

¹³C SOLID STATE NMR INVESTIGATION OF NATURAL RESINS COMPONENTS.



IX International Macromolecular
Colloquium



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Introduction

The natural resins are multiphase systems because of its high chemical complexity¹. The objective of this work is to establish an analytical methodology as a routine using solid state nuclear magnetic resonance (NMR) techniques to investigate the mainly chemical components presented in the natural resins in bulk². And also to evaluate the molecular behavior of these resins. The routine solid state techniques allow us to assign the main compounds presented in the resins. Therefore, applying specialised techniques, like variable contact time (VCT), delayed contact time (DCT), dephasing time and proton spin lattice relaxation time in the rotating frame ($T_1^H\rho$), more information about chemical structure and molecular dynamic is available^{3,4}.

The application of faster MAS with short delay time permits us to detect high-speed molecular motions of individual components. The use of CPMAS allows us to characterize the total solid phase present in the sample. The CPMASDD is able to evaluate part of the sample, like non-protonated carbons, but some very mobile carbons are also detected. NMR relaxation studies have been widely used to probe molecular dynamics. Normally the approach is to measure one or more relaxation times and then attempt to interpret the

data. $T_1^H\rho$ is an alternative method to obtain the response of the dynamic molecular of the role sample⁵⁻⁷.

Experimental

Five natural resins named as aroeira vermelha (AV), aroeira branca (AB), cedro rosa (CR), jatobá (JA) and barbatimão (BB) were analyzed by ¹³C solution and solid state NMR.

All solid state spectra were obtained on a VARIAN INOVA 300 spectrometer operating at 75.4 MHz for ¹³C. All solid NMR experiments were done at ambient probe temperature and were performed using gated high decoupling. A zirconium oxide rotor of 7mm diameter was used to acquire the NMR spectra at rates of 5.5 kHz. The ¹³C NMR spectra were carried out in the cross-polarization mode with magic angle spinning. For the variable contact-time experiment, a range of contact time was established from 100 to 8,000 μ s. Proton $T_1\rho$ values were determined from the intensity decay of ¹³C peaks with increasing contact-times and by delayed contact-time experiment, where the range of spin-locking was from 200 to 8,000 μ s.

Results and Discussion

As the ^{13}C NMR solution was not able to give us the chemical structure or the type of components presented in the NR. The solid state measurements showed more information on that resins and a change in the methodology proceedings is necessary.

From the ^{13}C solid state NMR spectra of all resins, several useful informations have been extracted. The AV resin presented a poor CPMAS spectrum. However signals from polysaccharide and ester were detected. The cross polarization with variable contact time was carried out from short contact time (μs) to long contact times (ms). As was expected the efficiency was not good, only wide signals located at short contact times were detected. From these responses we can suppose that this resins is amorphous and rigid, this rigidity is related to the sample spatial conformation and may present a metal in its structure, which contributes to the difficulties of the polarization transfer, making the signals wider. The assumption of the metal in this structure can be supported by the fact that the ^{13}C MAS spectrum with short delay time, did not present signals, because this sample do not have a domain in this time scale, probably because it is a rigid amorphous polysaccharide complexes with a metal. The $T_1^{\text{H}\rho}$ values determined for the resolved carbons are shorter than the values determined for the other resins, due to the rigidity of the sample.

The AB resin CPMAS ^{13}C showed signals from the polysaccharide and from a oil, probably a triacylglycerol. The signals from polysaccharide reveals that these resin presents a crystalline and an amorphous polysaccharide and other signals comes from an ester.

When the BB resin was analyzed by CPMAS ^{13}C it showed signals from polysaccharide and an ester. The polysaccharide signals are not well resolved as was detected for AB resin. The two signals detected for an ester indicates that these came from acetate.

Analyzing CR resin, the CPMAS ^{13}C showed the same signals found for BB resin, indicating that these two different type of resins can be constituted by the same components, or at least very similar.

Comparing all distribution form of the CPMAS ^{13}C decays, during the variable contact time experiment it is clear that the AV resin is very much rigid than the other resins, the optimum contact time

was around $100\ \mu\text{s}$ and it is also amorphous presenting the NMR signals very wide. The CR is rigid and amorphous as well, and the signals were broad. The AB and BB presented higher molecular mobility and the best contact time for the polarization transfer was about $1000\ \mu\text{s}$ for the BB and $600\ \mu\text{s}$ for the AB.

Conclusions

Indeed, solid state NMR techniques exceeds solution state NMR because more information can be extracted from solid state due to anisotropic interaction and because there is less averaging from mobility at the molecular level.

In this work we have first chosen to use liquid NMR to try to identification the components in the natural resins. Therefore, the solid state NMR techniques give much more information about the resins than solution NMR. So, the first approach must be the application of solid state NMR techniques to continue the identification process. The ^{13}C signals were much better detected and additional information on the NR was also obtained.

Acknowledgements

The authors are indebted to PETROBRAS/CENPES/Gerência de Química for the use of solid state NMR spectrometer.

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