

Le Corps professoral de
Gembloux Agro-Bio Tech - Université de Liège vous prie
de lui faire l'honneur d'assister à la défense publique de la dissertation originale que

Monsieur BHAGGAN Krishnadath,

Titulaire d'un diplôme *in Scheikune*,

présentera en vue de l'obtention du grade et du diplôme de

DOCTEUR EN SCIENCES AGRONOMIQUES ET INGENIERIE BIOLOGIQUE,
le 22 octobre 2018, à 15 heures précises (personne ne sera admis après cette heure),
en l'auditorium G (Bioindustries, bât. 9),
Passage des Déportés, 2, à 5030 GEMBOUX.

Cette dissertation originale a pour titre :

« Characterization, polymorphism and structuring properties of trisaturated triacylglycerols containing palmitic and stearic acids ».

Le jury est composé comme suit :

Président : Prof. A. RICHEL, Professeur ordinaire,

Membres : Prof. S. DANTHINE (Promoteur), Prof. M.-L. FAUCONNIER, Prof. C. BLECKER,
Mme L. GAMBELLI (Bunge Loders Croklaan), M. K. W. SMITH (Fat Science Consulting Ltd).

Summary

Pure tripalmitoylglycerol (PPP), 1,3-dipalmitoyl-2-stearoyl-*sn*-glycerol (PSP), 1-palmitoyl-2,3-distearoyl-*sn*-glycerol (PSS) was successfully synthesized according to a newly developed enzymatic processing route. The kinetic phase behavior and phase transformation paths of these pure TAGs and binary and ternary mixtures thereof, were investigated at 10.0°C min⁻¹ (fast cooling) and 1.0°C min⁻¹ (slow cooling) cooling rates, and re-heating at 5.0°C min⁻¹ and 1.0°C min⁻¹ by differential scanning calorimetry and X-Ray diffraction. Polarized light microscopy was used to study the microstructure of different model application blends. Binary mixtures with $X_{\text{PSP}} = 0.1$ increments were studied in terms of polymorphism, crystallization and melting behavior. At the higher cooling rate, all samples crystallized in α polymorph, while at the lower cooling rate, a different behavior was observed. For pure PPP, the most stable form obtained was the β -form, whereas for PSS and PSP, the most stable form achieved was the β' -form.

In the PPP-PSP binary mixture, samples containing $X_{\text{PSP}} \leq 0.3$ crystallized in the α -polymorph and samples containing $X_{\text{PSP}} \geq 0.4$ crystallized in the β' -polymorph. During heating all samples transformed to a more stable β' -form and melted finally in the β -form ($X_{\text{PSP}} \leq 0.3$) or in the β' -form ($X_{\text{PSP}} \geq 0.4$). Kinetic phase diagrams were constructed by using the melting and transformation peak temperatures from the DSC heating thermograms and XRD patterns and displayed an apparently typical eutectic behavior with a eutectic point at $X_{\text{PSP}} = 0.3$, irrespective of the rate at which the samples were cooled and re-heated. The eutectic temperature was independent of the cooling and heating rates used.

In the PPP-PSS and PSS-PSP binary systems, all samples crystallized in the α -polymorph and transformed into the more stable β' -form via crystallization from the melt or direct recrystallization from the α -phase. In PSS-PSP, samples containing $X_{\text{PSP}} \geq 0.5$ tended to crystallize in the β'_2 -form and transformed during heating to the more stable β'_1 -form. In PPP-PSS, samples containing high PPP concentration ultimately transformed to the most stable β -form. The kinetic phase diagram of PPP-PSS mixtures displayed an apparently typical eutectic behavior with a eutectic point at $X_{\text{PSS}} = 0.3$, when the samples were melted at the higher heating rate, which shifted to higher concentration, $X_{\text{PSS}} = 0.5$, when the lower heating rate was applied. The eutectic temperature ($\sim 58.4^\circ\text{C}$) was independent of the cooling and heating rates used. The kinetic phase diagram of PSS-PSP mixtures displayed two types of behavior, a probable monotectic behavior in the most stable phase and a eutectic behavior in the meta-stable phase when the samples were melted at higher heating rate.

To study the most stable form, samples were incubated at different temperature and incubation time. At lower incubation temperature (15°C), most stable forms were not obtained, whereas when stored at temperature (50°C) close to the melting point of the least stable polymorph, samples transformed to the most stable form, although for samples containing higher amount of PPP a mixture of polymorphs was observed.

Different ternary blends were derived based on the composition of hydrogenated palm oil. These ternary blends showed similar phase behavior as was observed for the binary mixtures. For these blends, β' -form is desired for food application, but when the PPP, content was high, the mixtures transformed to the β -form during incubation period. These results showed that samples having high PPP content are not suitable for use as hard stock fat for structuring purposes.