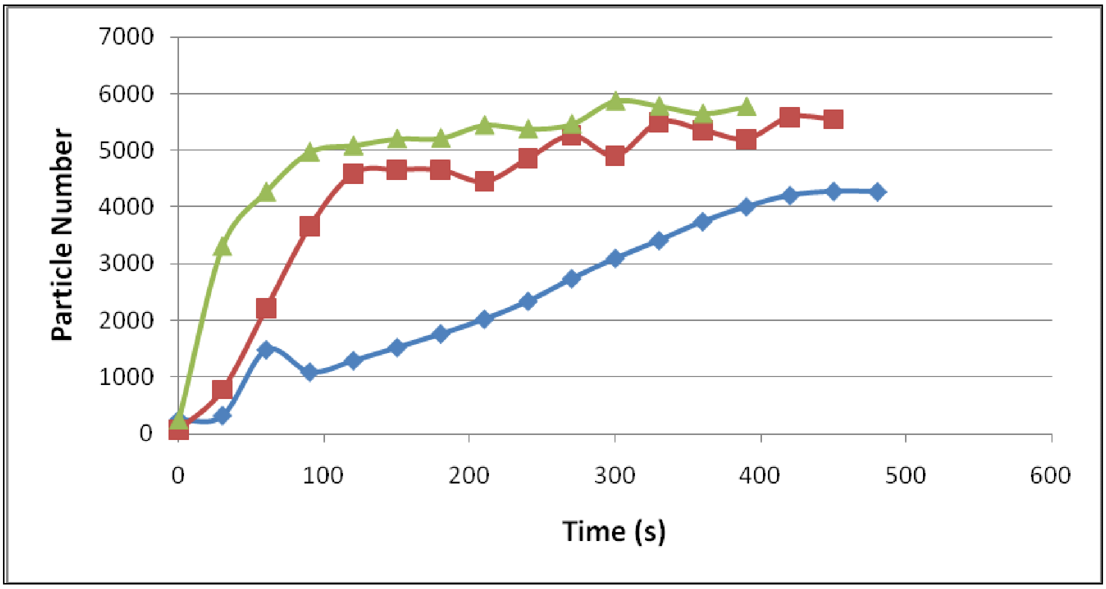

Figure 3.20 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3.20; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn't show a significant crystal formation, which is also proven by the light microscope photos.

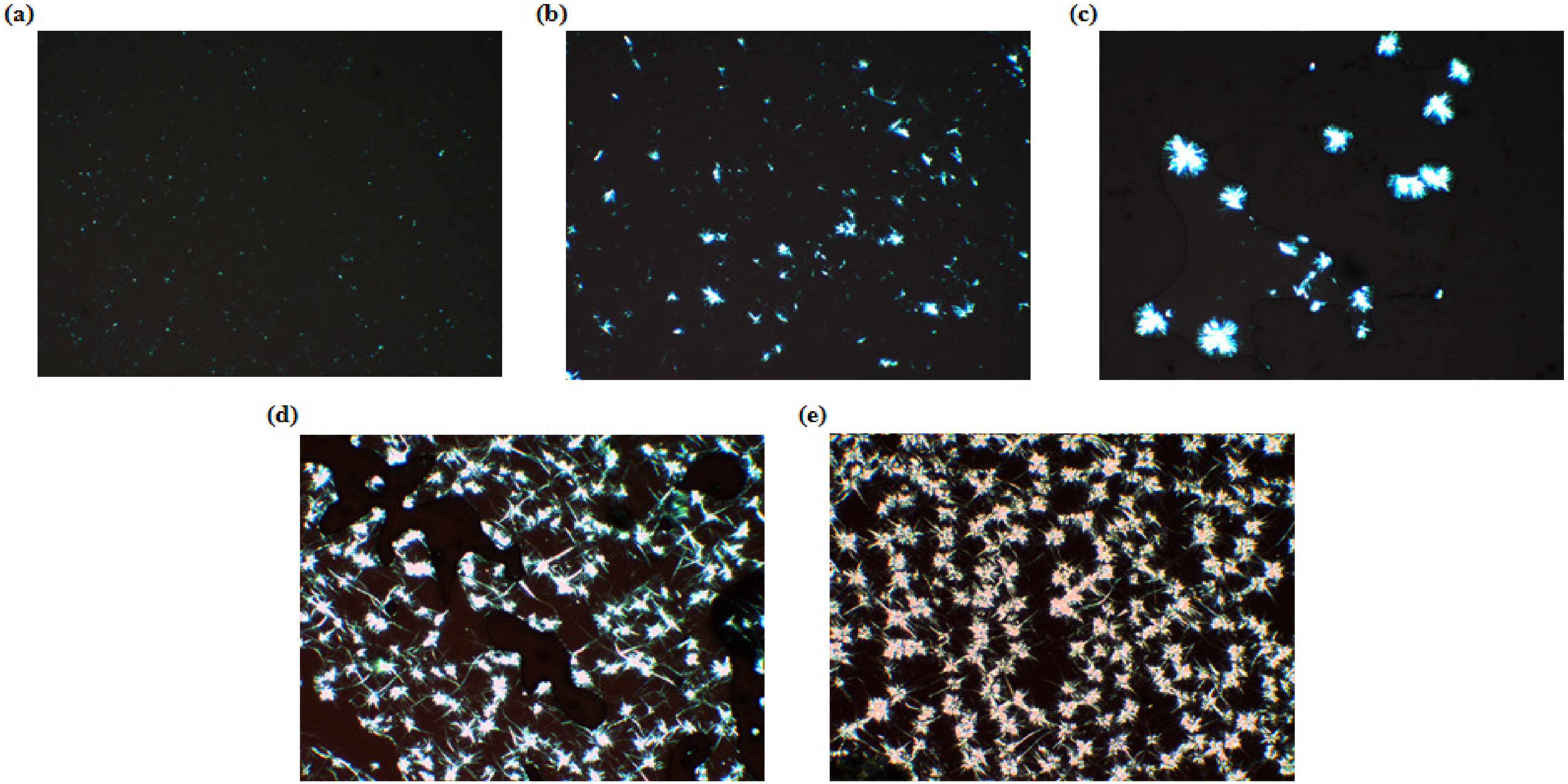

Figure 3.21 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 1000 ppm active nickel concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times, stored at 20 ºC for 2 days.

The photos in the Figure 3.21 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 60, 80 and 100 minutes. The ones hydrogenated for 20 and 40 minutes didn't show a considerable crystal formation.

2.3.2 Hydrogenation with 2000 ppm active nickel

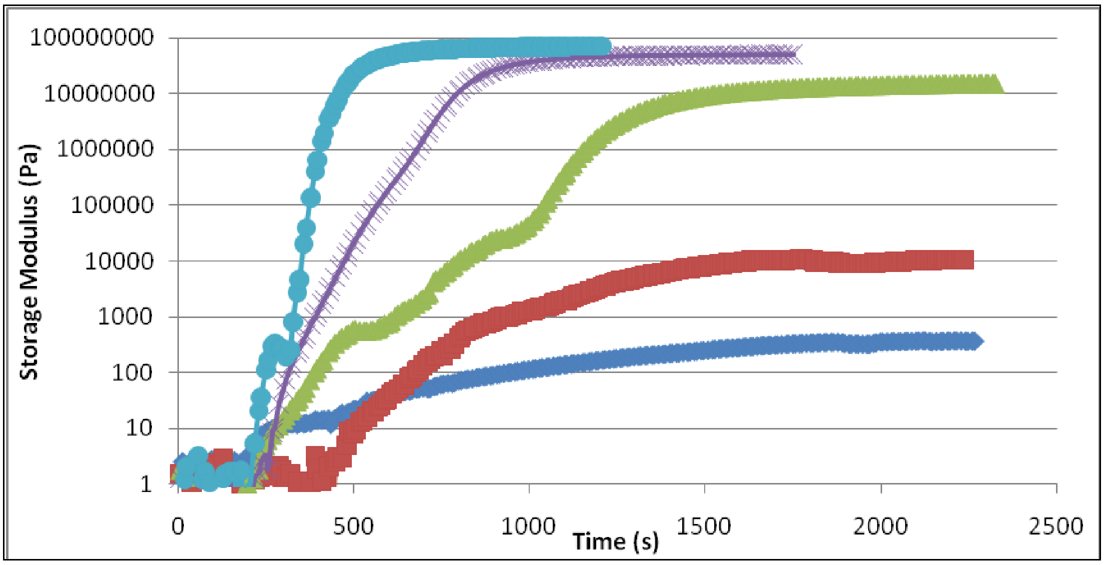

Figure 3.22 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 20 minutes (♦), 40 minutes (■), 60 minutes (▲), 80 minutes (×) and 100 minutes (●) of hydrogenation times

Figure 3.22 presents that the plateau values of the storage moduli for the samples hydrogenated for 20, 40, 60, 80 and 100 minutes are 370.2, 10610, 15360000, 50400000 and 71960000 Pa respectively. Sample hydrogenated for 100 minutes shows a narrow plastic range and the ones for 20, 40, 60 and 80 minutes show a broad plastic range.

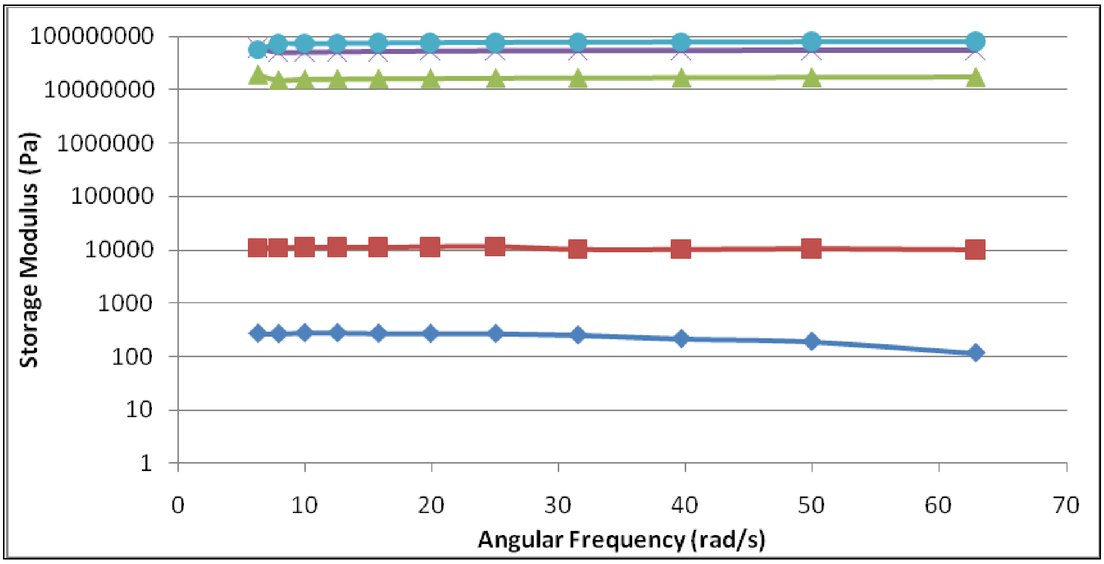

Figure 3.23 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 20 minutes (♦), 40 minutes (■), 60 minutes (▲), 80 minutes (×) and 100 minutes (●) of hydrogenation times

Figure 3.23 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 20, 40, 60, 80 and 100 minutes are 116.6, 10140, 17430000, 55410000 and 80510000 Pa respectively.

