

Inferring the physical properties of maltodextrin / water systems in glassy state from the fitting parameters of the Free Induction Decay

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Introduction

The examination of the structure/properties relationships of carrier matrices commonly used in pharmaceutical, flavour or fragrance encapsulation systems, drives the control of the release mechanisms of active molecules.

When encapsulation systems are considered, a correlation between the Characteristic Time Distribution (CTD) and the mobility of active molecules "trapped" in the matrix is strongly expected. However, the extraction of the CTD from the Low Field Nuclear Magnetic Resonance Free Induction Decay (LF NMR FID) with maximum robustness is a key first step in this direction.

Efforts are here concentrated towards the significance of FID on maltodextrin/water glassy systems to identify the contribution of each relevant proton species and give a scientific insight into CTDs.

Materials

¹H NMR measurements were performed on a Resonance MARAN Ultra spectrometer (23 MHz) at 27°C. The 90° pulse duration was 6.3 μs and the deadtime 17.1 μs.

Three grades of maltodextrin samples (2DE, 10DE, 19DE) were studied to account for the influence of the molecular weight distribution on the signal characterisation. Each maltodextrin sample was mixed with appropriate amount of deionised water.

FIDs were averaged over 4 scans having 4096 data points prior to assessment of water content using the conventional Karl Fischer stoichiometric protocol. The FIDs were normalised by the mass of sample and then fitted using the solver option of Excel® software.

Experimental strategy

A fitting equation is used to extract characteristic relaxation times and amplitudes of individual components contribution.

$$I = A_1 \exp\left(-\frac{t^2}{T_{21}^2}\right) \frac{\sin(bt)}{bt} + A_2 \exp\left(-\frac{t}{T_{22}}\right)$$

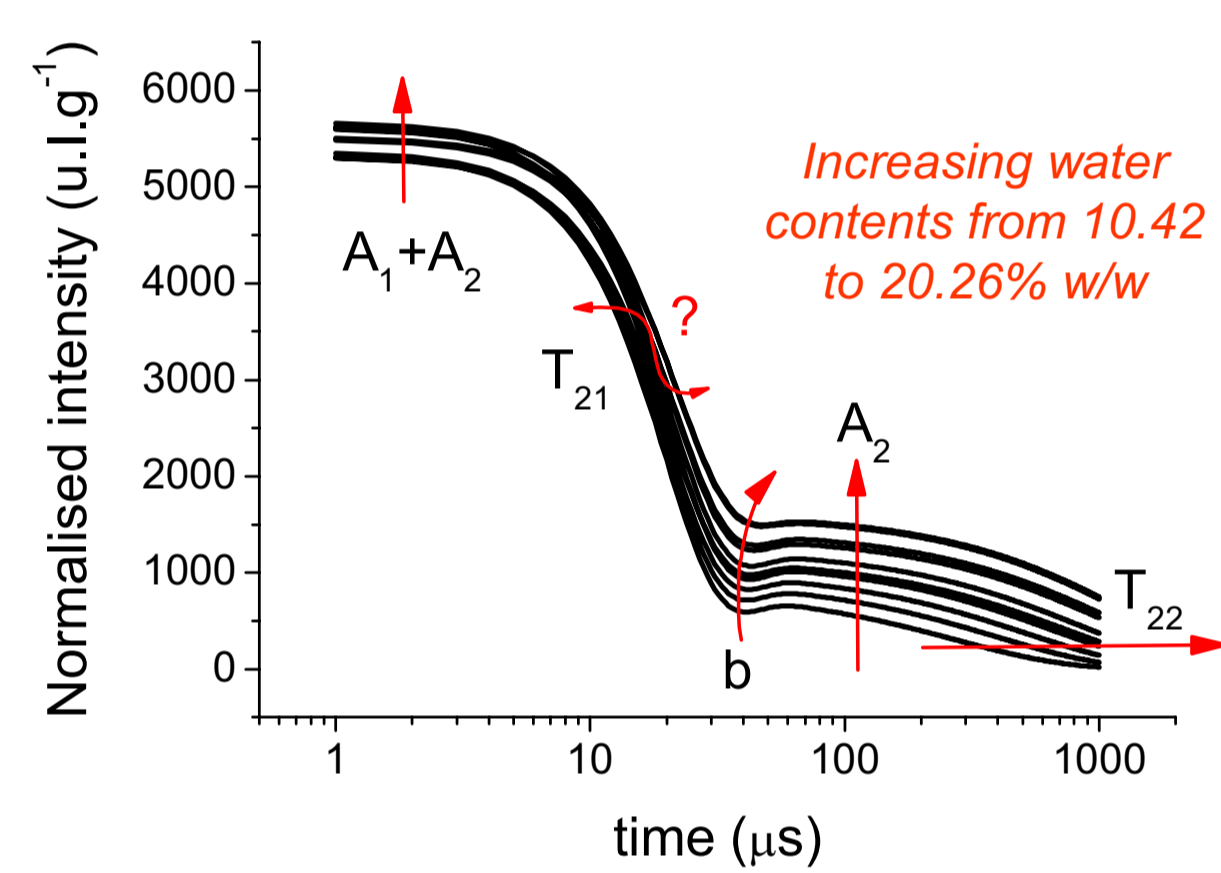
I is the signal intensity observed, A_1 and T_{21} are the amplitude and the characteristic time T_2 of the "low" mobility protons of the sample respectively, b characterizes a forced damped oscillation and A_2 and T_{22} represent the amplitude and T_2 of the "high" mobility protons.

