Dynamics of moisture migration in structured fat as moisture barrier in food

Thesis

Presented in Partial Fulfillment of the Requirements for the Honors Program of

College of Food Agricultural and Environmental Sciences

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2014

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1. Introduction

Moisture migration is a great concern for the food industry because it can shorten the shelf-life of the product, making it unappealing to the consumers in terms of safety and quality. Moisture migration can occur between different phases in a multi-component food system, and between food and the atmosphere. In a food system that contains a mixture of domains with different moisture levels, such as raisin bran and cream-filled pastry, moisture migration proceeds from domain that has high moisture content to domain that has low moisture content until an equilibrium is reached (Ghosh and others 2005). The force governing the transfer of water is not a differential in concentration or volume, but a differential of the chemical potential of water generally expressed by its activity, mole fraction or partial pressure for gaseous phases (Roudaut and Debeaufort 2010). There are some ways to prevent moisture migration in a complex food system. For example, by making the domains to have the same moisture content and using packaging that is impermeable to moisture. However, setting food components to have the same moisture content is undesirable in most cases because the different food components would have exact same texture, which could decrease consumer liking. Packaging would work to limit moisture migration from food to the atmosphere, although it cannot limit moisture migration within the food. A feasible solution to limit moisture migration is the application of an edible barrier to prevent water movement within the food components.

An edible film is defined as any type of material used for coating various foods to extend shelf-life of the product that may be eaten together with food with or without further removal (Pavlath and Orts 2009). There are various materials that can be made into edible films, such as polysaccharide, lipid, and protein. However, lipid might be the best candidate for moisture migration barrier because of its hydrophobicity. Several studies have shown that edible lipid

films can limit water vapor transfer efficiently (Martini and others 2006a, Martini and others 2006b, Ghosh and others 2005). There are some factors that affect moisture permeability of lipid films, such as their structure, chemical arrangement, hydrophobicity, physical state, conditions of testing and film preparation (Borlieu and others 2009). Water vapor permeability (WVP) of lipid films can be decreased by increasing solid fat content (SFC) which also means increasing tightness of crystalline packing (Ghosh and others 2005). This might be caused by the water particles travelling more slowly due to the lack of space within the lipid structure. Polymorphism can also affect moisture permeability of the lipid film. α polymorph is more permeable than β polymorph and β' polymorph because of its lower melting point and thermodynamic instability (Ghosh and others 2002). Increased thickness of the lipid film and low incubation temperature decreases moisture migration because of the longer pathway that water particles have to go through and decrease in water vapor mobility and increase in SFC at lower temperatures (Ghosh and others 2005). Film preparation that allows good distribution of lipid particles would decrease WVP of the film and medium-level adhesion to the product that allows room for expansion when the product absorbs moisture would decrease the tendency of the film to crack (Morillon and others 2002). The modification of these various lipid properties is important to maximize the capacity of a lipid film as a moisture barrier.

Another major factor that could affect moisture diffusivity of a lipid film is ingredient interaction. In many food products, lipid is usually combined with other ingredients before being applied to food products. For example, cocoa butter, the most widely-used material for edible lipid film, is usually mixed with sugar, lecithin, and cocoa powder to improve its flavor, appearance, and taste (Ghosh and others 2005). The property of each type of ingredient in the film could affect its hydrophobicity and moisture diffusivity of the film. Hydrophilic ingredients,

such as dextrose, might absorb much moisture that would cause structural changes to the film (Ghosh and others 2005). Even though controlling ingredient interaction is not an easy task, physical modification of lipid could be used to enhance lipid film's moisture barrier capacity.

