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PHASE CHANGE UNDER STATIC ELECTRICAL FIELD; IN THE CASE OF LIPIDS

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ABSTRACT

Phase change in biological tissues may be affected by electrical and magnetic disturbances. Freezing under static electric field of water, aqueous solution and pork meat has been investigated by the authors, showing the ability of this process to refine ice crystals in frozen matrices. SEF affects the supercooling, which is usually reduced with SEF. SEF also triggers the nucleation. The use of radiofrequencies and microwaves has also been used recently by researchers to promote refined ice crystallization in food systems. A focus is proposed on recent experiments done on solidification of a vegetable fat mix (Vegetaline® – France) under static electric field (SEF). Results showed that SEF affects the supercooling and the phase change temperature of the fat mix indicating a possible impact on the crystalline structure of the solidified fat.

1. INTRODUCTION

Crystallization is a common process practiced in chemical and process engineering (Yan, Neve & Collins, 1997). Crystallization comprises of two processes, namely, nucleation and crystal (or nuclei) growth. Nucleation process during crystallization process can be affected by some traditional techniques like agitation, mechanical shock, friction and extreme pressure within solutions and melts (Yan et al., 1997). Many researchers have used some new methods, such as; pressure shift, ultrasound, electric field and microwave assisted freezing and cooling process (Yan et al., 1997; Chevalier, Le Bail, & Ghoul, 2000; Li & Sun, 2002; Orłowska, Havet, & Le-Bail, 2009; Xanthakis, Havet, Chevallier, Abadie, & Le-Bail, 2013; Xanthakis, Le-Bail, & Ramaswamy, 2014). The findings related to various novel methods assisted cooling and freezing is presented in Table 1. Application of static electric field during cooling and freezing affects the heat and mass transfer for dielectric crystallization during overall crystallization process (Yan et al., 1997).

In the case of lipids, polymorphism is associated with difference in packing of the hydrocarbon chains and their angle of tilt (Marangoni, 2010). In fats, crystals primarily form three major polymorphs: α , β' and β (C Lopez, Lesieur, Bourgaux, & Ollivon, 2005; C

Lopez, Lesieur, Bourgaux, Keller, & Ollivon, 2001; Marangoni, 2010; Rønholt, Kirkensgaard, Mortensen, & Knudsen, 2014; Ronholt, Kirkensgaard, Pedersen, Mortensen, & Knudsen, 2012). The alpha form is metastable and will thus transform into more stable forms. Two crystalline forms are called monotropic when one is more stable than the other, and recrystallization will take place in the direction of the more stable form only.

Table 1. Studies related to cooling and freezing assisted by various novel methods.

Method	Sample	Mechanism	Effect	Authors
Pressure shift freezing	Gelatin gels	Manipulates the melting point of water by shifting the operating pressure	Increases the degree of supercooling; produces smaller crystals	Chevalier et al., 2000
Ultrasound	Potato	Induces nucleation due to cavitation	Increases the degree of supercooling; produces smaller crystals	Li et al., 2002
DC electric field	Butter	Induces nucleation due to realignment of molecular orientation	Increases the degree of supercooling; produces stable crystals, highest heat flow was observed for butter treated cooled under electric field	Yan et al., 1997
	Distilled water		Decreases the degree of supercooling; produces smaller crystals	Orlowska et al., 2009
	Pork meat			Xanthakis et al., 2013
Microwave	Pork meat	Disrupts water pentamers, resulting in increasing the number of nucleation sites.	Decreases the degree of supercooling; produces smaller crystals	Xanthakis et al., 2014

Degree of supercooling (or undercooling) acts as a driving force for nucleation for fat crystals. When a high degree of supercooling is provided, molecules have less time to pack in the most thermodynamically stable configuration and thus metastable form crystals are formed. Metastable forms have a lower free energy on nucleation ($\Delta G_n^\#$) than the more stable forms as shown in Figure 1. Long hydrocarbon chain generally takes long time align for stable configuration. Crystal growth of TAG molecules depends on a number of factors, such as; degree of supercooling, melt viscosity, the rate of molecular diffusion to the crystal surface, and the time required for TAG molecules to fit into the growing crystal lattice. Growth rate is inversely proportional to melt viscosity, which tends to increase with decreasing temperature. Faster cooling rate favours formation of small crystals with firmer (rigid) crystal network, whereas slow cooling results in larger and stable crystals with less contact points resulting in soft network (Rønholt et al., 2014). Rønholt et al. 2014 reported that butter produced from fast cooled cream had higher G' value compared to slow cooled one.