The strength of the dipolar interaction M_2 was calculated as:

$$M_2 = \frac{2}{T_{21}^2} + \frac{1}{3}b^2$$

Fitting of the FID signals

Five parameters describe the maltodextrin/water FIDs, two of them are amplitudes (A_1 and A_2) and therefore related to concentrations and three are related to energetic contributions (T_{21} , T_{22} and b), therefore to the physical state of the sample.



Typical shift behaviours in FID signals for 2DE maltodextrin/water mixtures in glassy state when increasing water content.

For a constant sample mass, the total intensity of the FID (A_1+A_2) increases as the water weight fraction increases, due to the higher density of water protons as compared to maltodextrin.

T_{21} increases when increasing water content whereas b decreases and probably vanishes for very high water content. A_2 and T_{22} both increase when increasing water content.

Amplitude parameters of the FID signal (A_1 and A_2)

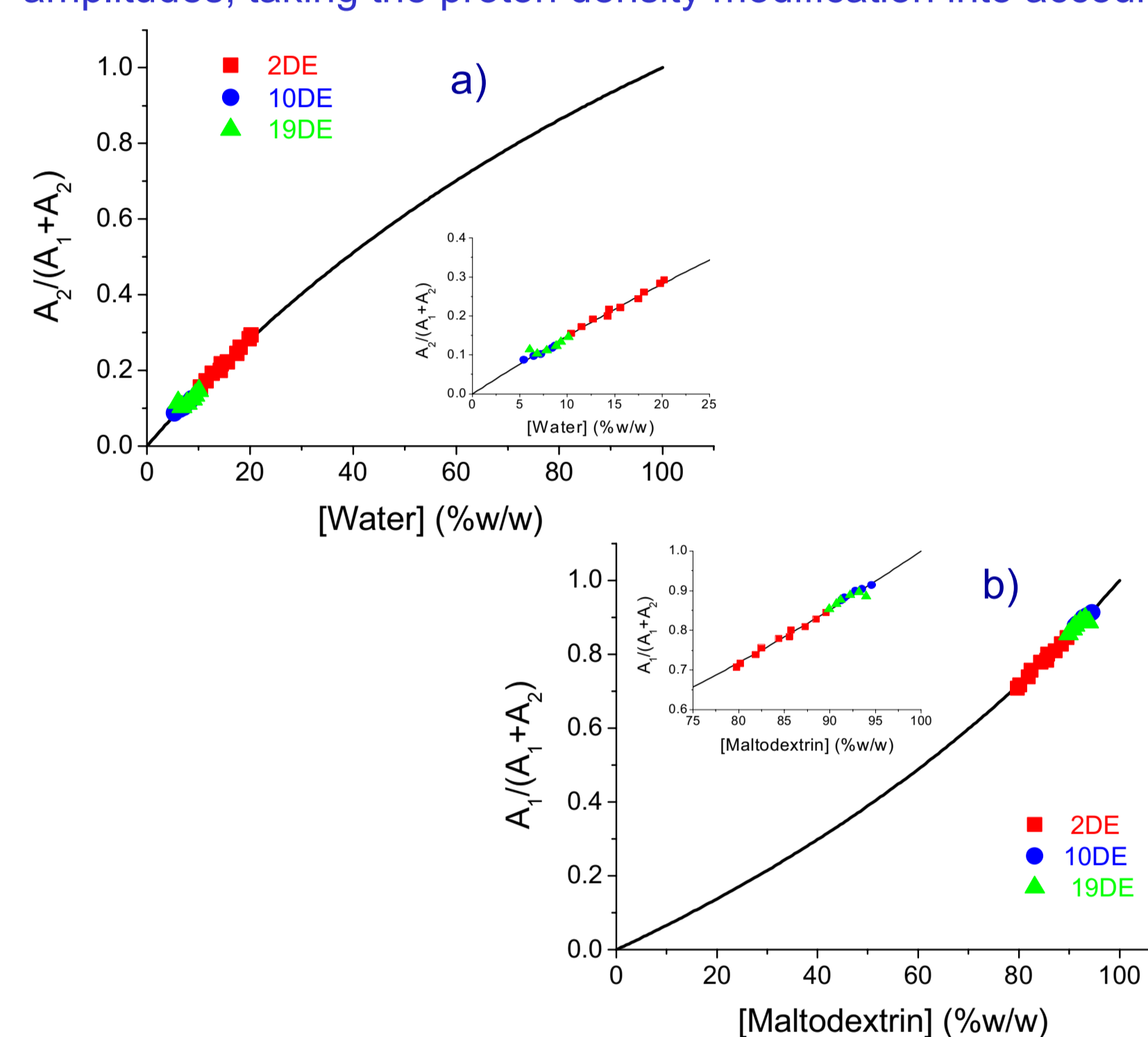