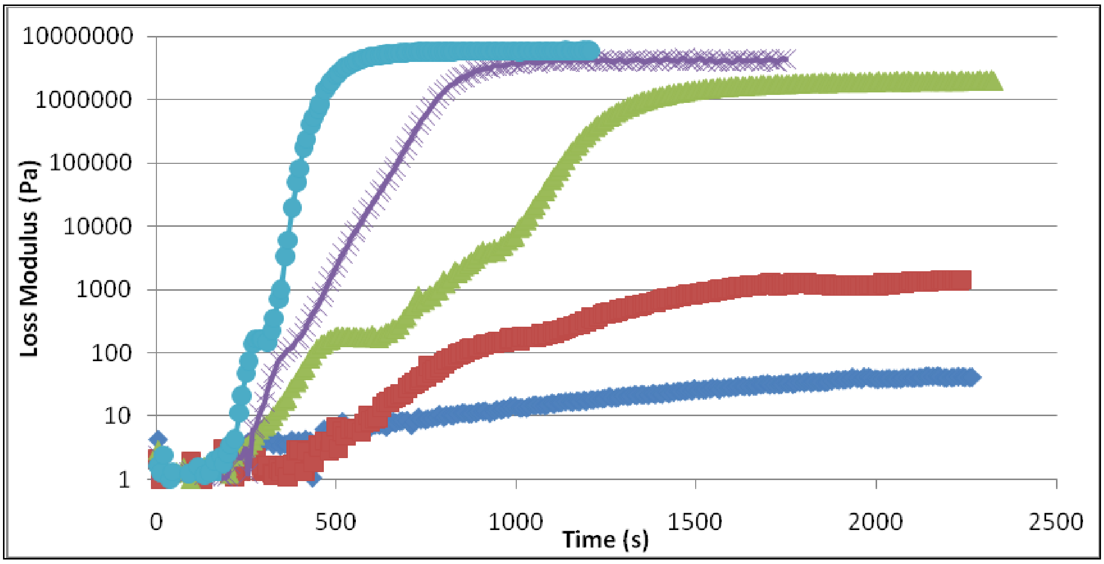

Figure 3.24 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 20 minutes (♦), 40 minutes (■), 60 minutes (▲), 80 minutes (×) and 100 minutes (●) of hydrogenation times

Figure 3.24 presents that the plateau values of the loss moduli for the samples hydrogenated for 20, 40, 60, 80 and 100 minutes are 40.26, 1424, 1956000, 4375000 and 5895000 Pa respectively. Sample hydrogenated for 100 minutes shows a narrow plastic range and the ones for 20, 40, 60 and 80 minutes show a broad plastic range.

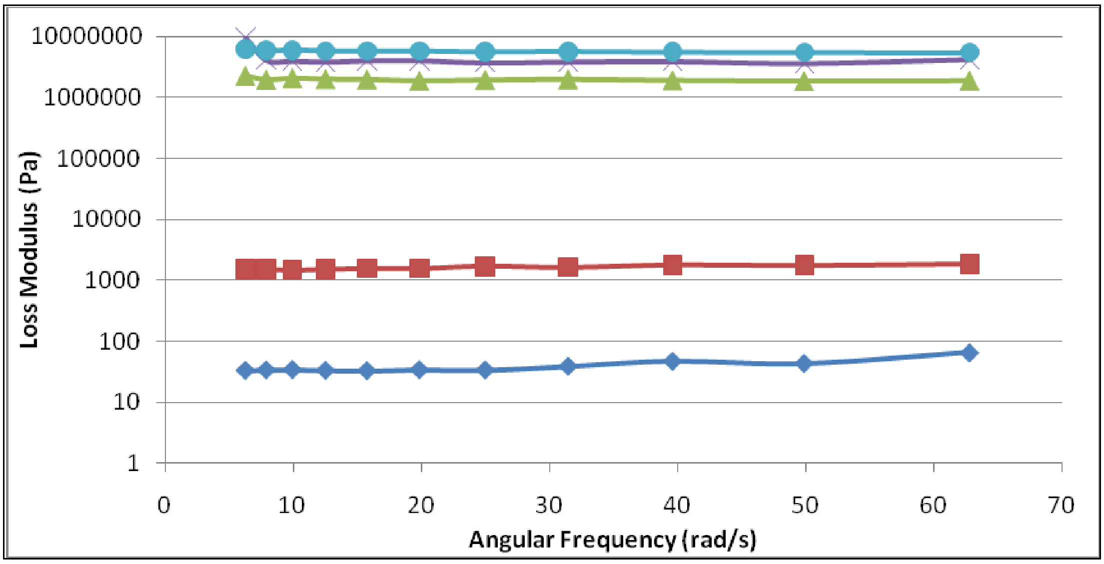

Figure 3.25 Frequency sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 20 minutes (♦), 40 minutes (■), 60 minutes (▲), 80 minutes (×) and 100 minutes (●) of hydrogenation times

Figure 3.25 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 20, 40, 60, 80 and 100 minutes are 65.19, 1843, 1869000, 4254000 and 5465000 Pa respectively.

Fatty acid contents and iodine values of the samples hydrogenated for 20, 40, 60, 80 and 100 minutes, are given in Table 3.8.

Table 3.8 Change in the fatty acid distributions of soy oil samples, hydrogenated for 20, 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration

Time (min)	**0**	**20**	**40**	**60**	**80**	**100**
Iodine number	130.1	115.2	96.4	80.3	75.9	71.3
18:0	3.77	4.31	4.99	6.05	7.85	10.37

Table 3.8 (continued)

18:1 trans	0.00	6.52	26.21	47.46	59.76	67.74
18:1 cis	30.70	34.82	32.37	26.89	15.97	8.07
18:2 trans	0.00	14.69	19.49	8.59	5.71	3.12
18:2 cis	46.40	24.13	4.55	0.06	0.00	0.00
18:3 trans	0.00	2.29	0.44	0.12	0.02	0.00
18:3 cis	8.46	1.08	0.17	0.00	0.00	0.00
Total trans	0.00	24.94	47.20	56.31	65.49	70.86
Conjugated linoleic	0.00	1.44	1.06	0.14	0.00	0.00

As can be seen from Table 3.8, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Stearic acid reaches to 10.37% and trans 18:1 acid increases up to 67.74% where total trans fatty acids are at 70.86% at 100. minute. Cis 18:1 and cis 18:2 acids both decreased throughout the reaction and are present 39.97% and 0.00% respectively at the end of the reaction. Trans 18:2 acids increased at the first 40. minute of the reaction and then decreased down to 3.12% at the 100. minute. Cis and trans forms of 18:3 acid and conjugated 18:2 acid are completely eliminated until the end of the reaction. The iodine number decreased down to 71.3 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 20, 40, 60, 80 and 100 minutes, are given in Table 3.9.

Table 3.9 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 20, 40, 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration

Time (min)	**SMP (ºC)**	**Solid fat content (%)**				
		$N_{0^{\circ}C}$	$N_{10^{\circ}C}$	$N_{21.1^{\circ}C}$	$N_{33.3^{\circ}C}$	$N_{40.6^{\circ}C}$
20	<15	5.2	3.9	0.9	0.0	0.0
40	22.2	39.7	23.9	6.4	0.0	0.0

Table 3.9 (continued)

60	29.5	76.0	65.1	30.2	1.0	0.0
80	33.0	89.6	85.3	57.1	7.0	0.0
100	34.0	92.2	89.8	67.5	14.0	0.2

Solid fat contents of the samples hydrogenated for 20, 40, 60, 80 and 100 minutes, are plotted in Figure 3.26.

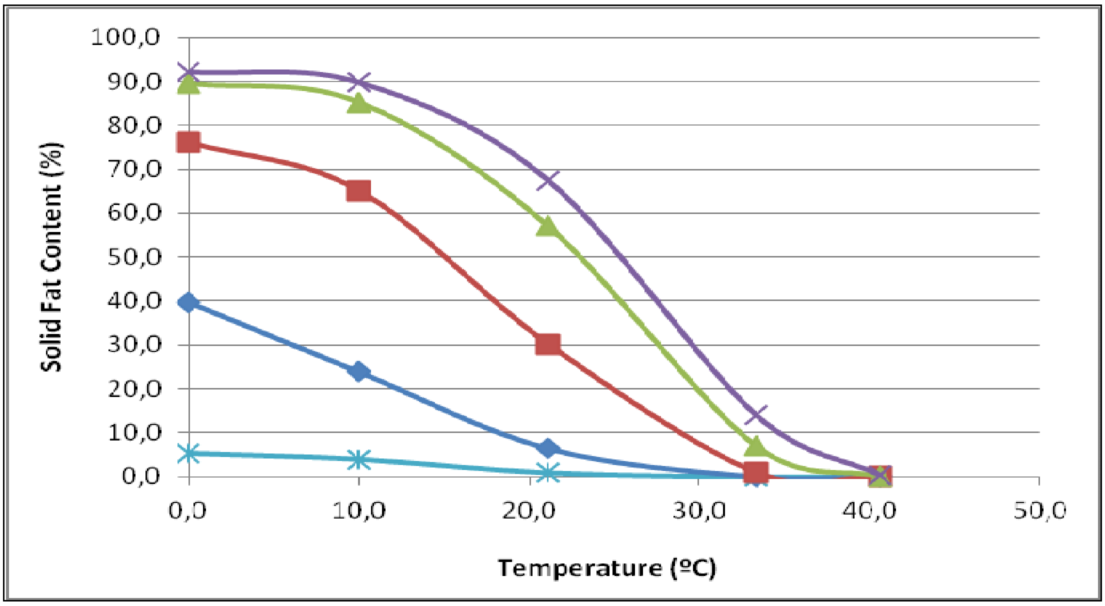

Figure 3.26 Change in solid fat contents of soy oil samples, hydrogenated under 165 ℃ temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 20 minutes (♦), 40 minutes (■), 60 minutes (▲), 80 minutes (×) and 100 minutes (●) of hydrogenation times

Table 3.9 and Figure 3.26 show that, slip melting point of the sample exceeded 20 ℃ after 40 minutes of hydrogenation and reached to 34.0 ℃ at the end of 100. minute. Until 100. minute all the samples taken at 40.6 ℃ are liquid; whereas at 100. minute, solid fat contents of the samples are 92.2% at 0 ℃, 89.8% at 10.0 ℃, 67.5% at 21.1 ℃, 14.0% at 33.3 ℃ and 0.2% at 40.6 ℃.

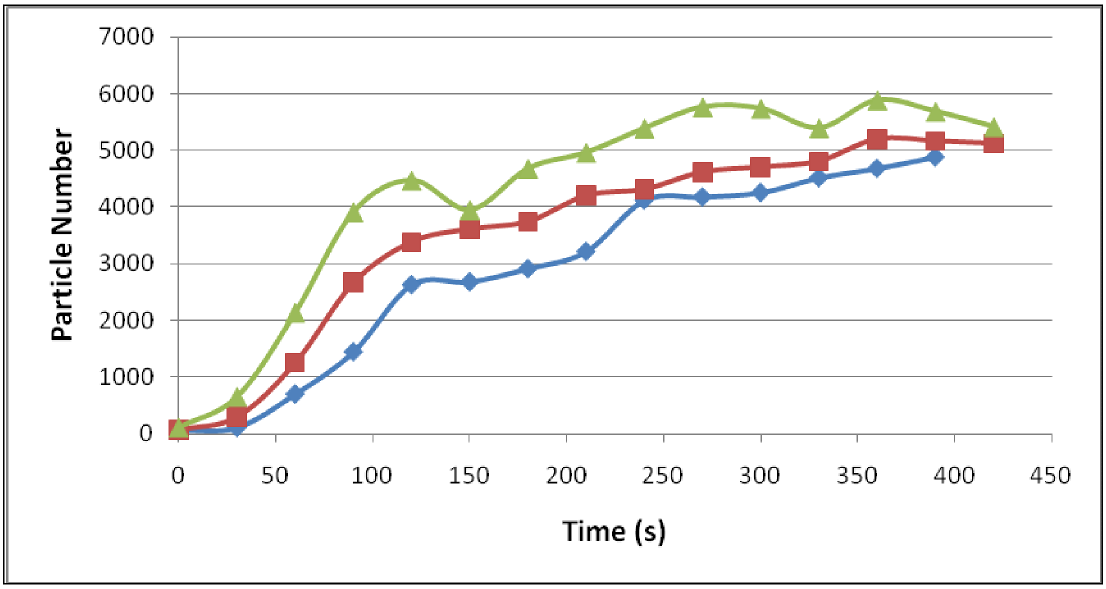

Figure 3. 27 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 2000 ppm active nickel concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3. 27; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn’t show a significant crystal formation, which is also proven by the light microscope photos.