It has been shown that modification of lipid structural properties influences oil migration (Lipp and others 2000). Physical properties of lipid film can be modified by using mechanical action, such as shearing. Mazzanti and others (2008) showed that shearing application on milk fat reduced the onset time of α to β' phase transition. Since the β' formation is more stable than α formation, shearing might help in improving impermeability of lipid films. Shearing can also arrange lipid crystallites to be oriented in a direction parallel to the external shear field, reduce the size of crystal clusters, and lower the density of the lipid (Maleky and others 2011; Maleky and others 2012). These changes reduce oil permeability of lipid. For example, sheared cocoa butter was shown to have lower rate of oil diffusion compared to cocoa butter that was statically crystallized (Maleky and others 2012). Bolliger and others (1999) found that increasing shear speed during tempering of cocoa butter increased viscosity and melting enthalpy, consequently decreased solidification time. And shearing might also reduce moisture permeability of lipid because it was expected that water vapor and oil move through the same route through the film. It is important, therefore, to investigate the effect of shearing on lipid barrier moisture permeability because there are many properties that can be influenced by shearing. The findings could then be used to maximize the potential of lipid layer as a moisture barrier.

The objective of this research was to evaluate if there was a difference in moisture migration through lipid barriers that were structurally modified (sheared) and moisture migration through lipid barriers that were not structurally modified (static) in a controlled humidity environment.

2. Materials and Methods

2.1 Preparation of Structured Fat Samples

Two different lipid samples, including pure cocoa butter (Peter's Chocolate, Lititz, PA) and a mixture of canola oil and IHCO (60% IHCO w/w and 80% IHCO w/w) were used. All of the samples were heated sufficiently to allow complete melting and destruction of crystal memory. Cocoa butter was melted at 70°C and held at 50°C for 10 min. IHCO was melted and held at 80°C for 30 min, and liquid canola oil was added after IHCO had been melted completely. Each of the samples were then divided into 2 groups, cooling under laminar shear application and cooling in the absence of laminar shear (static condition). For the cocoa butter sheared samples, the cooling process was done for 12 minutes in a beaker immersed in a 22°C water bath while the shearing blade was running at a shear rate of 180 s^{-1}. The cooling conditions were set the same for IHCO sheared samples. However, because of the faster crystallization property of this sample, the cooling process was done for 4 minutes at a shear rate of 260 s^{-1}. The samples were then molded into thin discs and were used in moisture migration monitoring. For the static samples, the melted lipid was pipetted into the molds and therefore the crystallization process happened on the molds.

2.2. Moisture Loss Monitoring

The procedure was based on the procedure used by Martini (2006b). A mixture of 37.5% w/w of silica gel (Fisher Scientific Pittsburgh, PA), 3% w/w of hydroxypropyl methyl cellulose (The Dow Chemical Co., Midland, MI), 13.2% w/w of saturated solution of MgCl2 • 6H2O (Fisher Scientific, Pittsburgh, PA), and 46.3% w/w of deionized water was prepared in order to obtain 95% of relative humidity (RH) as a model ambient humidity. The crystalized samples were put on top of plastic cups filled with the silica gel mixture and sealed with additional lipid

material. They were then stored at 5°C and 30°C in desiccators with controlled RH at 33% using a saturated MgCl2 • 6H2O solution. The pressure gradient (4.14 mmHg) was calculated based on procedures by Ghosh and others (2005). The WVP was calculated for each replicate separately and then averaged. Five replicates of the samples were weighed everyday until day 10, then periodical weighing was done until day 46 for cocoa butter samples and day 56 for IHCO samples. Weight loss was calculated at each time point and a plot of weight loss vs time was constructed.

2.3 Water Vapor Permeability Calculation

WVP is a state of material that allows water vapor to pass through it (Martini and others 2006a). The physical state of the lipid component has a strong influence on the WVP of the film; water is less soluble in solid lipid than it is in liquid lipids (Ghosh and others 2005). In this study, WVP will be determined by first calculating water vapor transmission rate (WVTR). WVPR will be calculated by the equation:

$$WVPR = slope/A$$

where slope is the slope of a straight line portion of the plot of weight loss vs time (g/days) and A is the area of the film used, which was calculated as the area of the AQUALAB cups (11.95 cm^2). WVPR will be reported in g days-1 cm-2. Then, WVP will be calculated using the equation:

$$WVP = WVTR \bullet \Delta x/\Delta p$$

where Δx is the thickness of the film (mm) and Δp (mmHg) is the vapor pressure difference between both sides of the film. The units for WVP will be g mm days-1 cm-2 mmHg-1. WVP will be calculated for each replicate and the average will be taken.

