

Evaluation of Sorva Latex by ^1H NMR Relaxometry

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Abstract: Solid state nuclear magnetic resonance ^1H relaxation times using a low field spectrometer are useful to evaluate the heterogeneity of samples, intermolecular interactions and domain formation, since changes in relaxation parameters will reflect changes in the macromolecular behaviour. In this work proton spin-lattice (T_1) and spin-spin relaxation (T_2) times were measured to determine domains formation in the solid latex found in *Couma utilis* (sorva), after moisture has been controlled. The results showed that both relaxation times allowed characterization of most of the components of the latex domains, such as free water (mobile domain); triacylglycerides (intermediate domain); polysaccharides, and polyisoprene (rigid domain).

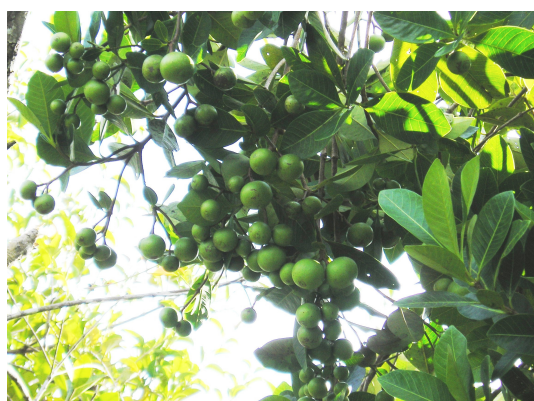
Introduction

Latex is the protective fluid contained in tissue beneath the bark of the rubber tree, *Hevea brasiliensis* and *Couma utilis*, for example. Natural latex is a complex emulsion in which many substances, such as proteins, polysaccharides, sugars, oils, gums and cis-1,4-polyisoprene can be found. This fluid is usually white; but it can be yellow, orange, or scarlet. Sorva is a sort of fruit that grows in the Amazon, Brazil. In the trunk, when sorva is in the unripe state, it contains white latex, a liquid similar in appearance to cow's milk (see Figure 1). Indeed, this liquid is consumed by the inhabitants of the Amazon region as milk and also as a medicine for some diseases. Despite such applications, scientific studies on these materials are scarce. As for the physico-chemical characterization of latex, analyses such as emulsion stabilization according to the particles size; coagulation process; processing temperature; domain interactions and chemical

constitution,¹⁻³ can provide useful information. Additionally, nuclear magnetic resonance (NMR) spectroscopy has played an important role in the compositional study of food and complex samples, such as latex.⁴⁻¹⁰ NMR is non-invasive and includes a wide range of techniques that can be applied together to develop an analytical methodology for natural products. Particularly, solid state NMR has become an essential technique for food characterization, as it can both differentiate between the solid forms of materials and is sensitive to their structural and dynamical properties.⁸⁻¹⁶ The focus of this work is to investigate the molecular dynamics of the components of sorva latex. The methodology developed for this study was the measurement of NMR relaxation times, as proton spin-lattice and proton spin-spin nuclear relaxation times. They can reveal details of the phase behavior of the materials as a consequence of intermolecular interaction.



(a)



(b)



(c)

Figure 1. (a) Sorva flour; (b) sorva fruit and (c) sorva latex

Experimental

Latex extraction

The latex of *Couma utilis* tree was extracted from the trunk using a special knife. Its natural polymerization occurred after 24 hours of exposure to environmental conditions. After polymerization, it was dried in an oven with circulating air at 50°C for three days. Water loss was monitored by infrared (IR) spectroscopy. After this treatment, the material was stored in a desiccator.

NMR measurements

All relaxation measurements were carried out on a Resonance Maran Ultra 23, operating at 23 MHz for ^1H . The samples were placed in a tube of 18mm diameter to acquire relaxation data. Proton T_1 and T_2 data were determined from inversion-recovery and Carr-Purcell-Meiboom-Gill (CPMG) sequences, respectively. Inversion-recovery (recycle delay $180^\circ - \tau - 90^\circ$ acquisition) was acquired using 20 data points for a range of τ varying from 0.1 to 5,000 of milliseconds with 5s of recycle delay and 4 scans for each. The CPMG pulse sequence (recycle delay of $90^\circ - \tau - 180^\circ$ acquisition) was carried out with three values of τ were used (50, 100, 200 microseconds) with recycle delay of 5s, and 9600 acquisitions were accumulated. All relaxation data were recorded at two temperatures, 25°C and 35°C. Relaxation values and relative intensities were obtained by fitting the exponential data with the aid of WINFIT program. Distributed exponential fittings as a plot of relaxation

amplitude versus relaxation time were performed by using WINDXP software.