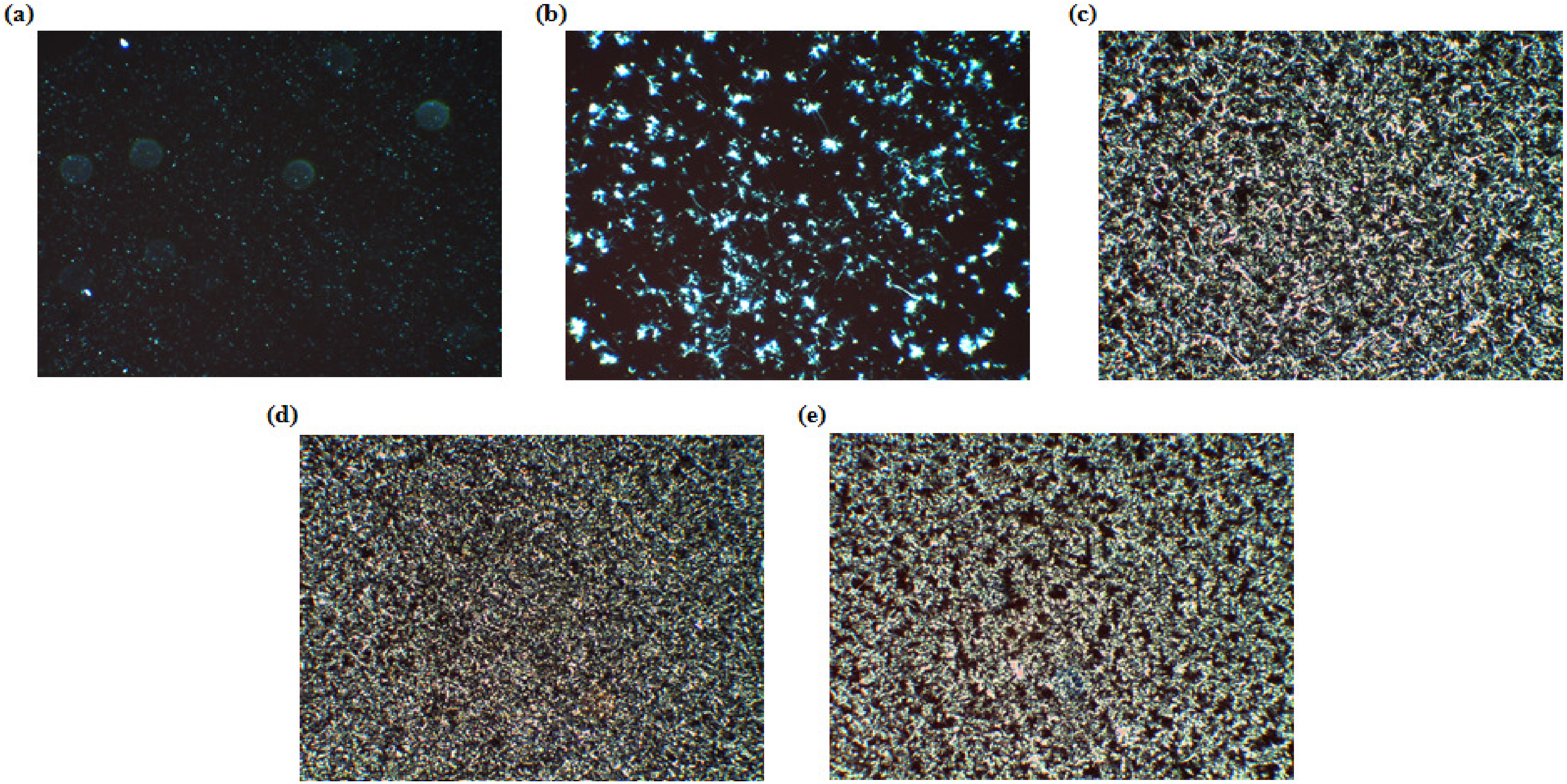

Figure 3.28 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 2000 ppm active nickel concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times, stored at 20 ºC for 2 days.

The photos in the Figure 3.28 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 40, 60, 80 and 100 minutes. The one hydrogenated for 20 minutes didn't show a considerable crystal formation.

3.4 Hydrogenations with Pd/A catalyst

Hydrogenations with Pd/A catalyst are performed in the presence of 25 and 50 ppm active palladium in the oil to be processed.

3.4.1 Hydrogenation with 25 ppm active palladium

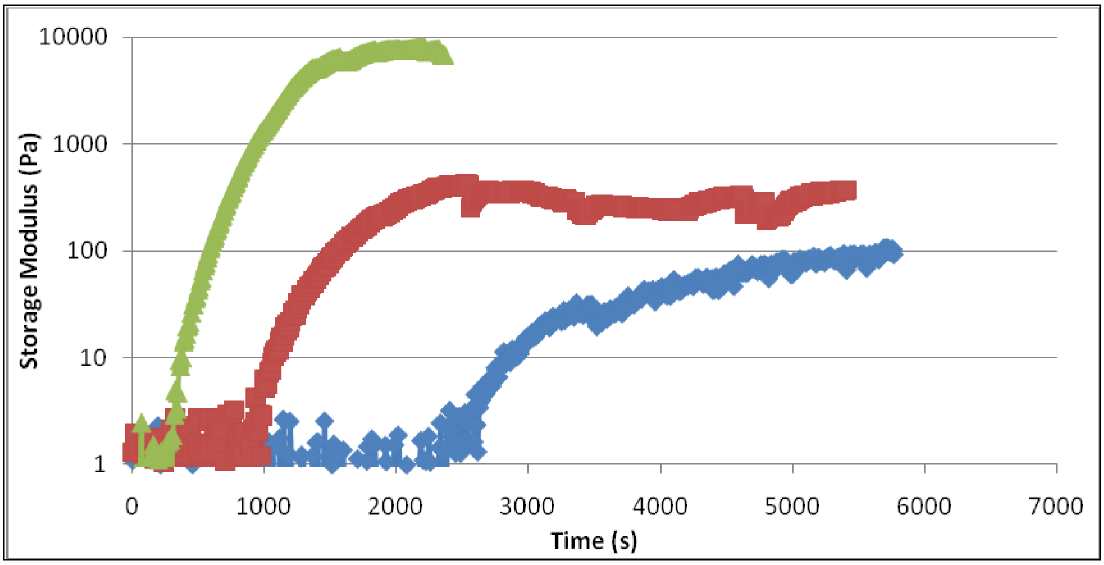

Figure 3.29 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.29 presents that the plateau values of the storage moduli for the samples hydrogenated for 60, 80 and 100 minutes are 92.9, 372.5 and 6895 Pa respectively. Sample hydrogenated for 100 minutes shows a narrow plastic range and the ones for 60 and 80 minutes show a broad plastic range. Also the samples hydrogenated for 20 and 40 minutes didn’t have a regular and stable storage modulus behaviour.

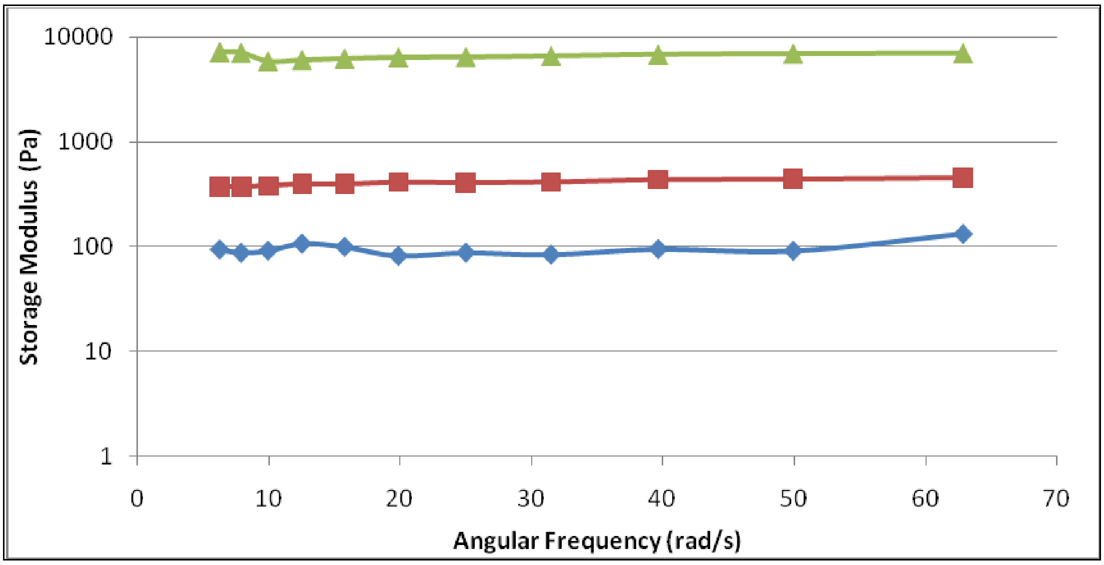

Figure 3.30 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.30 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 60, 80 and 100 minutes are 131.2, 456.9 and 6977 Pa respectively. Also the samples hydrogenated for 20 and 40 minutes didn’t have a measurable storage modulus.

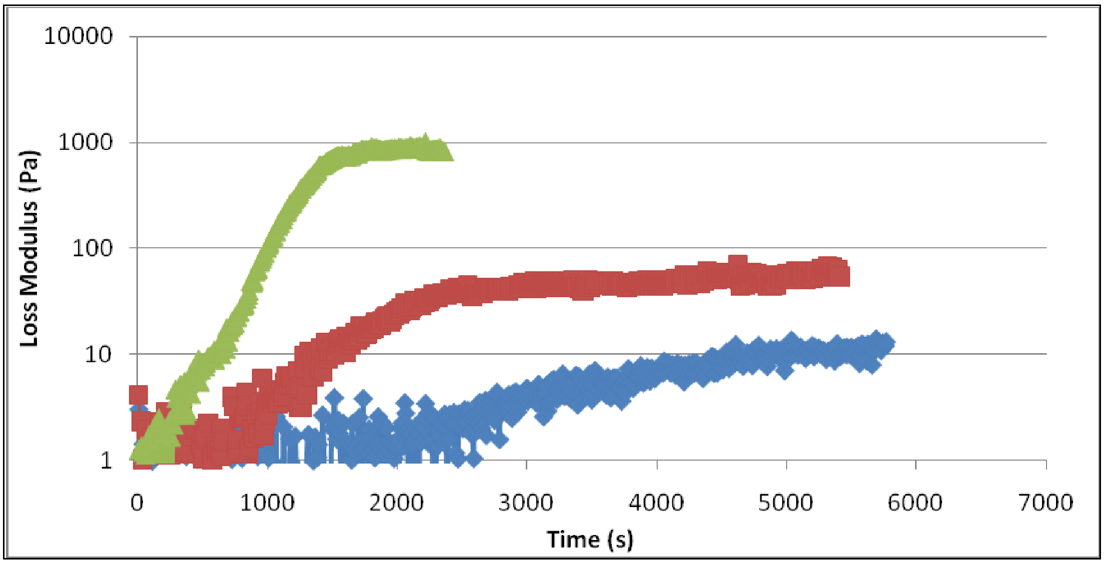

Figure 3.31 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.31 presents that the plateau values of the loss moduli for the samples hydrogenated for 60, 80 and 100 minutes are 13.3, 53.96 and 823.7 Pa respectively. Sample hydrogenated for 100 minutes shows a narrow plastic range and the ones for 60 and 80 minutes show a broad plastic range. Also the samples hydrogenated for 20 and 40 minutes didn't have a regular and stable loss modulus behaviour.