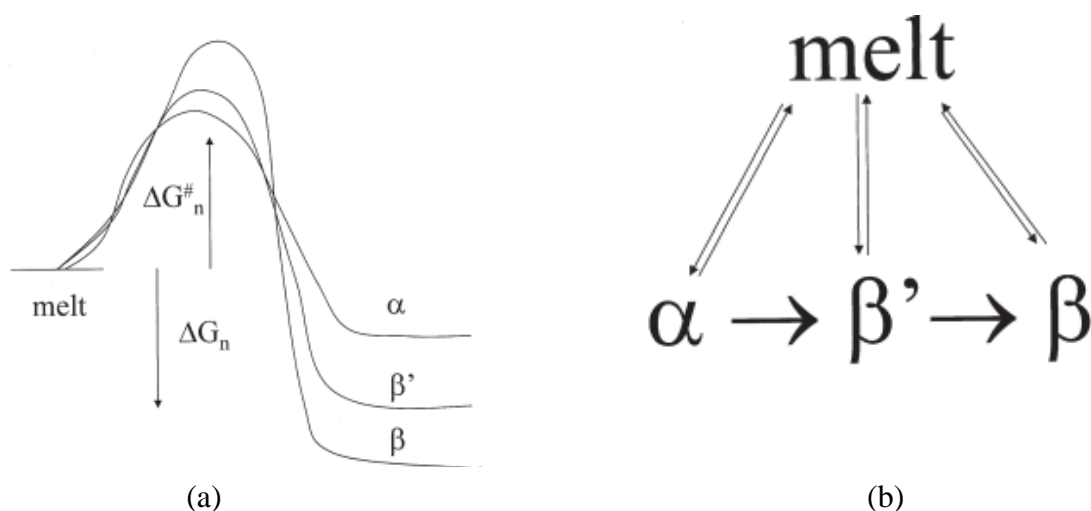


Figure 1. (a) Diagram depicting the free energy of activation (kinetics of formation) for the formation of a particular polymorph as well as the free energy difference between products and reactants (thermodynamic stability), (b) Dynamics of polymorphic crystallization and recrystallization in fats.

Table 2. Characteristics of the different polymorphic forms in TAGs (Marangoni, 2010).

Characteristic	α Form	β' Form	β Form
Chain packing	Hexagonal	Orthorhombic	Triclinic
Short spacing(s)	0.415 nm	0.38 and 0.42 nm	0.46 nm
IR Spectrum (-CH ₂ -) rocking vibration	Singlet at 720 cm ⁻¹	Doublet at 727 cm ⁻¹ and 719 cm ⁻¹	Singlet at 717 cm ⁻¹
Density	Least dense	Intermediate	Most dense
Melting Point	Lowest	Medium	Highest

This study aims at studying the impact of static electric field on the crystallisation of a commercial mix of hydrogenated copra oil and palm oil (Vegetaline® - France), which is known to develop beta prime fat crystals.

2. MATERIAL and METHODS

Vegetaline (France) has been used for the tests; this commercial fat mix is made of hydrogenated coconut oil and palm oil. The system used to solidify the fat has been presented in previous paper of Orłowska et al. (2009). The sample holder, was made of Ertacetal (DSM EPP). A square hole was machined in the centre of the holder (named as measurement cell). The sample was installed in this cavity (volume 1.6 ml). The internal dimensions of the measurement cell were as follows: 3 mm depth, 20 mm in length, 20 mm in width. An aluminium electrode (50 x 50 x 2 mm – length x width x thickness) was placed 2 mm above the sample surface. The ground electrode was the metal plate of the MPA100. A Peletier element was used (Melcor, USA) on which sample holder was assembled. The high voltage was provided by DC voltage generator connected to the upper electrode. Voltage applied in the experiments ranged from 0 kV to 10 kV corresponding to SEF of 0 to 4·10⁶ V/m respectively. The sample was cooled by the Peletier element connected to the temperature controller Eurotherm 2408. A real-time measurement of the temperature was obtained with a Luxtron 790 Fluoroptic Thermometer equipped with optical fiber (Luxtron, model: 00-11511-4th IIR International Conference on Sustainability and the Cold Chain, Auckland, New Zealand, 2016