Results and Discussion

Sorva latex from the trunk coagulates very rapidly at room temperature, which makes difficult liquid characterization by NMR. Therefore, solid state analyses can be carried out using relaxation measurements of the sample in the natural coagulation state and after being dried in an oven, for example.

The molecular mobility and domain formation studies of coagulated natural latex and coagulated natural dried latex extracted from the trunk sorva tree were carried out using relaxation data in a low field spectrometer. Structural changes after water loss, the coagulated natural latex, and coagulated natural dried latex were investigated by T_1 and T_2 , relaxation times. Table 1 shows the proton T_1 values of coagulated natural latex and Table 2 exhibits the proton T_1 values of coagulated natural trunk dried latex.

Table 1. Proton spin-lattice relaxation time of coagulated natural latex at 25°C

T_1 (ms)	Intensity
3	19
69	38
240	43

Table 2. Proton spin-lattice relaxation time of coagulated natural dried latex at 25°C and 35°C

25°C		35°C	
T_1 (ms)	Intensity	T_1 (ms)	Intensity
18	14	17	14
123	37	129	26
431	49	440	60

Comparing the relaxation parameters listed in Tables 1 and 2, one can see that the values of T_1 changes dramatically, after water loss. This is associated with changes in the interaction process caused by changes related to the non stabilized process.

As for the T_1 values shown in Table 2, they did not change significantly for both temperatures, as absorbed water did not interfere in the structural organization. The three values determined for T_1 were attributed to low value derived from free water protons; the intermediate value is associated to the hydrogen of water and mobile chains such as triacylglycerides and saccharides. The high value is derived from rigid domains, which can consist of polysaccharides and polyisoprene. An increase in the intensity values for both intermediate and high T_1 values determined at 35°C can be, probably, due to the loss of mobility. It may be attributed to water loss in the intermediate region and/or domains reorganization.

Figures 2 and 3 show relaxation domain distribution curves for the hydrated and dehydrated latex, respectively. From these Figures, it can be seen that relaxation domains become more resolved after dehydration. Therefore, two peaks of free water can also be observed in Figure 3.

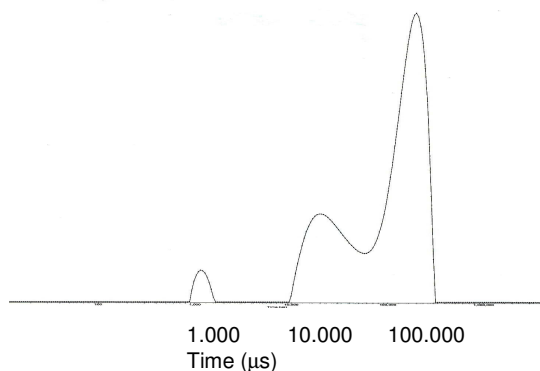


Figure 2. T_1H relaxation domain distributions for the hydrated latex

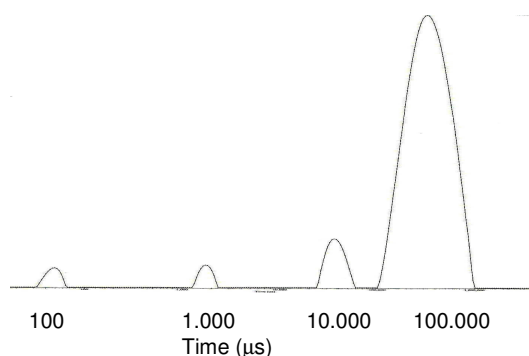


Figure 3. T_1H relaxation domain distributions for the dehydrated latex

Spin-spin relaxation time was also determined for the samples to evaluate changes in domains due to water presence. Table 3 shows the proton T_2 values of coagulated natural latex trunk and of coagulated natural dried latex, at 25 °C, using τ value 50 μsec .

Table 3. T_2 values for the coagulated natural trunk latex (CNL) and coagulated natural dried latex (CNDL)

T_2 (ms)	
CNL	CNDL
0.1	0.1
0.3	0.3
1.4	2.0
5.0	5.0

Table 3 shows no difference at all in the T_2 values for both coagulated natural and dried trunk latex indicating that the water present in the sample is an internal domain, and it was not removed at the temperature used. It also needed higher temperatures. The behavior of T_2 parameter is in accordance with the literature¹⁶ and corroborates the T_1 data.

Conclusions

According to the values determined for each relaxation time, both spin-lattice and spin-spin relaxation times, made possible to characterize the components present in the different regions of sorva latex emulsion.

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