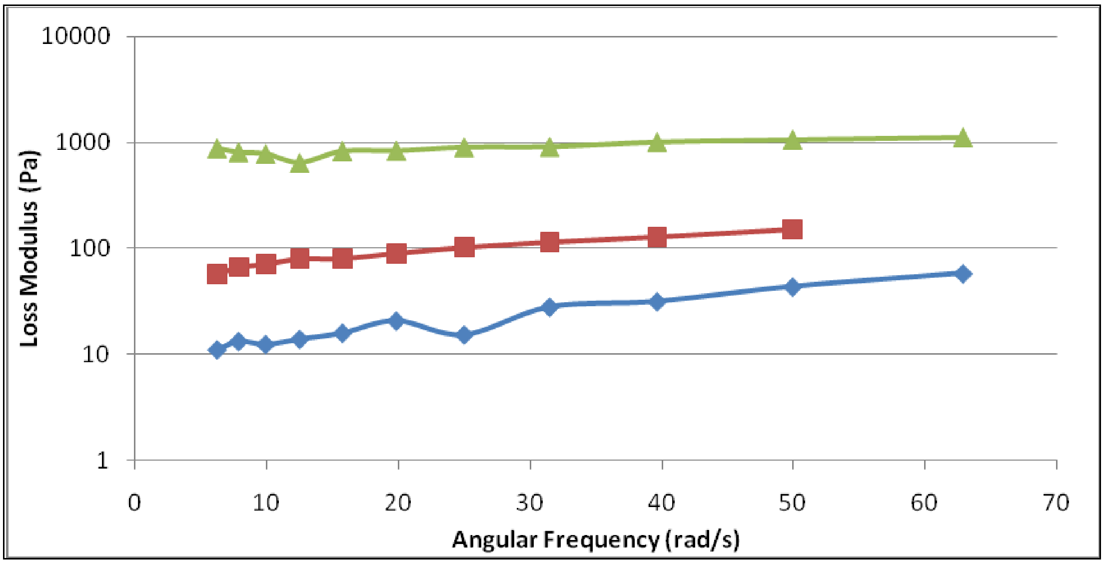

Figure 3.32 Frequency sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.32 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 60, 80 and 100 minutes are 58.24, 178.1 and 1119 Pa respectively. Also the samples hydrogenated for 20 and 40 minutes didn't have a measurable loss modulus.

Fatty acid contents and iodine values of the samples hydrogenated for 60, 80 and 100 minutes, are given in Table 3.10.

Table 3.10 Change in the fatty acid distributions of soy oil samples, hydrogenated for 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration

Time (min)	**0**	**60**	**80**	**100**
Iodine number	130.1	117.8	112.8	109.0
18:0	3.77	4.42	4.81	5.11
18:1 trans	0.00	8.40	12.01	14.44

Table 3.10 (continued)

18:1 cis	30.70	31.90	32.27	32.84
18:2 trans	0.00	6.42	7.43	8.48
18:2 cis	46.40	32.31	27.73	24.18
18:3 trans	0.00	0.85	0.79	0.72
18:3 cis	8.46	4.65	3.80	3.19
Total trans	0.00	16.01	20.66	23.98
Conjugated linoleic	0.00	0.34	0.44	0.33

As can be seen from Table 3.10, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Stearic acid reaches to 5.11% and trans 18:1 acid increases up to 14.44% where total trans fatty acids are at 23.98% at 100. minute. Cis 18:1 and trans 18:2 acids both decreased throughout the reaction and are present 32.84% 8.48% respectively at the end of the reaction. Cis 18:2, trans 18:3 and cis 18:3 acids all decreased down to 24.18%, 0.72% and 3.19% at the 100. minute. Conjugated 18:2 acid increased to 0.44% at 80 minutes and again decreased down to 0.33% until the end of the reaction. The iodine number decreased down to 109.0 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 60, 80 and 100 minutes, are given in Table 3.11.

Table 3.11 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration

Time (min)	**SMP (ºC)**	**Solid fat content (%)**				
		$N_{0^\circ C}$	$N_{10^\circ C}$	$N_{21.1^\circ C}$	$N_{33.3^\circ C}$	$N_{40.6^\circ C}$
60	<15	8.8	5.2	0.0	0.0	0.0
80	<15	15.9	10.1	0.9	0.0	0.0
100	15.5	23.1	16.0	2.9	0.1	0.0

Solid fat contents of the samples hydrogenated for 60, 80 and 100 minutes, are plotted in Figure 3.33.

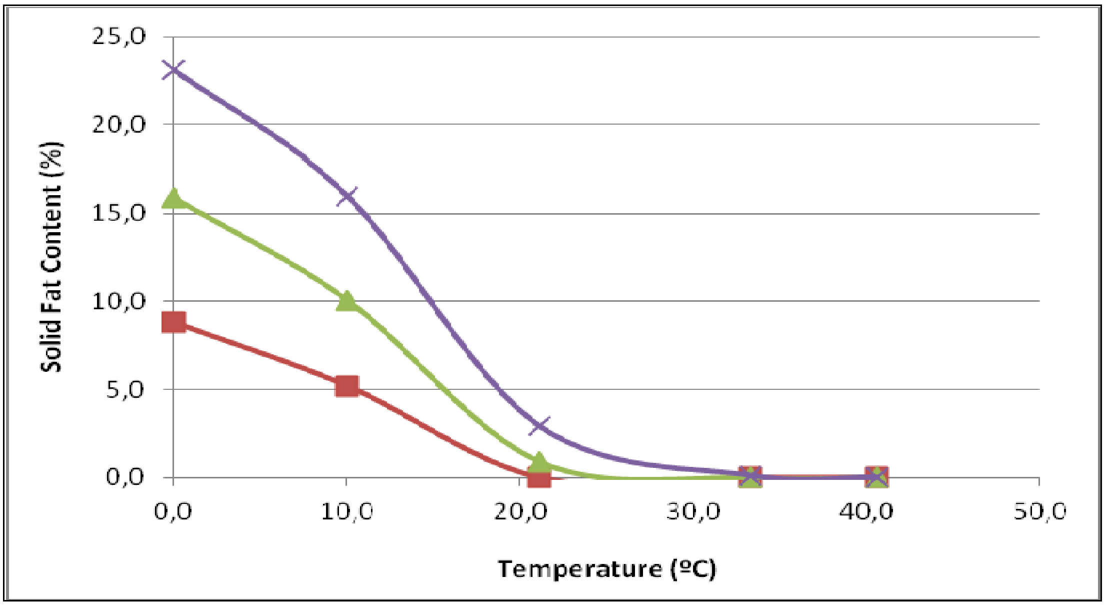

Figure 3.33 Change in solid fat contents of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Table 3.11 and Figure 3.33 show that, slip melting point of the sample couldn't exceed 20 ºC even after 100 minutes of hydrogenation and could only reached to 15.5 ºC at the end of 100. minute. Until 100. minute all the samples taken at 33.3 ºC and 40.6 ºC are liquid; whereas at 100. minute, solid fat contents of the samples are 23.1% at 0 ºC, 16.0% at 10.0 ºC, 2.9% at 21.1 ºC, 0.1% at 33.3 ºC and 0.0% at 40.6 ºC.

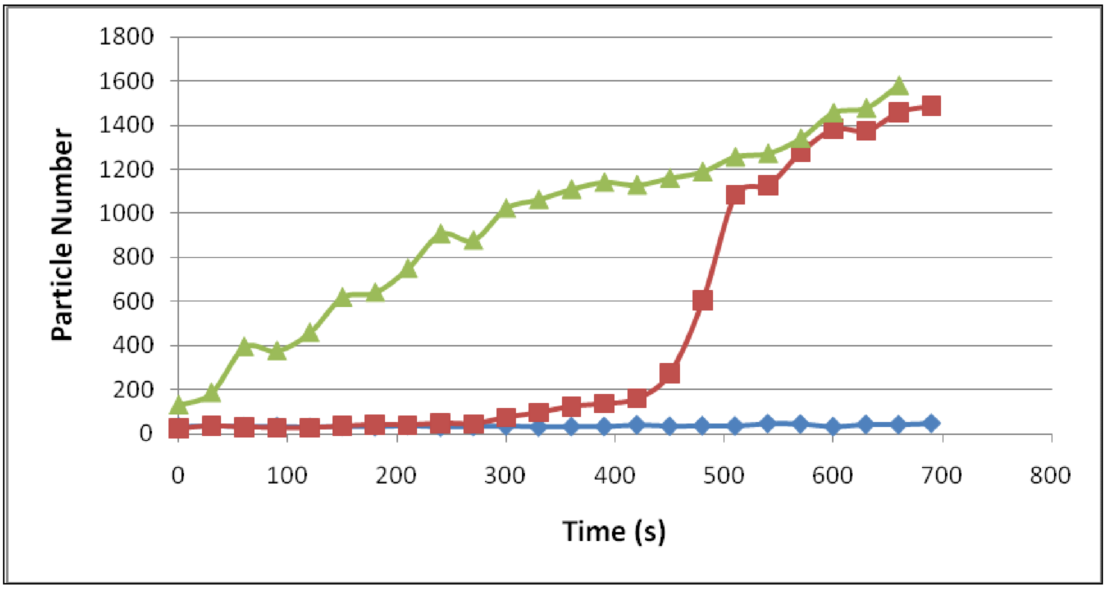

Figure 3.34 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 25 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3.31; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn't show a significant crystal formation, which is also proven by the light microscope photos.

