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FFC APPLICATION NOTE: FOOD

Fast Field Cycling to monitor the crystallization in alimentary fat

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The FFC technique

Fast field cycling (FFC) NMR relaxometry is a low-field magnetic resonance technique which measures the dependence of the spin-lattice relaxation rate $\mathbf{R_1}$ (= $\mathbf{1/T_1}$) on the magnetic field over a wide range of field strengths, with just one instrument (Kimmich and Anoardo, 2004) [**1**].
The important information extracted from the relaxation dispersion curves (NMRD profiles) concerns molecular motions (molecular dynamics) described by means of a spectral density $\mathbf{J(\omega) \propto R_1}$.

The case study: the fat and confectionery industry

Low-field NMR (20 MHz) is currently used in the confectionery and fat industry for determining what is called solid fat content (SFC), *i.e.* the proportion of crystalline material present in a sample.
However, this technique is not sensitive enough at lower SFC values resulting in the need of complementary techniques if crystallization studies, rather than melting profiles, are sought. FFC NMR has been shown to be sensitive to different types of molecular motions by allowing the access to a wider range of lower frequencies (<20 MHz) that are not usually attainable using other type of NMR instruments. These frequencies are interesting because they show the slower molecular motions that are usually invisible using other set-ups, such as that of structuring, or orientation that occur during the formation or transformation of liquid crystal phases [**2**] and lipid bilayers [**3**]. This therefore raised the question of whether these lower frequencies would be able to detect the initial stages of crystallization that are not observable using the SFC method.

Application of FFC to detect the crystallization in chocolate butter

By heating cocoa butter and then cooling it step-wise, Ladd-Parada, *et al.* [**4**] were able to estimate the self-diffusion coefficient and its temperature dependence using the well-known method by Kruk, *et al.* [**5**].
However, once the sample was cooled and held isothermally at 20 °C, molecular motions other than self-diffusion became more dominant with time, particularly at frequencies below 1 MHz (**FIG. 1**). Here it was observed a strong increase in the spin-lattice relaxation rate ($\mathbf{R_1}$) values, suggesting a phase transition, *i.e.* crystallization.

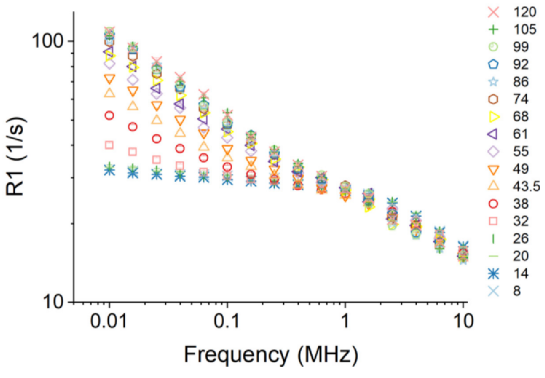

FIG. 1:
Relaxation profile as a function of time of cocoa butter previously heated to 50°C, cooled to 20°C and held isothermally at this temperature. Time increases from the bottom (8 min) to the top (120 min), the key on the right-hand side is indicative of the time (minutes) at which the relaxation measurements finished. (Adapted from [4]).

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Notably, when holding the sample at 20 °C, Ladd-Parada, *et al.* (2019b) [**6**] observed that by using the standard SFC technique, they could not pick-up crystallization until after 50 mins (**FIG. 2**), whereas, when plotting the $\mathbf{R_1}$ value at 10 KHz vs time, it was seen to increase immediately, reaching a first plateau, followed by a second increase and plateau as previously observed in literature using X-ray scattering (van Malssen, et al. (1996) [7]. It must be noted that the time-dependency of the relaxation rate is not used for modelling crystallization kinetics using the Avrami nor Gompertz models as is common in literature, when analysing DSC data, for example.

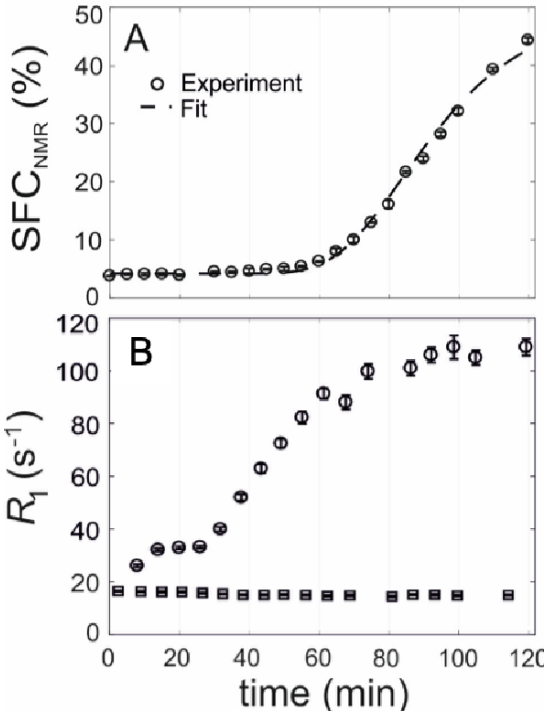

FIG. 2:
Crystallization of cocoa butter at 22°C.
(A) *SFCNMR turnover and the corresponding Gompertz fit.*
(B) *R_1 values at 10 kHz (circles) and 10 MHz (squares). [Adapted from (6)].*

However, it is notable that when the $\mathbf{R_1}$ starts plateauing for the second time, it coincides with the increase of the SFC curve, showing that measurements below 1 MHz are complementary to those at 20 MHz, helping to determine the time of start of the phase transition.

Conclusions

It has been shown that tracking the $\mathbf{R_1}$ values at 10 kHz allowed the observation of the initial stages of crystallization, as it is sensitive to the amount of orientationally ordered TAG molecules (*i.e.* triacylglycerols, which are the main components of fats) and their associated dynamics in the sample.
In summary, using lower frequencies might prove advantageous for studying the early stages of crystallization.

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