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Evaluation of Cinnamon by Solid-State NMR Employing Relaxometry

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Abstract

To evaluate the molecular dynamics and the molecular regions presented in the cinnamon types it was chosen to evaluate them without any treatment, and for that it was used low-field nuclear magnetic resonance (NMR) through the pulse sequence such as MSE-FID, an NMR sequence in the time domain, and from the longitudinal relaxation time (with a time constant T_1), employing the inversion-recovery pulse sequence. The low-field NMR results indicate that the techniques chosen were a very good alternative to evaluate these types of samples food and their structural organization according to their constituents. The molecular mobility is different.

Keywords

Cinnamon, Low-Field NMR, NMR Relaxation, Functional Food

1. Introduction

To analyze the substances or materials in the solid state some techniques can be used, one of them is NMR spectroscopy, since this technique permits us to evaluate the sample without any treatment [1] [2] [3] NMR is used to characterize different materials type, especially low-field NMR [4] [5]. Molecular mobility of materials, especially food in the solid state can be determined by NMR relaxation measurements [6] [7]. The analysis of proton spin-lattice relaxation time (T_1H) and proton spin-spin relaxation time (T_2H) are good tools to evaluate.

The time-domain NMR technique (TD-NMR) was used to analyze the cinnamon types to obtain information on the molecular structure/organization and properties of the material, as well as the molecular dynamic that may infer about crystalline and amorphous domain [1] [2] [3] [8] [9].

2. Experimental

2.1. Materials

In this work, three types of cinnamon were bayed from the market and were analyzed as was received.

2.2. NMR Analyzes in the Time Domain

The solid samples were analyzed employing the time domain nuclear magnetic resonance (TD-NMR) pulse sequence, in order to determine the nuclear relaxation data. Maran Ultra 23 equipment was used, operating at a frequency of 23 MHz (for the hydrogen nucleus) and equipped with an 18 mm probe, the analyses were carried out at temperature of approximately 30˚C.

2.2.1. MSE-FID Pulse Sequence

The Magic Sandwich Echo pulse sequence (MSE-FID) was used to measure the transverse relaxation time (T_2^*H), which is sensitive to the segmental dynamics of the sample constituents. For the acquisition of each decay signal, 140 points spaced by 2 μs through 64 scans with a waiting time of 5 s were used.

2.2.2. Inversion-Recovery Pulse Sequence

The Inversion-Recovery pulse sequence was used to determine the longitudinal relaxation times of hydrogen nuclei (with a time constant—T_1H) in diffusion domains of approximately 20 nm. A logarithmic list with 40 values was used, recovery times between 0.1 and 5000 ms, with a recycle time of 5 s between each value. From the relaxation curve obtained, an Inverse Laplace Transform was performed to obtain the distribution curves of relaxation domains for each sample with the aid of the WinDXP® software (1.8.1).

3. Results

Relaxation Data and MSE-FID Analyses

To study the molecular dynamic of the materials to understand the differences among them, we used pulse sequences MSE-FID (Magic-sandwich echo—Free induction decay) a sequence of nuclear magnetic resonance in the time domain.

Table 1 and Table 2 present respectively, the results obtained by Inversion-Recovery and MSE-FID for the 3 cinnamon samples.

Figure 1 shows the distribution graphs of longitudinal relaxation domains (T_1) obtained by inversion-recovery cinnamon types.

Cinnamon samples showed 4 to 5 domains of longitudinal relaxation (T_1H), as can be observed in Figure 1. Domains with a shorter relaxation time, located between approximately 1 and 10 ms, can be associated with the fiber fraction of cinnamon with a higher content of essential oil and water. The domains between 10 and 500 ms are assigned to the fibrous fraction with less water and oil content. And the domain between 1000 and 1500 corresponds to the fraction of free water, present in the surface region and with little or no interaction with the matrix.

Table 1. T_1H values and percentages of each domain obtained by Inversion-Recovery.