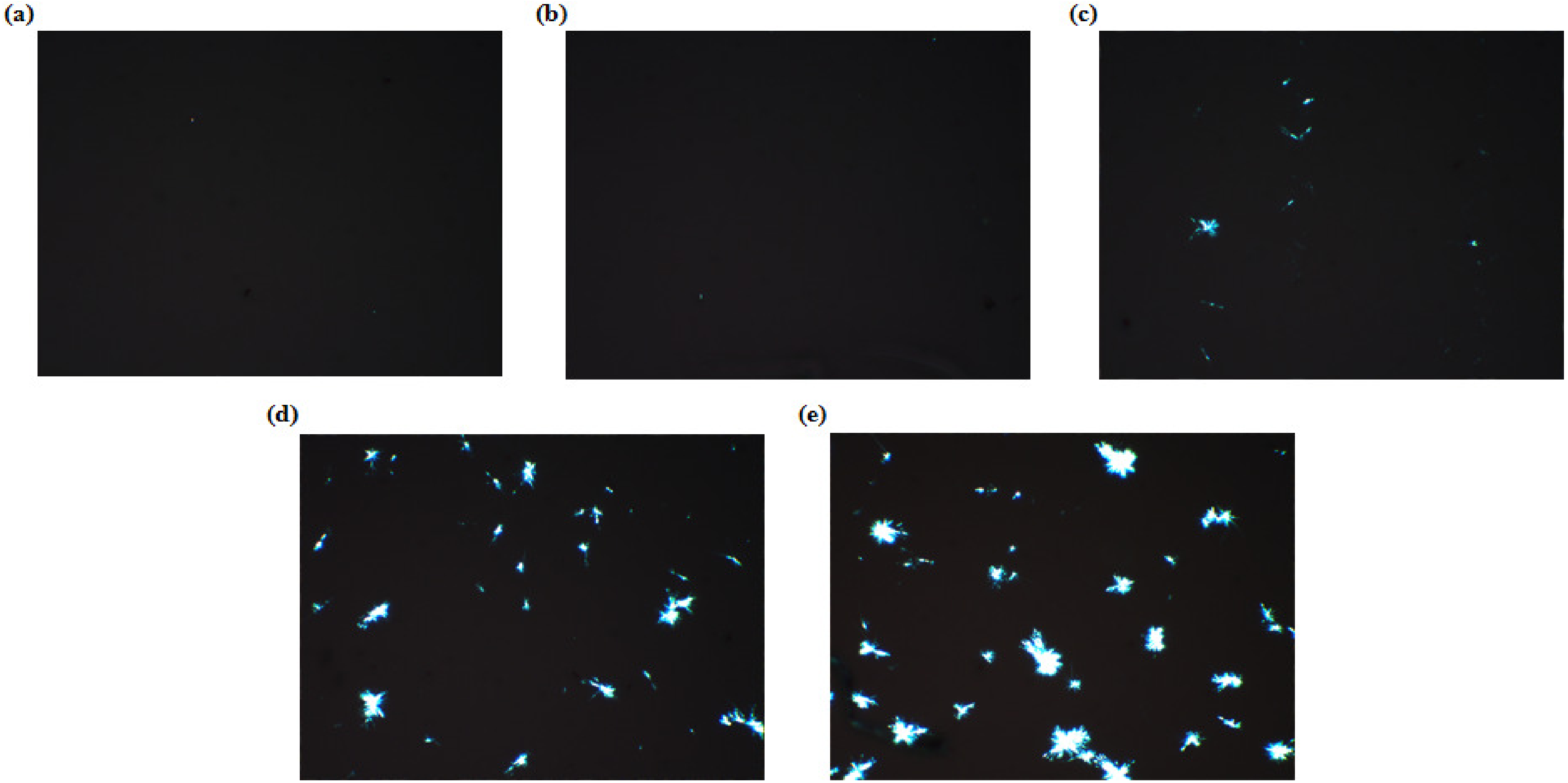

Figure 3.35 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 25 ppm active palladium concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times, stored at 20 ºC for 2 days.

The photos in the Figure 3.35 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 80 and 100 minutes. The ones hydrogenated for 20, 40 and 60 minutes didn't show a considerable crystal formation.

3.4.2 Hydrogenation with 50 ppm active palladium

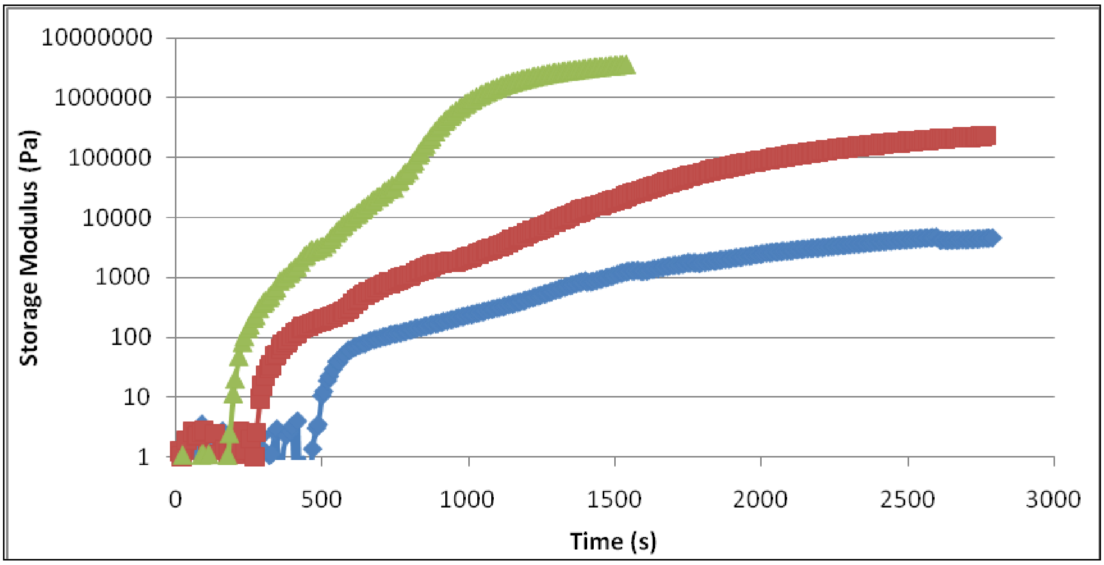

Figure 3.36 Time sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.36 presents that the plateau values of the storage moduli for the samples hydrogenated for 60, 80 and 100 minutes are 4608, 231900 and 3669000 Pa respectively. Samples hydrogenated for 80 and 100 minutes show a narrow plastic range and the one for 60 minutes shows a broad plastic range. Also the samples hydrogenated for 20 and 40 minutes didn't have a regular and stable storage modulus behaviour.

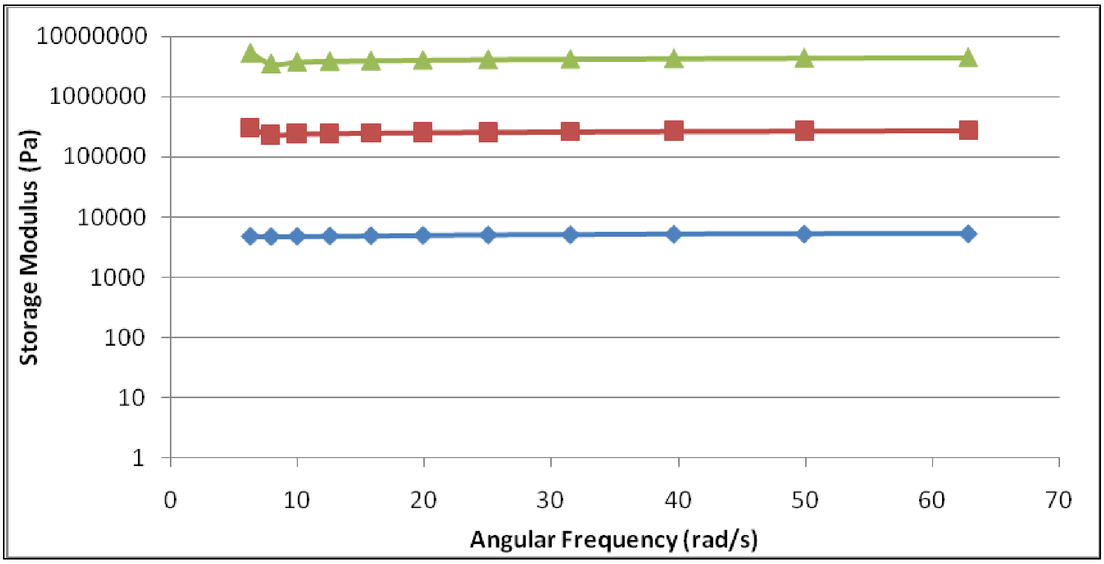

Figure 3.37 Frequency sweep curve for the storage moduli of soy oil samples, hydrogenated under 165 °C temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.37 shows that storage moduli of none of the samples are frequency dependent. The constant values of the storage moduli for the samples hydrogenated for 60, 80 and 100 minutes are 5300, 277300 and 4462000 Pa respectively. Also the samples hydrogenated for 20 and 40 minutes didn’t have a measurable storage modulus.

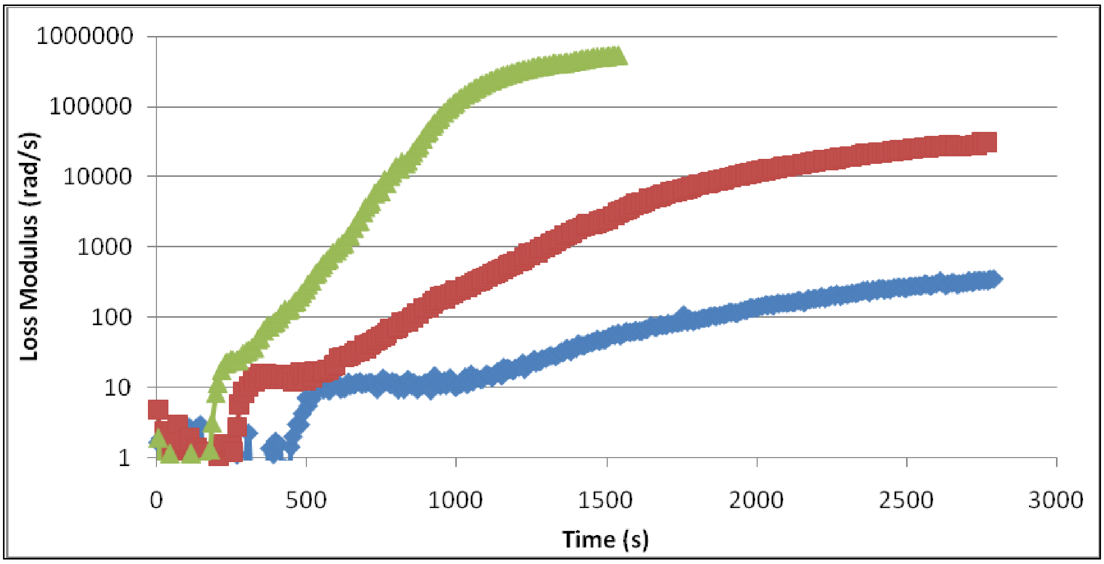

Figure 3.38 Time sweep curve for the loss moduli of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.38 presents that the plateau values of the loss moduli for the samples hydrogenated for 60, 80 and 100 minutes are 356, 31300 and 549100 Pa respectively. Samples hydrogenated for 80 and 100 minutes show a narrow plastic range and the one for 60 minutes shows a broad plastic range. Also the samples hydrogenated for 20 and 40 minutes didn’t have a regular and stable loss modulus behaviour.