2.4 X-ray diffraction (XRD)

The polymorphism of the crystallized samples was determined at the beginning and the end of gravimetric test with X-ray diffraction. A Rigaku Miniflex X-ray diffractometer (Rigaku, Tokyo, Japan) was utilized. The apparatus had a 1.25° divergence slit, a 1.25° scatter slit, and a 0.3mm receiving slit. For the copper tube, accelerating voltage was 30 kV and current was 15 mA. Testing materials were sliced thinly and gently packed into sample disks that came with the instrument. Disks were then placed into sample holder and scanned from 50 to 300 at rate of 2°/min. The results were analyzed using Jade 8.0 software (Materials Data Incorporated, Livermore, California). At least one scan of one replicate in each sample set was performed.

2.5 Polarized light microscopy (PLM)

Lipid films that had not been incubated were viewed under PLM (Carl Zeiss Microscopy, LLC, Oberkochen, Germany) to visualize the crystal structures. The samples were dissolved in canola oil in a 1:2 w/w ratio. Small portion of the mixtures were then transferred onto microscope slides and viewed using the transmitted light.

2.6 Solid fat content measurement

Solid fat content (SFC) was measured by means of pulsed nuclear magnetic resonance (p-NMR) using a Bruker Minispec spectrometer (Bruker Optics Ltd., ON, Canada). Glass NMR tubes (10 mm diameter, 1 mm thickness, and 180 mm height) were filled with approximately 3 g of the crystallized samples (samples were cut in small pieces and placed in the tube). Crystallized samples were kept at the crystallization temperature, 20°C, for 7 days to monitor the SFC variation during storage.

3. Results and Discussion

3.1 Cocoa butter

Figure 1 and Figure 2 showed a bigger slope for static samples, meaning that more moisture escaped through static samples than it did through the sheared samples. The weight loss results corresponded to sheared cocoa butter having lower levels of WVTR and WVP compared to static cocoa butter (Table 1). A larger difference in WVP was observed in samples incubated at 5°C, with sheared samples having WVP of 0.021 g/day cm mmHg and static samples having WVP of 0.041 g/day cm mmHg. Overall, static and sheared cocoa butter samples that were incubated at 30°C had higher WVP compared to static and sheared cocoa butter samples that were incubated at 5°C. The observed lower WVP at lower temperature might be caused by decreased mobility of moisture and differences in lipid film structure that might impact its moisture permeability (Ghosh 2005). Morillon and others (2002) stated that there was a 10% increase in SFC when temperature was reduced from 26°C to 20°C. In this study, measurements of SFC showed a slight difference in sheared and static samples of cocoa butter, with the static samples having 1.3-1.8% higher SFC than sheared samples (Table 1).

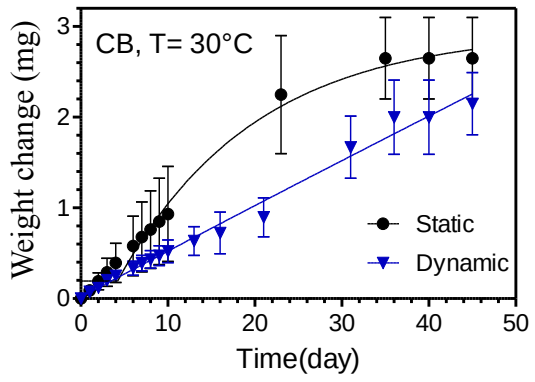

Fig. 1 Weight loss of static and sheared cocoa butter samples at 30°C.