A_1 and A_2 correspond to the amplitudes of the "low" and "high" mobility protons excitation (at time zero) respectively. The signal resulting from the excitation is proportional to the amount of protons being excited, which can be approached knowing the average molecular weight in number and the repeating unit of the maltodextrin.

$$\begin{cases} A_1 = k_1 n_{Hm} \\ A_2 = k_2 n_{Hw} \end{cases} \begin{cases} n_{Hm} = \frac{2}{18} \omega_w \\ n_{Hw} = \frac{10DP_n + 2}{162DP_n + 18} (1 - \omega_w) \end{cases} \begin{cases} n_H = \frac{1}{18} \omega_w \\ n_{OH} = \frac{3DP_n + 2}{162DP_n + 18} (1 - \omega_w) \end{cases}$$

n_{Hm} and n_{Hw} are the number of maltodextrin and water protons and are calculated for 1 g of sample of known weight fraction of water ω_w . n_H and n_{OH} are the number of water molecules and maltodextrin hydroxyl groups respectively.

Empirically, the averaged proportional constants k_1 and k_2 are found to be $84,830 \pm 2,050$ and $73,866 \pm 2,277$ respectively. The difference is thought to be linked to proton exchange properties. DP_n is the average degree of polymerisation of the maltodextrin (7, 9.7, 46 for 19DE, 10DE and 2DE).

From these values it is possible to model the evolution of both amplitudes, taking the proton density modification into account.



