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The Use of Low-Field Solid-State NMR Relaxation to Study the Latex Extracted from Brosimum *Parinarioides*

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Summary: The stability of the natural latex called Leite de Amapá, extracted from the Brosimum *paranarioides* tree, which is used as food and in popular medicine in Amazônia, was analyzed during an interval of twelve months. The molecular stability was monitored by proton spin-lattice (T_1H) and spin-spin (T_2H) relaxation times, which were measured with help of low-field nuclear magnetic resonance (NMR) with ^1H frequency at 23 MHz. According to the T_2H measurements, the latex degrades continuously and significant differences can be observed after 6 months of storage at ambient conditions, when no sort of chemical of physical treatment is employed.

Keywords: Brosimum *paranarioides*; characterization; latex; molecular dynamics; NMR

Introduction

The latex extracted from Brosimum *parinarioides*, named Leite de Amapá, is frequently used *in natura* as food and also as a popular medicine for treating tuberculosis and asthma in Amazônia.[1–4] However, fundamental studies about the chemical characteristics of Leite de Amapá have not been reported so far.

Nuclear magnetic resonance (NMR) is used frequently to characterize the chemical structure, the molecular dynamics and the molecular stability of samples.[2–15] Particularly, NMR analyses have been employed successfully to characterize the chemical composition of latexes, using different pulse sequences in high and low magnetic fields.[2–4,10–15]

Based on the previous remarks, the main objective of the present work was to monitor the stability of the Brosimum *parinarioides* latex at storage conditions at ambient temperature for a period of twelve months. In order to do that, low-field NMR analyses were used to determine the hydrogen relaxation parameters and monitor the stability of the latex. Monitoring of latex stability through NMR analyses is possible because spin-lattice and spin-spin relaxation times are sensitive to small changes of the molecular mobility, including modification of the water diffusion process and of the reorganization and reorientation of latex molecules, due to changes of the intermolecular interactions.[10–15]

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Experimental Part

Latex Extraction

The latex of Brosimum *parinarioide*s tree was extracted from the trunk and kept in sampling bottles at room temperature.

NMR Analyses

Aliquots containing 2.5 gram of latex were added to 18 mm NMR tubes. The sample was analyzed in a low-field NMR Maran Ultra (Resonance Oxford –UK), operating at 23 MHz for the hydrogen nucleus, to obtain data of spin-lattice relaxation time (180° - τ - 90°). The 90° pulse of 4.5 μs was

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calibrated automatically by the instrument software. The amplitude of the FID was sampled for twenty τ data points, ranging from 0.01 to 5000 ms, using 20 data points and 4 scans for each point. All measurements were carried out at 25 °C. The spin-spin relaxation time was determined by CPMG (Carr-Purcell-Meiboom-Gill) technique, using τ of 50 microseconds, recycle delay of 5 s and 4096 scans. The T_2 analyses were carried out for one year (twelve months). Relaxation values and relative intensities were measured by fitting the exponential data with the aid of the program WINFIT. Distributed exponential fittings as a plot of relaxation amplitude versus relaxation time were performed by using the software WINDXP. Both WINFIT AND WINDXP programs are commercial software that are provided by the manufacturer with the NMR equipment.

Results and Discussion

The low-field NMR analyses allowed us to establish a parameter to study the stability of the latex samples during the period of latex storage, at ambient conditions. The T_1H parameter can be useful for this purpose, since its value changes with the modifications of the molecular structure, being sensitive to water absorption and sample degradation. As reported in Table 1, no significant change of T_1H could be observed for a period of latex storage of six months. This was a strong indication that the sample did not change significantly during the considered storage time.

Based on the previous results, the spin-spin relaxation parameter was then monitored for 12 months. Obtained T_2H relaxation parameters are summarized in Table 2. As one can see, this parameter is more sensitive to latex changes than spin-lattice parameters, due to its sensibility to interactions with water and to motion of small molecules. Besides, it can also provide information about changes of the molecular reorganization, caused by changes of intermolecular and intramolecular interactions.

Table 1.
T_1H Values of the latex according to the time of storage.

Time of storage	T_1H (ms)		
Zero month	0.1	15	112
Six month	0.1	15	112

Table 2.
T_2H values for the latex according to the time of storage.

Time of storage	T_2H (ms)
Zero month	262
Six month	357
Twelve month	599

According to Table 2, T_2H increases with time, probably indicating changes of the water mobility inside and outside the cells, which cause modification of the hydrogen bonds and provoke molecular reorganization. These changes can also be caused by loss of small molecules, water absorption or other oxygen effects, as reaction with oxygen can cause changes of the molecular mobility and modification of the molecular bonds, leading to latex instability. According to the T_2H measurements, the latex degrades continuously and significant differences can be observed after 6 months of storage at ambient conditions, when no sort of chemical of physical treatment is employed. It is important to emphasize that the overall appearance of the latex did not change during the considered length of time.

Conclusion

Comparing both T_1H and T_2H data, it was verified that T_2H relaxation time were more sensitive than T_1H to characterize the stability of the latex of Brosimum *parinarioide*s, probably because of the higher sensitivity to changes of the water mobility. According to the T_2H measurements, the latex degrades continuously and

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significant differences can be observed after 6 months of storage at ambient conditions, when no sort of chemical of physical treatment is employed.

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