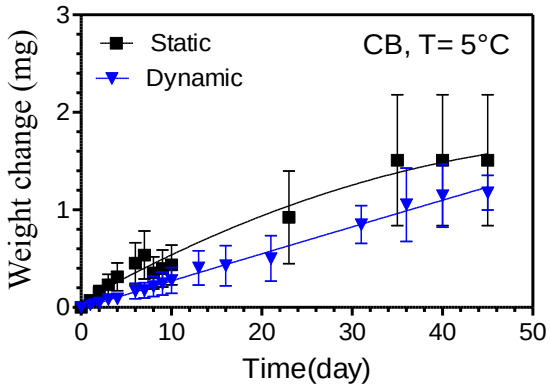

Fig. 2 Weight loss of static and sheared cocoa butter samples at 5°C.

Table 1. WVTR and WVP of static and sheared cocoa butter samples incubated at different temperatures.

Temperature		Static samples	Sheared samples
30°C	WVP (g/day cm mmHg)	0.072	0.040
	SFC (%)	78.5	77.1
5°C	WVP (g/day cm mmHg)	0.041	0.025
	SFC (%)	81.3	80.2

X-ray diffraction analysis showed no difference between sheared and static samples with all cocoa butter samples having β' polymorphism (Figure 3). This suggested that shearing did not have significant effects on the arrangement of crystal packing.

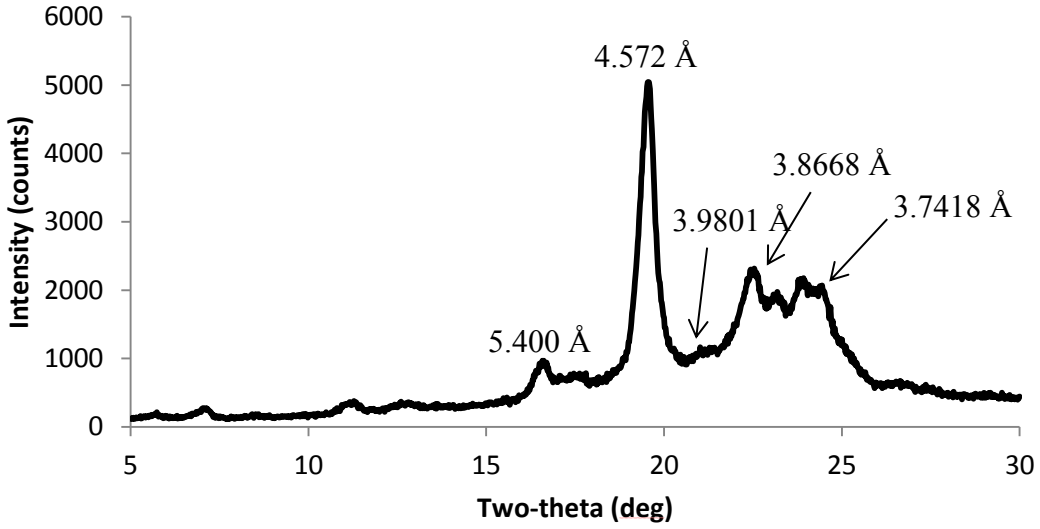

Figure 3. X-ray diffraction graph of cocoa butter showing β' polymorphism. Sheared and static samples had the same polymorphism.

Observation under PLM showed that there was a difference between sheared and static cocoa butter samples (Fig. 3). Visualization using 50X objective lens revealed that sheared sample had smaller crystalline structure compared to static sample. The smaller aggregates might influence moisture permeability of the sample since sheared cocoa butter sample was less permeable to moisture than static sample.