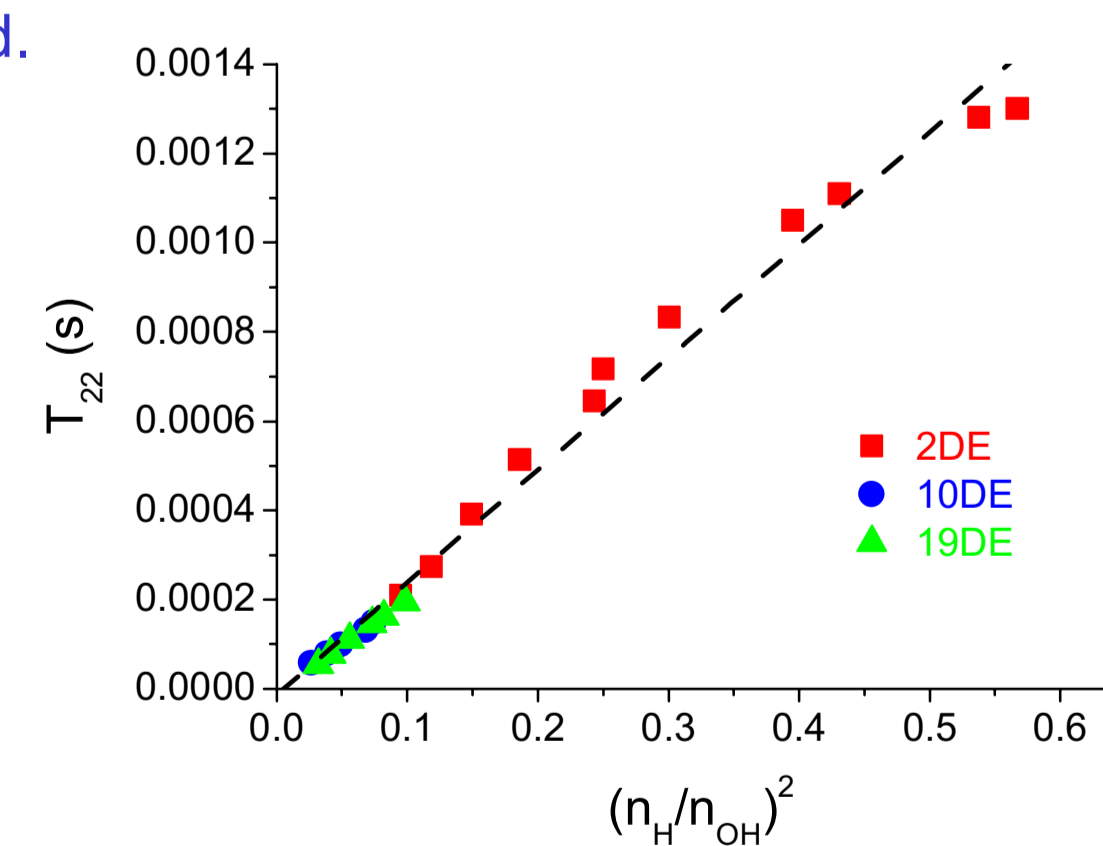
Correlation between the fraction of the "low" (a) and "high" (b) mobility protons phases over the total amplitude and water weight fraction for 2DE, 10DE and 19DE. Model (line) and experimental (scatters) data.

The maltodextrin molecular weight has no real influence on the results due to the low influence of the end chain hydrogen atoms. The longer the chain the lower is the impact of the end protons on the overall signal amplitude.

At "high" water content, water or even small sugars will not act like plasticizers anymore. The continuous trend is expected to show ruptures or saturations.

"High" mobility response of the FID signal (T_{22})