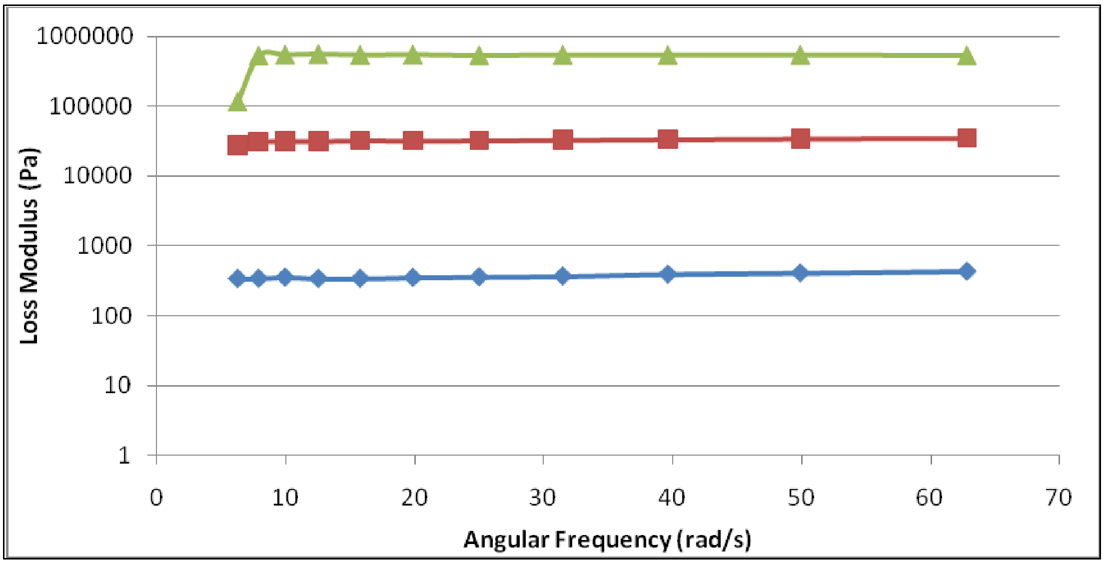

Figure 3.39 Frequency sweep curve for the loss modulus of soy oil, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Figure 3.39 shows that loss moduli of none of the samples are frequency dependent. The constant values of the loss moduli for the samples hydrogenated for 60, 80 and 100 minutes are 429.9, 35010 and 528000 Pa respectively. Also the samples hydrogenated for 20 and 40 minutes didn’t have a measurable loss modulus.

Fatty acid contents and iodine values of the samples hydrogenated for 60, 80 and 100 minutes, are given in Table 3.12.

Table 3.12 Change in the fatty acid distributions of soy oil samples, hydrogenated for 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration

Time (min)	**0**	**60**	**80**	**100**
Iodine number	130.1	106.2	98.8	92.1
18:0	3.77	4.85	5.40	6.53

Table 3.12 (continued)

18:1 trans	0.00	17.60	24.85	31.47
18:1 cis	30.70	32.63	31.53	29.86
18:2 trans	0.00	11.37	12.00	11.54
18:2 cis	46.40	19.57	13.41	8.38
18:3 trans	0.00	1.12	0.80	0.76
18:3 cis	8.46	1.98	1.19	0.72
Total trans	0.00	30.29	37.77	43.81
Conjugated linoleic	0.00	0.20	0.11	0.04

As can be seen from Table 3.12, stearic acid and trans 18:1 acid contents increase theroughout the hydrogenation. Stearic acid reaches to 6.53% and trans 18:1 acid increases up to 31.47% where total trans fatty acids are at 43.81% at 100. minute. Cis 18:1 and cis 18:2 acids both decreased throughout the reaction and are present 29.86% and 8.38% respectively at the end of the reaction. Trans 18:2 acid first increased until 80. minute, then devreased again to 11.54 at the end of the reaction. Trans 18:3 and cis 18:3 acids both decreased down to 0.76% and 0.72% at the 100. minute. Conjugated 18:2 acid decreased down to 00.04% until the end of the reaction. The iodine number decreased down to 92.1 at 100. minute.

Slip melting points and solid fat contents of the samples hydrogenated for 60, 80 and 100 minutes, are given in Table 3.13.

Table 3.13 Solid fat contents and slip melting points of soy oil samples, hydrogenated for 60, 80 and 100 minutes, under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration

Time (min)	**SMP (ºC)**	**Solid fat content (%)**				
		$N_{0^\circ C}$	**$N_{10^\circ C}$**	**$N_{21.1^\circ C}$**	**$N_{33.3^\circ C}$**	**$N_{40.6^\circ C}$**
60	16.6	21.9	13.6	1.4	0.0	0.0

Table 3.13 (continued)

80	21.6	36.3	28.5	7.5	0.0	0.0
100	25.6	53.6	43.6	17.2	0.0	0.0

Solid fat contents of the samples hydrogenated for 60, 80 and 100 minutes, are plotted in Figure 3.40.

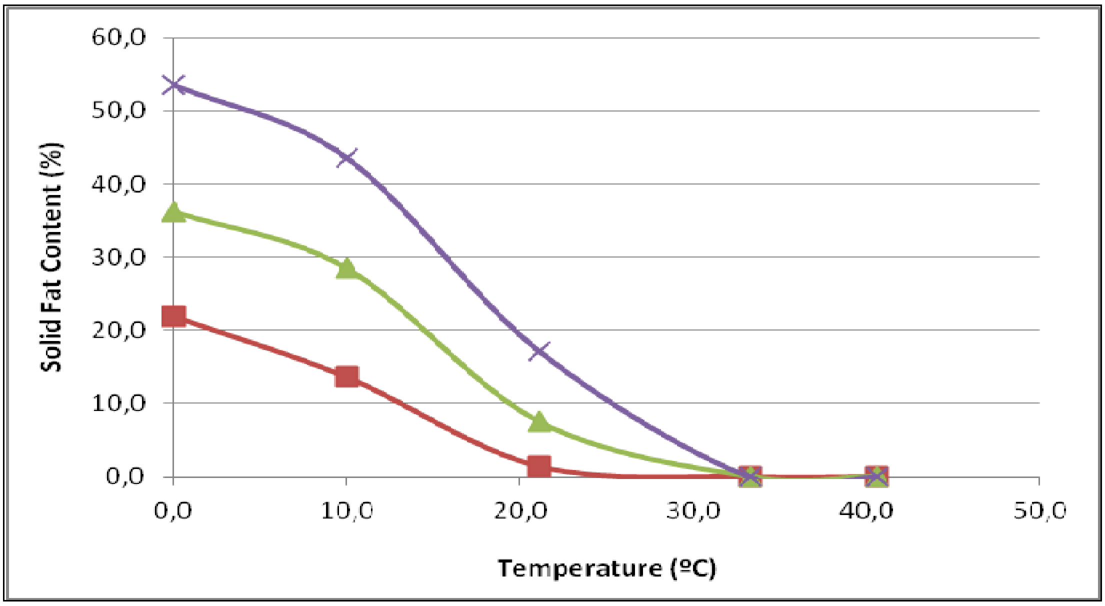

Figure 3.40 Change in solid fat contents of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 50 ppm active palladium concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times

Table 3.13 and Figure 3.40 show that, slip melting point of the sample exceeded 20 ºC even after 80 minutes of hydrogenation and reached to 25.6 ºC at the end of 100. minute. Until 100. minute all the samples taken at 33.3 ºC and 40.6 ºC are liquid; whereas at 100. minute, solid fat contents of the samples are 53.6% at 0 ºC, 43.6% at 10.0 ºC, 17.2% at 21.1 ºC, 0.0% at 33.3 ºC and 0.0% at 40.6 ºC.

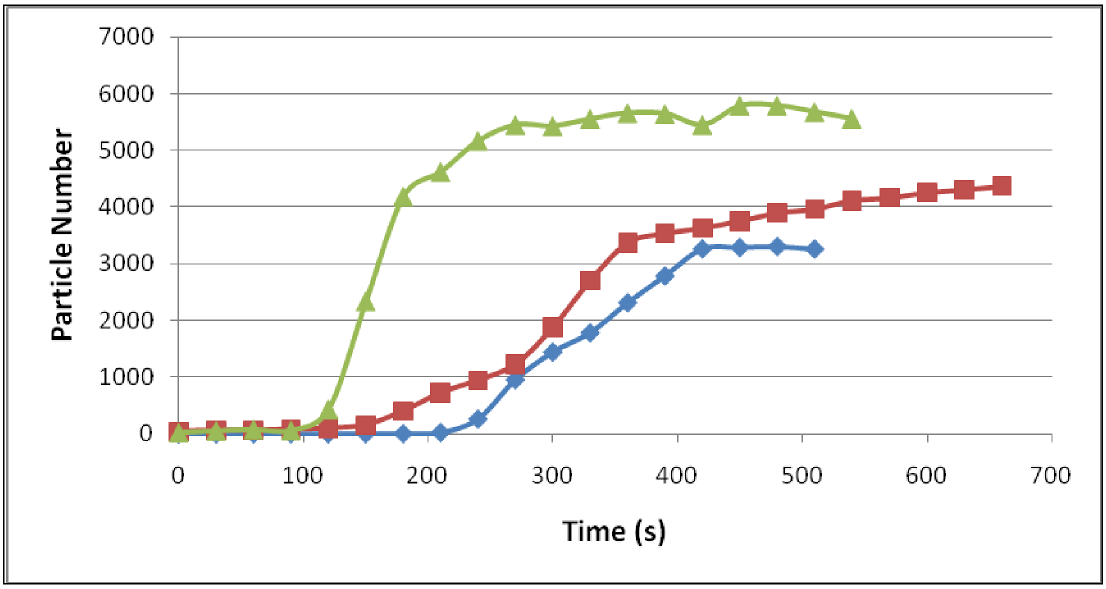

Figure 3.41 Change in particle number of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate and 1000 ppm active nickel concentration; for 60 minutes (♦), 80 minutes (■) and 100 minutes (▲) of hydrogenation times, depending upon cooling.

As it can be seen from the Figure 3.41; samples hydrogenated for 60, 80 and 100 minutes have an increasing crystal formation rate with increasing hydrogenation time; whereas the ones for 20 and 40 minutes didn’t show a significant crystal formation, which is also proven by the light microscope photos.