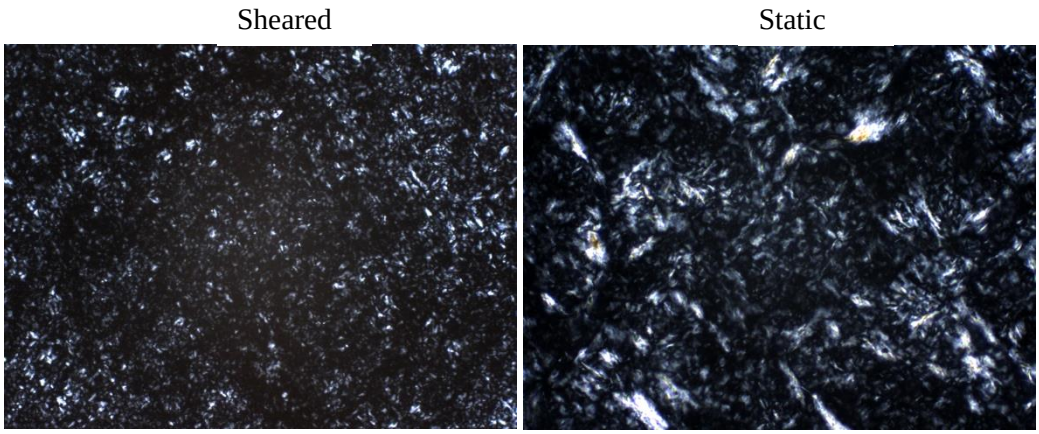

Figure 3. Observation by PLM (50X objective lens) of the physical structure of cocoa butter formed during crystallization under static and sheared cooling conditions.

3.2 IHCO blends

For the IHCO samples, static samples containing 60% IHCO had higher WVP compared to their sheared counterparts (Table 2). The opposite was observed in samples containing 80% canola oil. Sheared samples had a higher WVP of 0.319 g/day cm mmHg compared to static samples. This was reflected in the weight loss graphs. Figure 3 showed a steeper slope for static samples of 60% IHCO samples compared to sheared 60% IHCO and Figure 4 showed a more drastic weight loss for sheared 80% IHCO compared to the static samples. The WVP differences of sheared and static samples of 60% and 80% IHCO might be caused by variations in structure of the film as a result of the different ratios of liquid canola oil to IHCO. There might be an optimum ratio that could maximize the barrier performance. Static 60% IHCO had slightly higher WVP compared to static 80% IHCO, while sheared 60% IHCO had lower WVP compared to sheared 80% IHCO. As expected, SFC of 60% IHCO samples was lower than SFC of 80% IHCO samples. The SFC of sheared samples was slightly higher than SFC of static

samples.

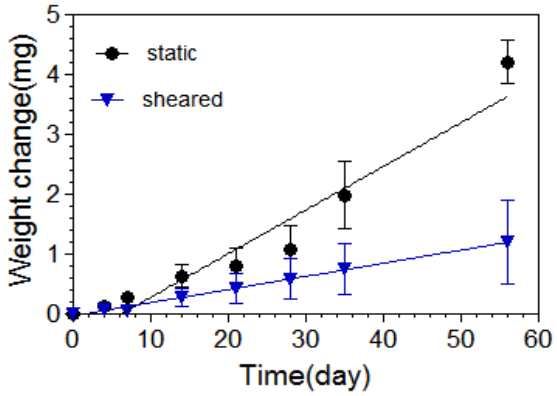

Fig. 4 Weight loss of static and sheared 60% IHCO samples 20°C.

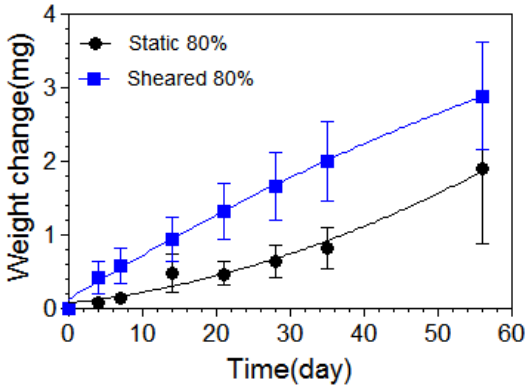

Fig. 5 Weight loss of static and sheared 80% IHCO samples 20°C.