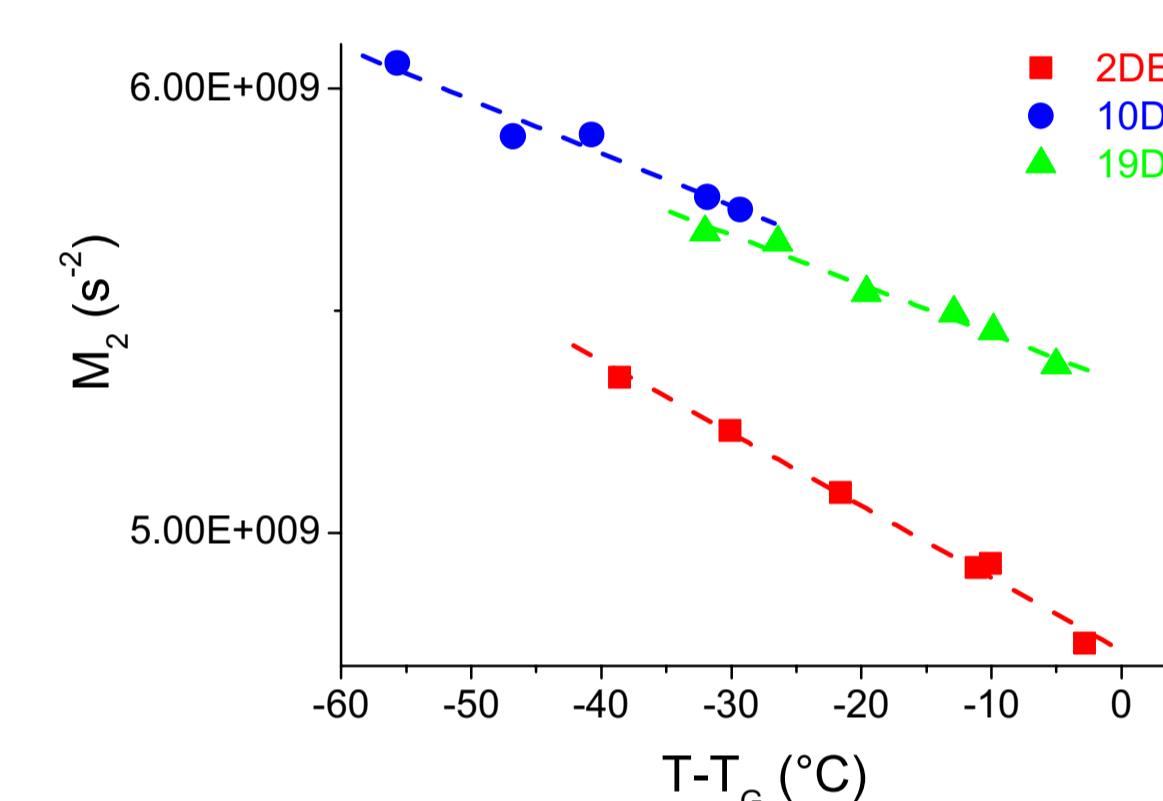
In the glassy state, T_{22} corresponds to the relaxation of water protons, all considered as bounded to the polymer by hydrogen bonds (no free water). An empirical relationship between T_{22} and the square of the molar fraction of hydroxyl group has been derived.



The correlation is independent of the maltodextrin species.

"Low" mobility protons response of the FID signal (T_{21} and b)

M_2 evolves linearly with $T-T_G$ where T_G is the glass transition temperature, which varies with water content. T_G is determined through Couchman's model and T is 27°C.



The slope of M_2 as a function of $T-T_G$ evolves with the type of maltodextrin and is function of the number average molecular weight M_n .

$$M_2 = K(M_n)^k \left(T - T_G \left(\frac{n_H}{n_{OH}} \right) \right) + C(M_n) + c$$

K , k , C and c are empirical constants.

T_{21} is very short when compared to the dead time inherent to the set up. It varies from 28.7 to 31.5 μs for different maltodextrins and at various water contents and no real trend is noticed.

Therefore, under the experimental conditions investigated here, T_{21} can be taken as a constant of the polymer independent of its molecular weight and characteristics of the solid state, whatever the mechanical properties.

b is representative of the material mechanical properties. As the water content increases, the compaction of the system decreases together with its elasticity and protons motion in the system increases, therefore b decreases. Ultimately, b is expected to evolve differently as the system overcomes the glass transition.

Thus,

$$\begin{cases} T_{21} = \sqrt{\frac{2}{c'}} = 28.3 \mu s \\ b = \sqrt{3 \left(K(M_n)^k \left[T - T_G \left(\frac{n_H}{n_{OH}} \right) \right] + C(M_n) + (c - c') \right)} \end{cases}$$