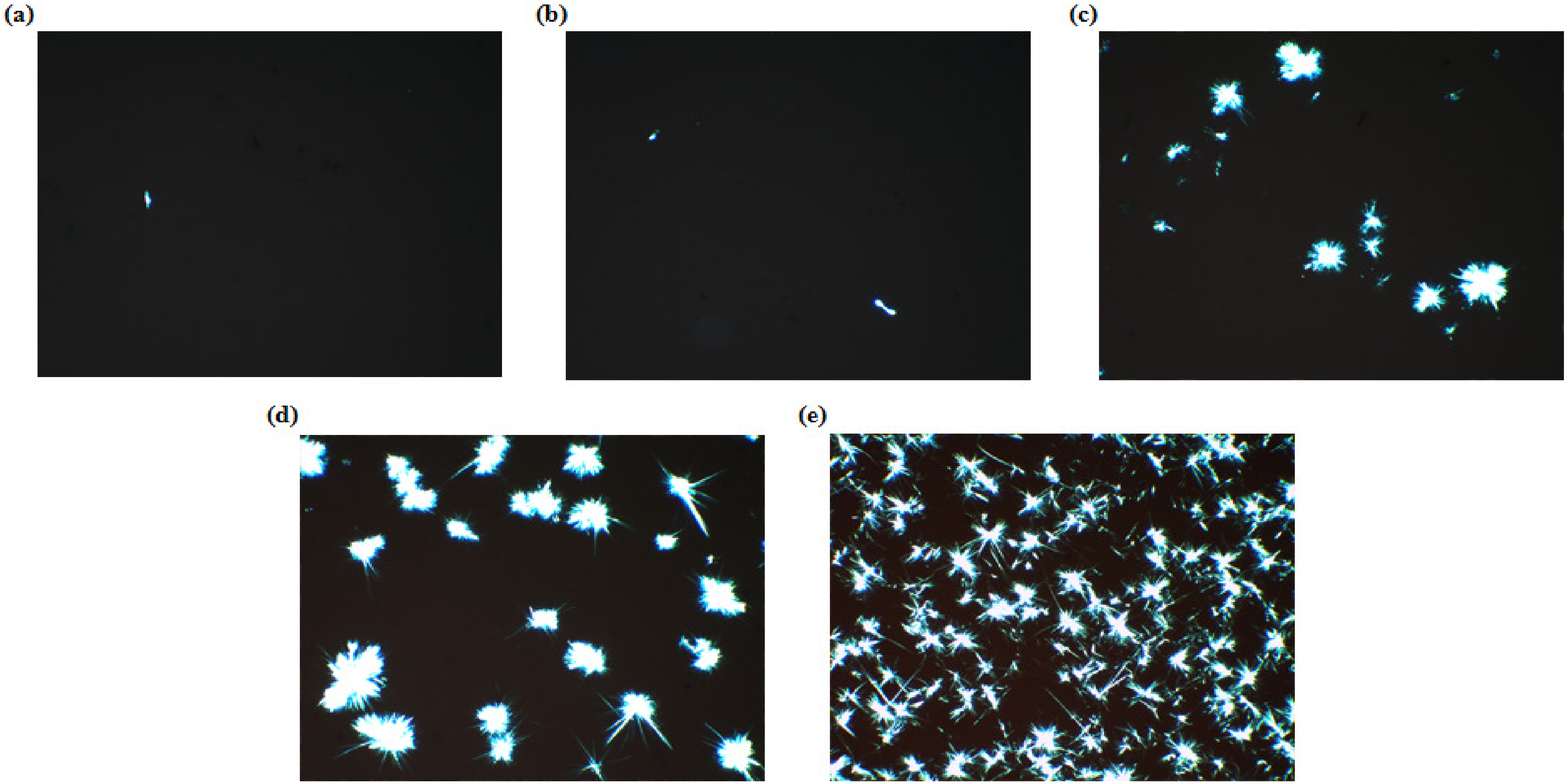

Figure 3.42 Microscopic observation of soy oil samples, hydrogenated under 165 ºC temperature, 2 bar H_2 pressure, 500 rpm stirring rate, 50 ppm active palladium concentration; for (a) 20 minutes, (b) 40 minutes, (c) 60 minutes, (d) 80 minutes and (e) 100 minutes of hydrogenation times, stored at 20 ºC for 2 days.

The photos in the Figure 3.42 show that; upon 2 days of storing, there observed a significant crystal formation in the samples hydrogenated for 60, 80 and 100 minutes. The ones hydrogenated for 20 and 40 minutes didn't show a considerable crystal formation.

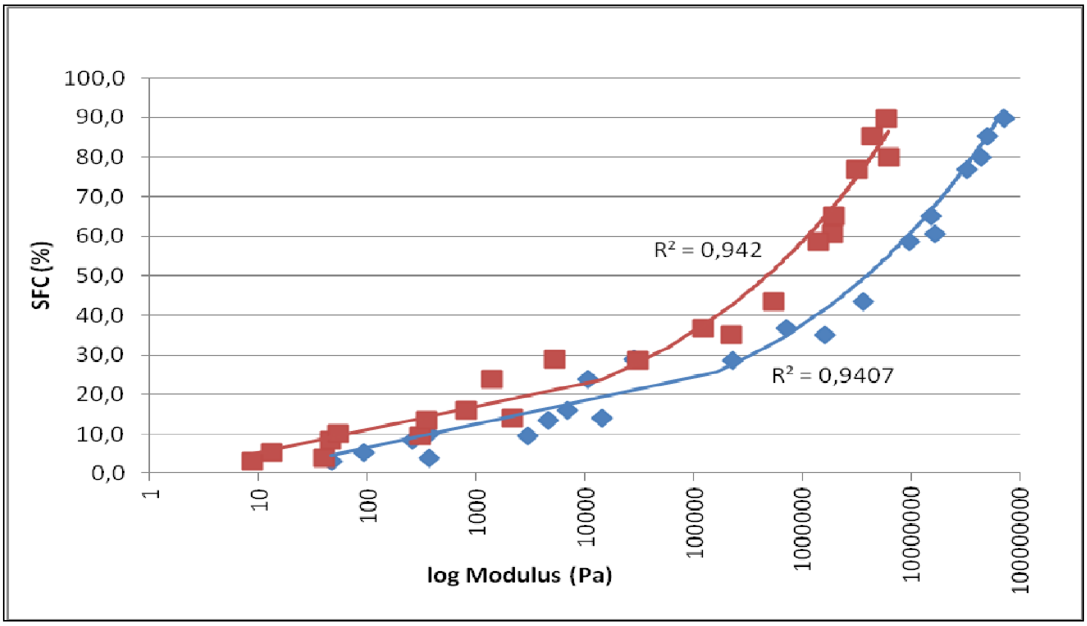

Figure 3.43 Dependency of storage (♦) and loss (■) modulus plateaus of the hydrogenated fat samples obtained from the time sweep tests; on their solid fat contents

Figure 3.43 indicates that moduli obtained from the frequency sweep tests have a considerable relationship (exponential) with the solid fat contents. This relationship also proves that the rheological nature of the fat samples is certainly determined by their solid fat content, as well.

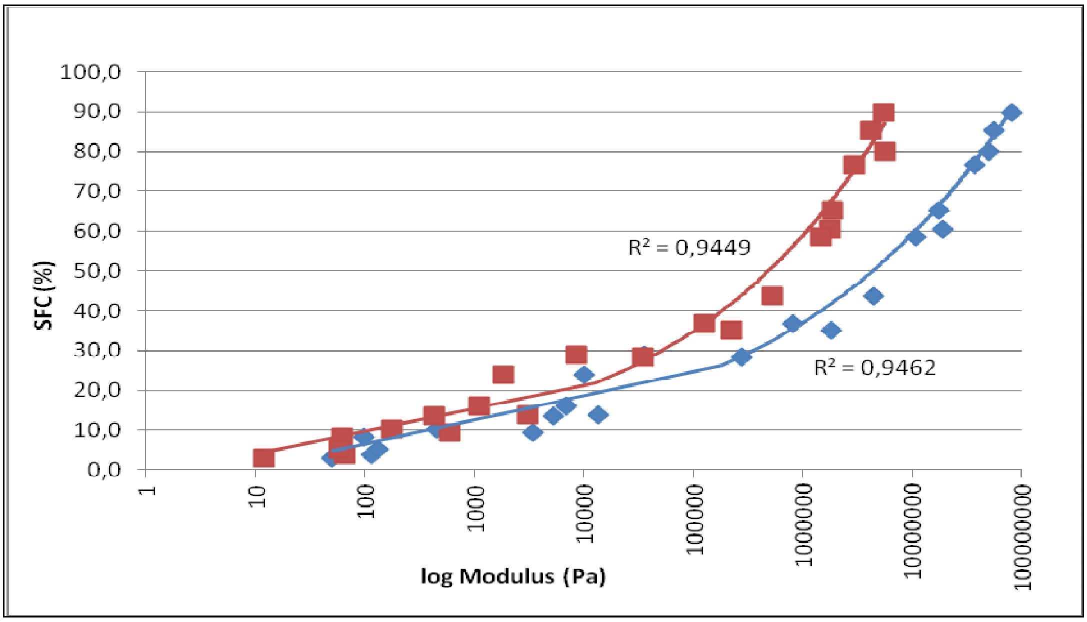

Figure 3.44 Dependency of storage (♦) and loss (■) modulus of the hydrogenated fat samples obtained from the frequency sweep tests; on their solid fat contents

Figure 3.44 represents that moduli obtained from the frequency sweep tests have a considerable relationship (exponential) with the solid fat contents. This relationship also shows that the solid fat contents of the fat samples is necessarily determined by their solid fat content, as well.

When the time and frequency sweep plots of loss and storage moduli of oils are reviewed in consideration of the fatty acid distribution and solid fat content tables, it can be seen that the cooling behaviour of the samples are in a strong correlation with the total trans and solid fat contents. 18:0 and trans 18:1 acids that have relatively higher melting points compared to the other fatty acids in the samples, determine the steepness of the curves, storage and loss moduli plateau. Increasing total trans and decresing iodine also explain this situation.

At 10 °C, which time and frequency sweep tests are carried, solid fat contents of the samples increases with the increase in their hydrogenation times. This is why the curve for the sample hydrogenated for a longer time is so steep and the one with a shorter hydrogenation time shows disordered rheological behaviour for a long time before reaching to a plateau. In other words, the more hydrogenated one has a narrower plastic range and is more tend to form crystal structure; than less hydrogenated one. The sample with the narrower plastic range has a steeper SFC profile whereasthe one having a wide plastic range has a flat SFC profile.

It can also be seen that all the samples have storage moduli greater than loss moduli, which are both almost frequency independent. This is because the elastic behaviour predominates the viscous behaviour, that the samples behave more solid-like and more likely to store the given energy than to dissipate it. Also, the samples hydrogenated by SP10 catalyst have highest storage moduli and the ones hydrogenated by Pd/A catalyst have lowest. This explains that SP10 produces more solid-like samples compared to Pd/A.

It has been previously stated by the research group of Prof. Dr. Muammer Kayahan, that the catalysts could be ordered as SP10>N222>Pd/A in the sense of forming total trans, 18:1 and 18:2 fatty acids. If the time and frequency sweep plots of loss and storage moduli of oils are compared, it could also be seen that even the sample hydrogenated for 20 minutes by SP10 of 1000 ppm show a regular and stable increase in storage modulus, whereas others do not. Also the microscope photos of oils catalysed by SP10 are much more crowded in crystals and the ones catalysed by Pd/A are scattered and loose.

Particle number while cooling plots also serve comfirmative information with the catalyst activity and rheology data. The samples catalysed by Pd/A have more gentle crystal formation curve, where the samples catalysed by SP10 are more tend to cooling and show a steeper cooling curve. The particle number plots of SP10 and N222 pretty much look alike each other because as crystallization proceeds, the crystalls start to cluster and overlap which makes it difficult to count the crystals. This is why some of the curves start decreasing after an instant. But if the plots of the ones hydrogenated for 60 minutes of each catalyst are compared to each other, it can be seen that SP10 produces samples that are more eager to crystallization.

CHAPTER 4

CONCLUSIONS AND RECOMMENDATIONS

Effects of different industrially available catalysts of several concentrations, on rheological and microstructural properties of fats are researched. To serve this purpose, three different industrailly available catalysts were used at two different concentrations in the hydrogenation of soybean oil. Soybean oil of definite initial fatty acid composition is subjected to hydrogenation in the presence of two nickel based (Nysosel 222 and SP 10) and one palladium based (Pd/Al_2O_3) catalysts and samples were taken at 20th, 40th, 60th, 80th and 100th minutes in order to monitor hydrogenation. Samples of previously measured fatty acid isomer composition, solid fat content, slip melting point and iodine values are subjected to rheological and microstructural analyses in order to determine whether there is a correlation in between.

Catalysts can be ordered according to the solid fat contents of the samples obtained by them, as SP10>N222>Pd/A. This order is parallel to the the one which, rheological tests and microstructural analyses exhibit. SP10-catalysed samples behave more elastic and are more readily crystallized; whereas Pd/A-catalysed samples behave less elastic and could barely crystallized.

The evidences of rheological and micro-structural tests were quite confirmative with the fatty acid distributions, solid fat contents, slip melting points and iodine values of the samples. The most selective catalyst was found to be SP10, with the products of the highest trans fatty acid concent and more solid-like; where the least selective one was Pd/A with lowest trans fatty acid content and least solid-like. Crystal number and properties, the behaviours of storage and loss moduli also supported trans fatty acid content of the samples. Also the moduli had a considerable parallelity with solid fat contents.

For the hydrogenation of general purpose vegetable oils, it is more proper to use catalysts with nickel as active metal than the ones in subsulfide form. Secondly, although polarized light microscopy gave sufficiently explicatory results for the microstructure of the fats upon cooling, more precise and detailed results can be obtained by transmission and scanning electron microscopy, X-ray scattering techniques and their combinations.