Table 2. WVTR and WVP of static and sheared IHCO samples incubated at different temperatures.

Percentage of canola oil		Static	Sheared
60%	WVP (g/day cm mmHg)	0.278	0.274
	SFC (%)	57.4	58.2
80%	WVP (g/day cm mmHg)	0.149	0.319
	SFC (%)	77.1	78.1

X-ray diffraction analysis showed that the sheared and static samples had the same polymorphic behavior (Figure 6). The β' polymorphism means implies that the samples were in a stable form compared to other possible polymorphisms. As in cocoa butter sample, shearing of IHCO did not affect its polymorphic behavior.

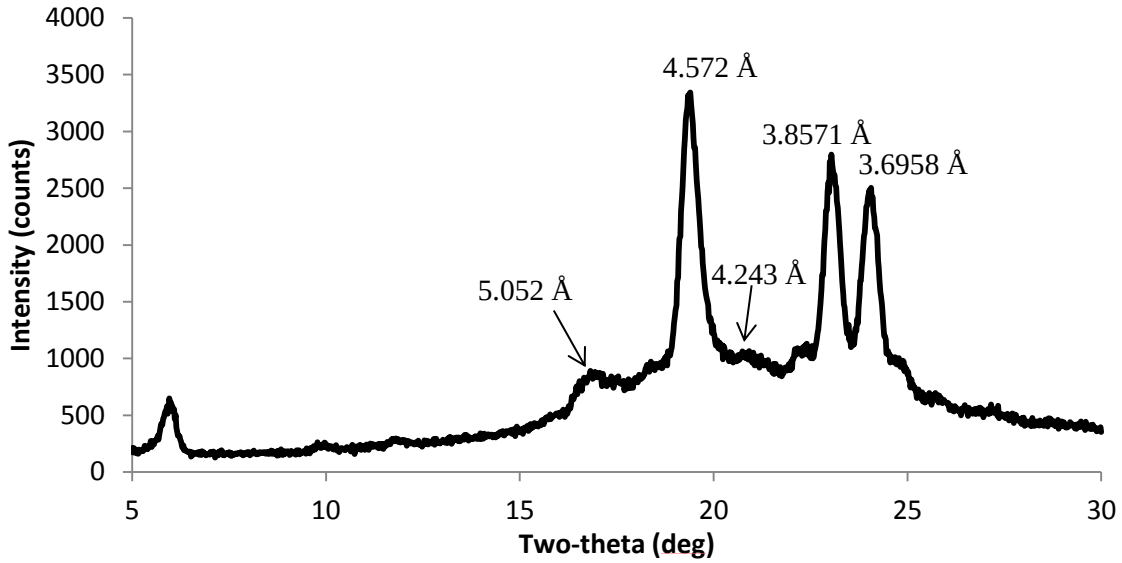

Figure 6. X-ray diffraction graph of IHCO showing β' polymorphism. Sheared and static samples had the same polymorphism.

Even though sheared and static IHCO samples had similar SFC values and polymorphism, observation under PLM showed that sheared and static IHCO samples had different micro structure. In sheared samples, the crystal structures had more distinct shape and pattern than those in static samples. The crystals in static samples were smaller and dispersed. Similar results were observed in 60% IHCO and 80% IHCO. Acevedo and others (2012) showed that a shear rate of 240 s^{-1} during crystallization of fully hydrogenated soybean oil can break the crystals, resulting in a more compact aggregation. This was consistent with the observed crystal structure of IHCO sheared samples which was tightly packed and organized.

