DOCTORAL THESIS

Influence of Tri-Saturated Glycerides on Crystallization and Melting Behavior of Coconut Oil

Summary

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The coconut oil (CO) has become popular in recent years because of its beneficial effects of medium-chain fatty acids on human health. However, CO also contains traces of long chain fatty acids. Many researchers have blended CO with other fats to expand its specific uses. In order to a wider application of CO, we must understand how to control a crystallization of CO by triacylglycerol (TAG) additives. Therefore, this study reports the effects of the existence of saturated TAGs on crystallization and melting behavior of CO from a variety of perspective. The addition of saturated TAGs in CO as a mixture and as a seed crystal was investigated with the purpose of clarifying the crystallization mechanism. Furthermore, the applying of saturated TAG seed in CO during fractionation process was also carried out in order to link to application uses. The study was conducted into 3 sections as follows:

Study 1: Effects of TAG additives on crystallization and melting behavior of CO

The crystallization behavior of CO with tripalmitin (PPP) and tristearin (StStSt) as additives was investigated. The effects of cooling rates and TAG concentrations on crystallization and melting behavior of CO were studied by differential scanning calorimetry (DSC) and optical microscopy. Polymorphs were also determined by synchrotron radiation X-ray diffraction (SR-XRD). The results are summarized as follows:

1. From DSC results, two exothermic peaks for CO crystallization indicated two compositions in CO. From SR-XRD results, the α form crystallized first at a high crystallization temperature (HTc) followed by β′ crystallization at low temperature (LTc). Both HTc-α and LTc-β′ transformed into the β′ form of CO (CO-β′) solid solution during heating.

2. Although the addition of PPP increased crystallization temperature of CO, it did not change its polymorphic pattern. However, during slow cooling with the StStSt additive, CO-β′ crystallization was induced from the melt directly.

3. Under an isothermal condition, the crystallized StStSt spherulites induced nucleation of CO more than PPP did. Therefore, PPP increased the crystallization temperature of CO in both HTc and LTc fractions without changing the polymorph of CO, while StStSt promoted crystallization of CO directly into CO-β′.

The study in this part reported that the nucleation of CO was promoted by the PPP and StStSt, which priory crystallized as seed crystals. The incremental improvement in crystallization rate through the use of high melting additives could decrease process costs, especially in products requiring rapid crystallization rates such as chocolate coatings and cookie fillings. However, it remains unclear which polymorphs of PPP and StStSt were most effective in promoting and controlling the crystallization behavior of CO. Therefore, the effect of seed polymorphs would be clarified in Chapter 4.

Study 2: CO crystallization on PPP and StStSt seed crystals with different polymorphs

The influence of the polymorphs of TAGs seed crystals on the crystallization of CO using seeding techniques was evaluated. The PPP and StStSt with three polymorphs (α, β', and β forms) were used as the seed materials. The two β forms were prepared by transforming in solid state from α form (β_α) and by annealing TAG powder (β_{ann}). The CO crystallization on the TAG seed crystals was observed at 20°C using differential interference contrast microscopy and SR-XRD. The effects of seed polymorphs are summarized as follows:

1. The seed crystals with different polymorphs of PPP and StStSt promoted the nucleation of the β' form of CO by heterogeneous nucleation.

2. The seed crystals with β' form were the most effective accelerators, indicating that polymorphic matching between seed crystals and CO strongly induced the nucleation of CO by epitaxial growth.

3. The high melting fraction of CO was specifically induced to crystallize on the surface of the single crystal-like morphology of the β_{ann} seed via the template effect with the same orientation as the seed.

These results indicate that the polymorph of seed crystals significantly affects the efficiency of CO crystallization. Efficient seedings can be used to improve the physical properties of CO via fractionation. The promotion of crystallization of CO high-melting fraction by β_{ann} seed is the most consideration for further fractionation in Chapter 5. The use of PPP and StStSt and other trisatulated TAGs in β_{ann} form as seeds supposes to increase the efficiency of the separation of TAGs with long chain-saturated fatty acids (LC-SFAs).

Study 3: Effects of TAG seeding on crystallization and melting behavior of CO-fractions obtained by dry fractionation

The dry fractionation of CO with crystal seeding technique was conducted. The effect of TAG seed crystals, trilaurin (LLL), trimyristin (MMM), PPP, and StStSt, and fractionation temperatures on the crystallization and melting behavior of CO fractions was investigated by DSC, SR-XRD, and optical microscopy. The fatty acid and carbon number contents of the CO fractions were analyzed by gas chromatography (GC).

1. The crystallization, melting, and chemical properties of the CO fractions strongly depends on the existence of TAG seeds and fractionation temperature, but not much affected by the type of TAG seeds. Fractionation temperature was found to play a key role in determining the quality of the CO-fractions.

2. The low yield of CO-oleins with low melting property enriched in medium chain-saturated fatty acids, including caprylic, capric and lauric acids, can obtained by dry fractionation at the lower fractionation temperature (23°C) with TAG seeds. This oleins also concentrated with low molecular weight of TAGs with carbon numbers (CNs) of 36 and 34, such as LLL.

3. The high yield of CO-stearins with high melting property enriched in LC-SFAs, especially palmitic acid, can obtained by dry fractionation at the higher fractionation temperature (25°C) with TAG seeds. The high molecular weight of TAGs with CNs of 48 (PPP) were increased in this stearins as well.

The CO fractions obtained by dry fractionation with TAG seeds will be a useful feedstock for medium chain triglyceride production as a food supplement. The CO-stearins with high melting property could be used to produce structured fats, spreads and confectionery fat formulation. However, the further studies in multi-step fractionation with crystal seeding and reproduced scaled-up fractionation from CO and CO fractions should be considered in order to increase the physical, chemical, and nutritional qualities of CO fractions.

It seems that the dry fractionation of CO carried out under conditions of this work is an effective process to separate the high-melting TAGs from low-melting TAGs. However, just some affecting factors, including seed crystal and fractionation temperature are studied. To obtain more unique and specific characteristic fat fractions, there are other affecting factors needed for further investigation, for example, holding time, cooling rate, agitation speed and separation technique, so on. Moreover, the impact of using CO fractions on food product quality, including texture, rheological, nutritional, and sensory properties, is also very important to study.

Key words: coconut oil, saturated triacylglycerols, crystallization, additive, seed crystal, fractionation, polymorphism