Amostra	$T_{1,1}$/%	$T_{1,2}$/%	$T_{1,3}$/%	$T_{1,4}$/%	$T_{1,5}$/%
Cinnamon 1	1.7 ms/15	6 ms/14	**43 ms/63**	944 ms/8	------
Cinnamon 2	1.5 ms/23	**17 ms/55**	102 ms/6	992 ms/6	------
Cinnamon 3	0.8 ms/19	3 ms/13	**18 ms/64**	186 ms/3	1420 ms/1

Table 2. Values of T_2^*H and percentage of each fraction from MSE-FID.

Amostra	F_R/%	F_{SR}/%	F_M/%	$<M_2>$
Cinnamon 1	20 µs/50	163 µs/24	254 µs/26	**4450 rad·ms^{-1}**
Cinnamon 2	19 µs/50	180 µs/27	245 µs/23	**4360 rad·ms^{-1}**
Cinnamon 3	**19 µs/64**	**200 µs/21**	**348 µs/15**	**3790 rad·ms^{-1}**

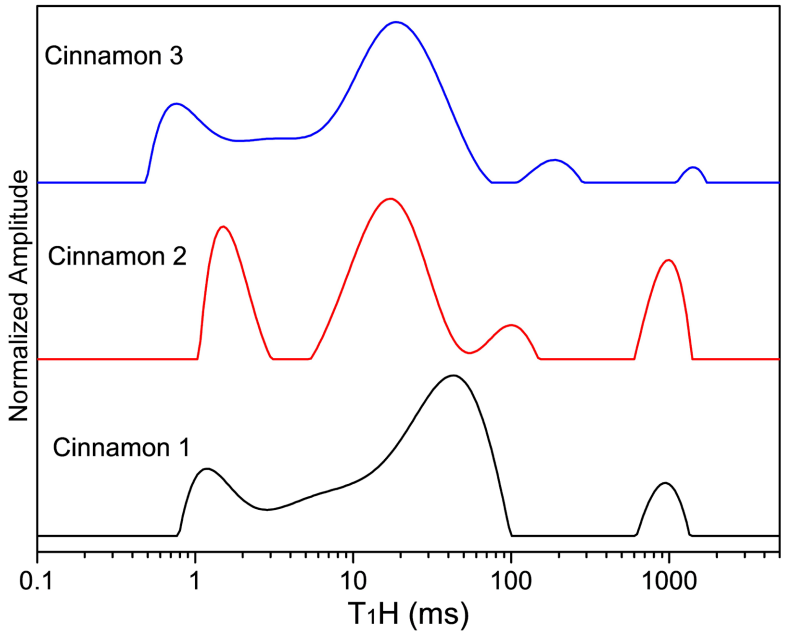

Figure 1. Distribution of longitudinal relaxation domains obtained by inverse-Laplace transform from inversion-recovery signals.

Measurements by MSE-FID identified 3 distinct molecular mobility regions of transverse relaxation (**Figure 2**), due to the chains movements. The rigid fraction, FR, corresponds to the fibrous fraction of cinnamon with little retention of essential oil and water. The semi-rigid fraction, FSR, is associated with the fibrous fraction with medium oil and water content. And the high mobility fraction, FM, can be assigned to the fraction with the highest water and oil content.

According to the results illustrated from **Figure 2** one can see that cinnamon 1 has 4 values of longitudinal relaxation domains and 3 values of transverse relaxation fractions that are very similar to cinnamon 2. However, the distribution of domains for cinnamon 1 indicates that this sample is more homogeneous matrix, with greater proximity between the different hydrogen populations, due to