01), data acquisition system (Datalog – AOIP-France). The temperature sensor was installed inside of the measurement cell in a central location (1 mm from upper and lower surface of the sample) and was therefore always immersed in the lipid. The optical fibre was calibrated against a reference platinum probe (Comptoir Lyon Allemand – Lyon-France). During measurements temperature changes of the sample were recorded every second with the data logger with an accuracy of ± 0.1 °C. New copra fat sample was used for each test; it was fully melted at 60°C for 10 min prior to any test to prevent the presence of any crystal ghosts. A set point of 15°C was imposed to the Peltier element and the test was stopped when the sample reached the temperature of 17°C. DSC tests have been performed using a Pyris 7 (Perkin Elmer – USA) at 2°C/min to determine the onset temperature, peak temperature and latent heat of the fat. Miniature sealed aluminium pans were used containing ca. 50 mg of fat. An empty pan was used as reference. The run started by a temperature equilibration at 5°C for 10 minutes followed by a temperature rise at 2°C/min up to 60°C to have a full melting of the fat. The DSC was previously calibrated using distilled water and indium. Dry nitrogen gas flow of 20 ml/min was used to prevent moisture condensation on the cells in the DSC. All tests were done in duplicate.

3. RESULTS

3.1. Experimental results during solidification under SEF

Time temperature history during cooling and solidification of the Vegetaline ® samples for different voltages (corresponding to different values of SEF) are shown in Figure 2. A temperature plateau was observed during the crystallisation of the fat mix. Supercooling was observed until 8 kV whereas in the case of 10 kV no supercooling was observed.

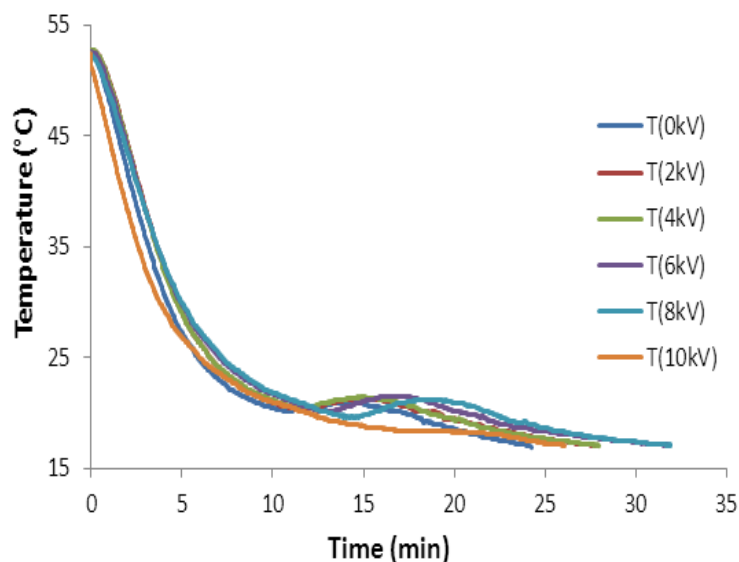


Figure 2. Experimental results for cooling the Vegetaline ® under influence of voltages.

The degree of supercooling, corresponding between the temperature difference between the lowest and highest temperature during the temperature rise observed at the onset of crystallization is plotted in Figure 3 showing an increase with increasing voltage.