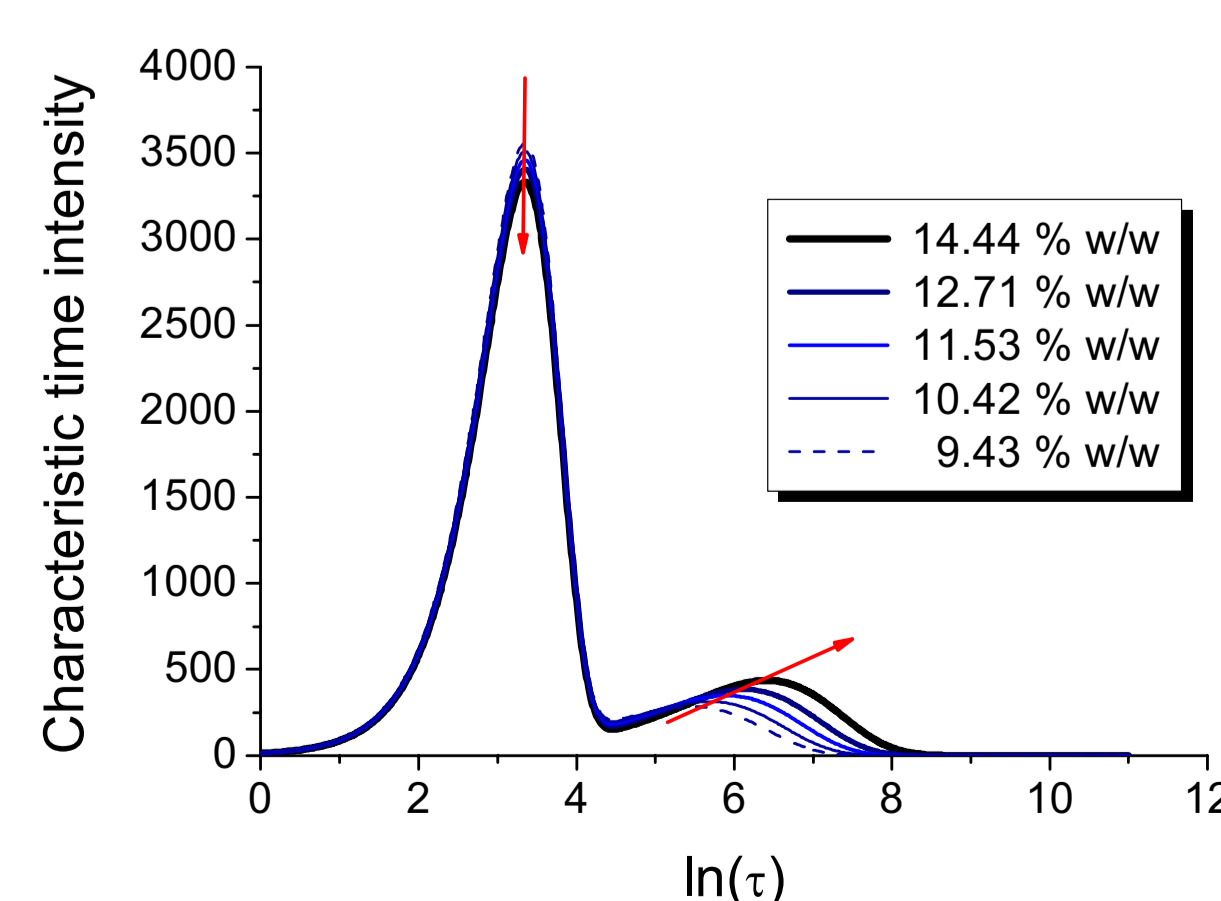
b is now accessible knowing M_n , n_H/n_{OH} and T .

Characteristic Time Distributions (CTD)

Modelling the FIDs and removing the contribution of b allows the representation of the characteristic time distribution evolution under various experimental conditions.

$$I^* = A_1 \exp\left(-\frac{t^2}{T_{21}^2}\right) + A_2 \exp\left(-\frac{t}{T_{22}}\right) \quad CTD_{(t)} = \left[\frac{dI^*}{d \ln t} \right]_{t=\tau}$$

As the water content increases, the amplitude of the "low" mobility protons contribution decreases whereas the amplitude for the "high" mobility protons contribution increases.



CTD for 2DE increasing water content

Conclusion

A fundamental approach to the FID fitting patterns of maltodextrin/water in the glassy state led to the physical understanding of all the initially used parameters. Therefore, the reconstruction of series of model FIDs is possible knowing the water content, the number average molecular weight of the maltodextrin and the temperature at which the measurement is performed.

Thus, it is possible to understand the evolution of the relaxation time distribution associated to the relaxation curve. This will certainly be valuable for further studies on the rubbery state of the same system.