REFERENCES

Bell, A., Gordon, M. H., Jirasubkunakorn, W., & Smith, K. W. (2007). Effects of composition on fat rheology and crystallisation. *Food Chemistry, 101*(2), 799-805.

Campos, R., Narine, S. S., & Marangoni, A. G. (2002). Effect of cooling rate on the structure and mechanical properties of milk fat and lard. *Food Research International, 35*(10), 971-981.

Cepeda, E. A., & Calvo, B. (2008). Sunflower oil hydrogenation: Study using response surface methodology. *Journal of Food Engineering, 89*(4), 370-374.

Cizmeci, M. (2007). Heterojen katalizorlerin hidrojenasyon sirasinda yag asitleri izomerleri olusumuna etkisi. (Doctorate, Ankara Universitesi). *Ankara Universitesi Fen Bilimleri Enstitusu, 1* (1), 1-114. (N/A)

Cizmeci, M., Musavi, A., Kayahan, M., & Tekin, A. (2005). Monitoring of hydrogenation with various catalyst ratios. *Journal of the American Oil Chemists' Society, 82*(12), 925-929.

Cizmeci, M., Musavi, A., Tekin, A., & Kayahan, M. (2006). Comparison of two palladium catalysts on different supports during hydrogenation. *Journal of the American Oil Chemists' Society, 83*(12), 1063-1068.

Enig, M., Pallansch, L., Sampugna, J., & Keeney, M. (1983). Fatty acid composition of the fat in selected food items with emphasis on trans components1. *Journal of the American Oil Chemists' Society, 60*(10), 1788-1795.

Erickson, D. R. (1995). In Erickson D. R. (Ed.), *Practical handbook of soybean processing and utilization* [Practical Handbook of Soybean Processing and Utilization] (D. R. Erickson Trans.). (1st ed.). St. Louis, Missouri: AOCS Press.

Fellows, P. (2000). Properties of foods and processing theory. In P. Fellows (Ed.), *Food processing technology* [Food Processing Technology] (P. Fellows Trans.). (2nd ed., pp. 16-17). Washington DC: CRC Press.

Fernández, M. B., Piqueras, C. M., Tonetto, G. M., Crapiste, G., & Damiani, D. E. (2005). Hydrogenation of edible oil over pd-Me/Al2O3 catalysts (Me = Mo, V and pb). *Journal of Molecular Catalysis A: Chemical, 233*(1-2), 133-139.

Fernández, M. B., Sánchez M., J. F., Tonetto, G. M., & Damiani, D. E. (2009). Hydrogenation of sunflower oil over different palladium supported catalysts: Activity and selectivity. *Chemical Engineering Journal, 155*(3), 941-949.

Fernández, M. B., Tonetto, G. M., Crapiste, G. H., & Damiani, D. E. (2007). Revisiting the hydrogenation of sunflower oil over a ni catalyst. *Journal of Food Engineering, 82*(2), 199-208.

Fernández, M. B., Tonetto, G. M., Crapiste, G. H., Ferreira, M. L., & Damiani, D. E. (2005). Hydrogenation of edible oil over pd catalysts: A combined theoretical and experimental study. *Journal of Molecular Catalysis A: Chemical, 237*(1-2), 67-79.

Gabrovska, M., Krstić, J., Edreva-Kardjieva, R., Stanković, M., & Jovanović, D. (2006). The influence of the support on the properties of nickel catalysts for edible oil hydrogenation. *Applied Catalysis A: General, 299*, 73-83.

Ghotra, B. S., Dyal, S. D., & Narine, S. S. (2002). Lipid shortenings: A review. *Food Research International, 35*(10), 1015-1048.

Gray, J., & Russell, L. (1979). Hydrogenation catalysts—Their effect on selectivity. *Journal of the American Oil Chemists' Society, 56*(1), 36-44.

Hsu, N., Diosady, L., & Rubin, L. (1989). Catalytic behavior of palladium in the hydrogenation of edible oils II. geometrical and positional isomerization characteristics. *Journal of the American Oil Chemists' Society, 66*(2), 232-236.

Hudlicky, M. (1996). Catalytic hydrogenation. In M. Hudlicky (Ed.), *Reductions in organic chemistry* [Reductions in Organic Chemistry] (M. Hudlicky Trans.). (2nd ed., pp. 3-17). Washington DC: ACS Monograph.

Izadifar, M., & Jahromi, M. Z. (2007). Application of genetic algorithm for optimization of vegetable oil hydrogenation process. *Journal of Food Engineering, 78*(1), 1-8.

Izadifar, M. (2005). Neural network modeling of trans isomer formation and unsaturated fatty acid changes during vegetable oil hydrogenation. *Journal of Food Engineering, 66*(2), 227-232.

Jacob, J., & Leelavathi, K. (2007). Effect of fat-type on cookie dough and cookie quality. *Journal of Food Engineering, 79*(1), 299-305.

Jovanović, D., Čupić, Ž., Stanković, M., Rožić, L., & Marković, B. (2000). The influence of the isomerization reactions on the soybean oil hydrogenation process. *Journal of Molecular Catalysis A: Chemical, 159*(2), 353-357.

Karabulut, I., & Kayahan, M. (1999). Palm cekirdegi yaginin hidrojenasyonu sirasinda bazi fiziksel ve kimyasal O…zelliklerindeki degismelerin arastirilmasi. *Turkish Journal of Agriculture and Forestry, 101*(4), 891-897.

Karabulut, I., Kayahan, M., & Yaprak, S. (2003). Determination of changes in some physical and chemical properties of soybean oil during hydrogenation. *Food Chemistry, 81*(3), 453-456.

Kayahan, M. (2002). In Kayahan M. (Ed.), *Modifiye yaglar ve uretim teknolojileri* [Modified Fats and Production Technologies] (M. Kayahan Trans.). (1st ed.). Ankara: ODTU Gelistirme Vakfi Yayincilik ve Iletisim A.S. Yayinlari.

Larsson, R. (1983). Hydrogenation theory: Some aspects. *Journal of the American Oil Chemists' Society, 60*(2), 275-281.

Li, T., Zhang, W., Lee, R. Z., & Zhong, Q. (2009). Nickel–boron alloy catalysts reduce the formation of trans fatty acids in hydrogenated soybean oil. *Food Chemistry, 114*(2), 447-452.

Liu, W. H., Stephen Inbaraj, B., & Chen, B. H. (2007). Analysis and formation of trans fatty acids in hydrogenated soybean oil during heating. *Food Chemistry, 104*(4), 1740-1749.

Mensink, R. P., & Katan, M. B. (1990). Effect of dietary trans fatty acids on high-density and low-density lipoprotein cholesterol levels in healthy subjects. *New England Journal of Medicine, 323*(7), 439-445.

Mondal, K., & Lalvani, S. (2008). Low temperature soybean oil hydrogenation by an electrochemical process. *Journal of Food Engineering, 84*(4), 526-533.

Musavi, A. (2006). Hidrojenasyon kosullarinin izomer yag asitleri olusumu uzerine etkisi. (Doctorate, Ankara Universitesi). *Ankara Universitesi Fen Bilimleri Enstitusu, 1* (1), 1-103. (N/A)

Musavi, A., Cizmeci, M., Tekin, A., & Kayahan, M. (2008). Effects of hydrogenation parameters on trans isomer formation, selectivity and melting properties of fat. *European Journal of Lipid Science and Technology, 110*(3), 254-260.

Narine, S. S., & Humphrey, K. L. (2004). A comparison of lipid shortening functionality as a function of molecular ensemble and shear: Microstructure, polymorphism, solid fat content and texture. *Food Research International, 37*(1), 28-38.

Ojijo, N. K. O., Kesselman, E., Shuster, V., Eichler, S., Eger, S., Neeman, I., et al. (2004). Changes in microstructural, thermal, and rheological properties of olive oil/monoglyceride networks during storage. *Food Research International, 37*(4), 385-393.

Pérez-Martínez, D., Alvarez-Salas, C., Charó-Alonso, M., Dibildox-Alvarado, E., & Toro-Vazquez, J. F. (2007). The cooling rate effect on the microstructure and rheological properties of blends of cocoa butter with vegetable oils. *Food Research International, 40*(1), 47-62.

Pernetti, M., van Malssen, K. F., Flöter, E., & Bot, A. (2007). Structuring of edible oils by alternatives to crystalline fat. *Current Opinion in Colloid & Interface Science, 12*(4-5), 221-231.

Piqueras, C., Bottini, S., & Damiani, D. (2006). Sunflower oil hydrogenation on Pd/Al2O3 catalysts in single-phase conditions using supercritical propane. *Applied Catalysis A: General, 313*(2), 177-188.

Rao, M. A. (2007). In Barbarosa Canovas G. (Ed.), *Rheology of fluid and semisolid foods* [Rheology of Fluid and Semisolid Foods] (G. Barbarosa Canovas Trans.). (2nd ed.). New York: Springer.

Ribeiro, A. P. B., Grimaldi, R., Gioielli, L. A., & Gonçalves, L. A. G. (2009). Zero trans fats from soybean oil and fully hydrogenated soybean oil: Physico-chemical properties and food applications. *Food Research International, 42*(3), 401-410.

Ribeiro, A. P. B., Basso, R. C., Grimaldi, R., Gioielli, L. A., dos Santos, A. O., Cardoso, L. P., et al. (2009). Influence of chemical interesterification on thermal behavior, microstructure, polymorphism and crystallization properties of canola oil and fully hydrogenated cottonseed oil blends. *Food Research International, 42*(8), 1153-1162.

Riesz, C., & Weber, H. (1964). Catalysts for selective hydrogenation of soybean oil.[1] II. commercial catalysts. *Journal of the American Oil Chemists' Society, 41*(6), 400-403.

Rylander, P. (1970). Hydrogenation of natural oils with platinum metal group catalysts. *Journal of the American Oil Chemists' Society, 47*(12), 482-486.

Santana, A., Fernández, X., Larrayoz, M. A., & Recasens, F. (2008). Vegetable fat hydrogenation in supercritical-fluid solvents: Melting behavior analysis by DSC and NMR. *The Journal of Supercritical Fluids, 46*(3), 322-328.

Santana, A., Larrayoz, M. A., Ramírez, E., Nistal, J., & Recasens, F. (2007). Sunflower oil hydrogenation on pd in supercritical solvents: Kinetics and selectivities. *The Journal of Supercritical Fluids, 41*(3), 391-403.

Sowmya, M., Jeyarani, T., Jyotsna, R., & Indrani, D. (2009). Effect of replacement of fat with sesame oil and additives on rheological, microstructural, quality characteristics and fatty acid profile of cakes. *Food Hydrocolloids, 23*(7), 1827-1836.

Wright, A. J., Mihele, A. L., & Diosady, L. L. (2003). Cis selectivity of mixed catalyst systems in canola oil hydrogenation. *Food Research International, 36*(8), 797-804.

Wright, A. J., Wong, A., & Diosady, L. L. (2003). Ni catalyst promotion of a cis-selective pd catalyst for canola oil hydrogenation. *Food Research International, 36*(9-10), 1069-1072.

Zajcew, M. (1960). The hydrogenation of fatty oils with palladium catalyst. IV. pilot-plant preparation of shortening stocks. *Journal of the American Oil Chemists' Society, 37*(3), 130-132.

Zárubová, M., Filip, V., Kšandová, L., Šmidrkal, J., & Piska, I. (2010). Rheological and crystalline properties of trans-free model fat blends as affected by the length of fatty acid chains. *Journal of Food Engineering, 99*(4), 459-464.