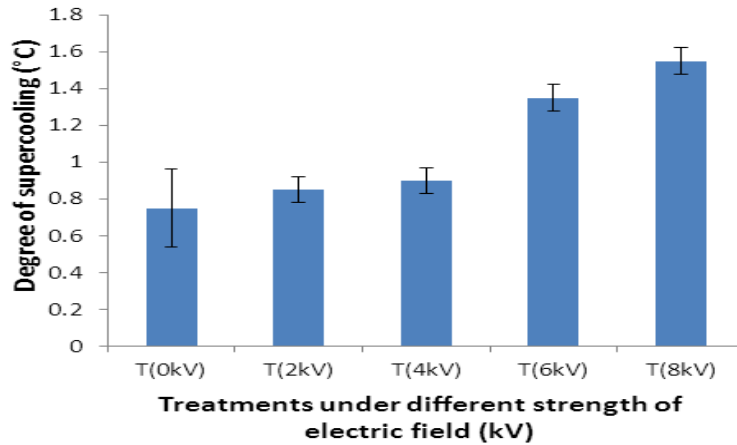


Figure 3. Evolution of the degree of supercooling in function of the voltage applied during solidification of the Vegetaline®. No supercooling was observed at 10 kV voltage.

3.2. DSC tests of the solidified fat

Following the tests, the solidified fat was studied in DSC. The tests were carried out just after the solidification (0 day or less than 2 hours after solidification tests) and after 1 day storage at 4°C to complete the solidification of the fat. Results are presented in Table 3. Results obtained after 1 day storage seemed to be steadier and were considered for analysis. For instance, the progressive increase in the latent heat of melting (measured between 5 °C and the termination of the endothermic peak at around 60 °C) observed at 1 day storage indicates that results obtained at 1 day storage are more logical and therefore more reliable. Completion of fat solidification requires some time due to the slow diffusion of non-solidified molecules towards the crystals initiated during the initial crystallization.

Table 3. Effect of electric field on the fat melting observed during DSC tests.

Treatments	T onset (°C)		Peak temperature (°C)		T offset (°C)		ΔH (J/g)	
	0	1	0	1	0	1	0	1
0 kV	14.13	18.93	28.35	28.80	34.08	33.62	99.83	100.47
2 kV	16.01	15.11	28.60	29.07	34.25	34.36	103.48	100.15
4 kV	13.86	15.07	28.70	29.17	34.26	34.52	99.40	100.95
6 kV	14.45	16.11	28.86	29.15	34.28	34.67	98.55	102.29
8 kV	14.68	16.28	29.37	29.46	34.60	34.98	98.82	102.29

Table 4. Crystallization behavior of fat cooled under different strength of electric field.

Time (s) taken for onset of crystallization					
Treatments	0 kV	2 kV	4 kV	6 kV	8 kV
	664.8	711	721.8	805.8	882
Time (s) spent in the plateau region during crystallization process					
Treatments	0 kV	2 kV	4 kV	6 kV	8 kV
	337.8	360	349.8	399	475.8
Time (s) to reach the final temperature of cooling (17 °C)					
Treatments	0 kV	2 kV	4 kV	6 kV	8 kV
	1455	1663.8	1677.6	1906.8	1914

3.3. Global analysis of results

As a global result, it appears that a higher supercooling was observed with increasing SEF. This is opposite to what was observed in the case of water (Orlowska et al., 2009). The melting enthalpy observed in Table 3 indicates that a more complete crystallization was observed with increasing SEF. This may be attributed to the impact of SEF which is known to increase the number of nucleation sites, which in turn may result in a higher degree of crystallization. Other values from this table showed that the peak temperature and offset temperatures are increasing with increasing SEF. This may be due to interactions between SEF and crystallization phenomena. Deconvolution of the DSC peaks may help in detecting the ratio of alpha, beta' and beta crystals for example. Further tests using X rays diffraction would be also needed to better understand the underlying phenomena.

4. CONCLUSION

Solidification tests of a commercial fat mix (hydrogenated coconut oil and palm oil) were carried out in a miniaturized cooling system equipped with a Peletier element. Results showed that SEF interacts with the crystallisation phenomena; supercooling as well as latent heat of the solidified fat increased with increasing voltage. Further tests are needed using deconvolution of the DSC signal and X rays diffraction to better understand if SEF affects the type of fat polymorphs forms during solidification.

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