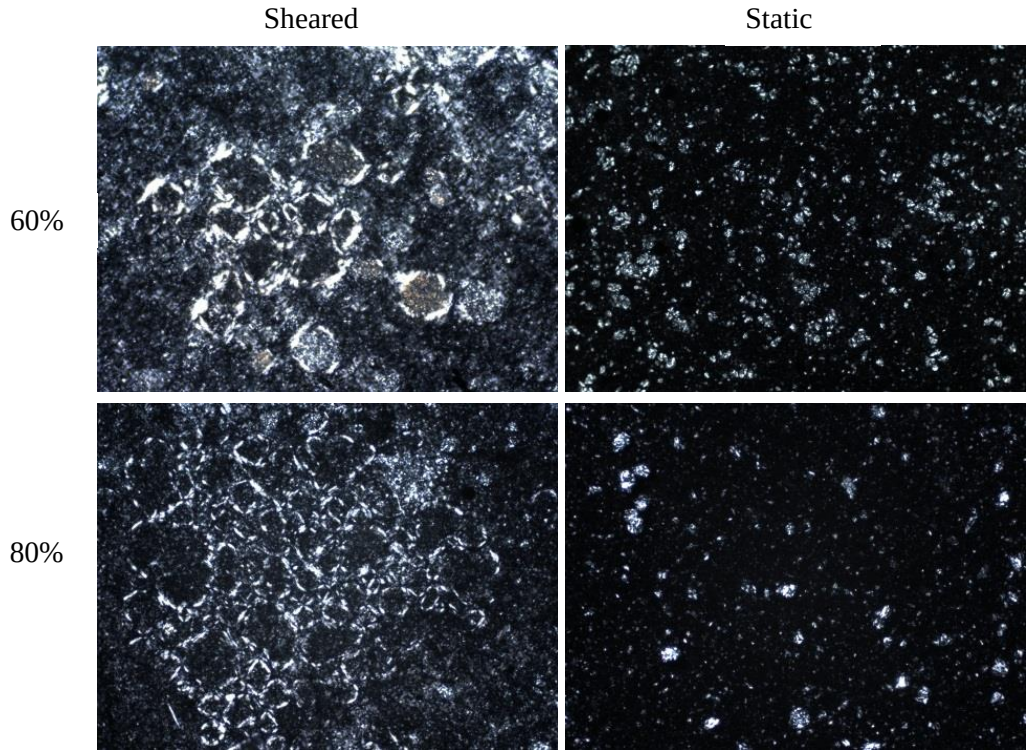

Figure 7. Observation by PLM (20X objective lens) of the physical structure of different IHCO blends formed during crystallization under static and sheared cooling conditions.

4. Conclusion

Studies have found that the application of physical force to lipid could change lipid nanostructures and its moisture permeability. Understanding this phenomenon is important to limit problems in the food industry concerning moisture migration in a complex food matrix. In this study, sheared cocoa butter film showed lower weight loss compared to static cocoa butter film. In other words, sheared samples had lower WVP than static samples. However, IHCO samples had mixed results, where at 60% IHCO, sheared samples had lower WVP, while at 80% IHCO, sheared samples had higher WVP. This suggested that shearing might have different effects for different canola oil concentrations. There might be an optimum ratio of liquid canola

oil and IHCO for maximum impermeability of the lipid film. SFC did not have a significant difference between sheared and static samples in both cocoa butter and IHCO, indicating that the shearing process had little to no effect on this property. Measurements by X-ray diffraction also showed similar polymorphism for sheared and static samples. Another lipid property that was analyzed in this study, crystal structure, might be highly affected by shearing. Visualization by PLM showed significantly different crystal structure of sheared and static samples. In cocoa butter, static samples had larger, randomly arranged crystal structures, while sheared samples had smaller crystalline. IHCO static samples were smaller and dispersed than IHCO sheared samples. Because of the similarity in SFC and polymorphism of the lipids while the samples showed different rate of moisture migration, this difference in structural property of the lipid might have high correlation to WVP of the samples.

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