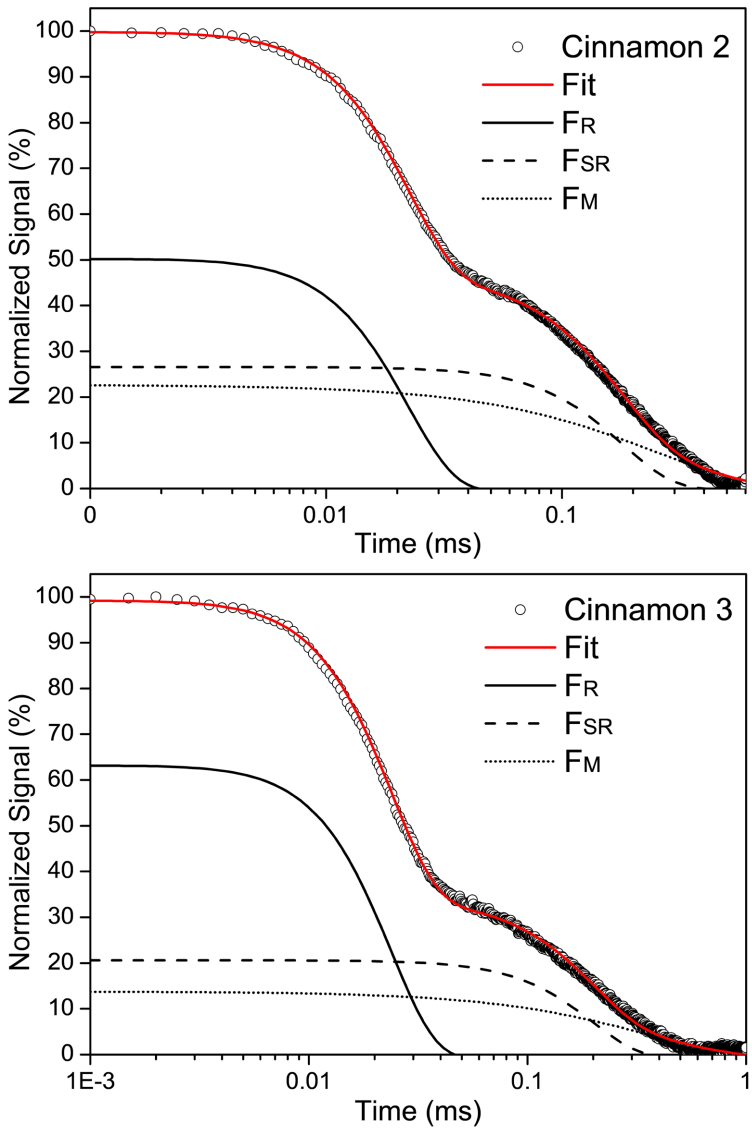

Figure 2. Transversal relaxation signals obtained by MSE-FID for all samples.

its molecular organization and the intra and intermolecular interactions. Cinnamon 2, in turn, presents the highest percentage for the $T_{1,4}$ domain (15%) associated with the unbound water fraction (absorption water). The results obtained by MSE-FID indicate that bound water and essential oil interact with the 3 fractions, leading to lower percentages of RF (50%) compared to cinnamon 3 (64%). The highest value of $<M_2>$ for spool 1 (4450 rad·ms^{-1}) indicates that this sample presents a rigid fraction with more compact and oriented fibers, slightly higher than the fibers of spool 2 (4360 rad·ms^{-1}), which indicates that its molecular organization is different from the others cinnamon type.

Cinnamon 3 has its water fraction more incorporated into the semi-rigid and mobile fibrous fractions and a lower unbound water content, indicated by the small $T_{1,5}$ domain at 1420 ms with only 1.1%. Through longitudinal relaxation this is observed by the minors of $T_{1,1}$, $T_{1,2}$, $T_{1,3}$ and $T_{1,4}$ suggesting greater mobili-

ty of the matrix promoted by the presence of water and essential oil in the internal structure of cinnamon. Through the MSE-FID, this sample presents more accentuated T_2^* values for FSR and FM, corroborating that in this cinnamon the water and oil fraction interacts more strongly with the semi-rigid and mobile fibers and less with the rigid fraction, which, consequently, presents a value of 64%. Therefore, due to the high mobility gain, the interaction between the chain segments of the cinnamon solid fraction becomes smaller, resulting in the lowest value of $<M_2>$ among the 3 samples.

4. Conclusion

In this work, the characterized cinnamon types, from NMR relaxation data one could see that the three types of cinnamon differ among them; the cinnamom 3 showed to be less rigid and very much heterogeneous. All of them are different due to the distribution of their major components such as: water, oil, and fibers. It also can be observed that the three types of cinnamon presented a particular molecular organization, and the low-field NMR relaxation data was a very good technique to show it.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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