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NMR Molecular Dynamic and Thermal Analysis Studies of Amescla Resin

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Natural resins have been a subject of the authors' research group since 2000 and a study involves a methodology to better analyze this type of sample was already published [1]. That study recommended that the first study should be done in the solid state. And in this case the authors decided to first investigate the molecular dynamic, using nuclear magnetic resonance from the measurements of proton spin-lattice and spin-spin relaxation time and the thermal parameters. The polymer relaxation processes occur over a wide range of time and length scales. A molecular-level understanding of such processes can lead to improved production methods and mechanical properties of the polymeric materials. The thermal motions, such as the glass transitions (T_g), occur at ~ 100 Å. This work has demonstrated that the molecular dynamic of natural resins, as amescla resin is very well characterized by the relaxation parameters, using both high and low field NMR techniques. The thermal measurements corroborate the NMR data.

Keywords: amescla resin, NMR, solid state

INTRODUCTION

Natural resins are composed mainly from polymeric terpenoids (polyterpenoids). However, there are many other compounds of intermediate and low molar mass. These intermediate and low molar mass compounds are in the natural resin and work as additives, increasing

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or decreasing the molecular mobility of natural resins. Besides that, other factors, such as molar mass and molecular structure of polymers, must be considered [1–3].

The Natural Resin of Amescla is a potential substitute for synthetic polymers. Because this NaRA is a polymer of renewable sources, its products have had more aggregate value because do not contribute for the production of CO₂.

The molecular dynamic of polymers is an important factor in the control of many properties of these materials. As a consequence, the use of any polymer depends on its molecular dynamics.

The importance of understanding the molecular dynamic increases for natural polymers. That is because their molar mass and chemical structure is unstable. For this reason, the understanding of dynamic molecular of amescla resin is very important.

Nuclear magnetic resonance spectroscopy (NMR) can provide very valuable information on local structure, conformational dynamics, and both structural and kinetic aspects of interactions with small molecules. NMR can give very detailed, highly localized information on molecules and materials. The ability to combine structural and dynamic information is one of the most important attributes of NMR in structural molecular context. Molecular dynamic studies derive from the interaction process, crystallinity ordination, molecular changes, and others mechanisms. Interaction studies using hydrogen NMR spin–lattice relaxation time measurements of a series of materials have been a subject of many researches. To further understand surface interactions at the solid interface on polymeric materials, the NMR techniques of relaxation have been combined. The combination of these techniques allows variations in NMR relaxation parameters such as proton spin–lattice (T_1) and proton spin-spin, (T_2) which are able to distinguish surface interaction changes. In solid state the interaction between chains is spatial through dipolar interaction mechanism, which allows the evaluation of the molecular dynamics because the relaxation times are sensitive to fast motion and can limit domains from 4 to 50 nm [1,4–10].

The thermal transitions, like glass and melting, are strongly dependent on processing conditions and dispersion in structural and chemical properties of polymers. Thus, a complete thermal analysis of a polymer material may give information concerning the behavior of the chemical composition and structure, the scale of the observation of thermal transition is about 100 nm.

The main purpose of this work is to evaluate the molecular dynamic of the amescla resin and its thermal behavior, because this natural material has been characterized for the first time.

EXPERIMENTAL

Sample

The amescla resin was collected in the Amazon forest zone of Sinop, in Mato Grosso state, Brazil. The resin was purified by extraction with ethanol and precipitation with water. After that, the resin was dehydrated.

Thermal Measurements

The thermal degradation temperature was determined in a Thermal Gravimetric analysis registered in a TGA 7 series, in nitrogen atmosphere at 10°C/min, from 30 to 700°C. The glass transition temperature (T_g) was measured by differential scanning calorimetry (DSC 7) at 20°C/min, from 40 to 200°C.

Solid State Measurements

The solid spectra were obtained on a VARIAN INOVA 300 spectrometer, operating at 75.4 MHz for ^{13}C , all solid NMR experiments were performed at ambient probe temperature using gated high decoupling. A zirconium oxide rotor of 7 mm diameter was used to acquire the NMR spectra at rates of 5.8 kHz. The ^{13}C NMR spectra were carried out in the magic angle spinning (MAS) using 60.000 Hz of spectral width and 0.023 s of acquisition time; cross-polarization magic angle spinning (CPMAS) with 2 s of recycle delay, 30.000 Hz of spectral width and 0.04 s of acquisition time, and for the variable contact-time (VCT) the recycle delay was 2 s and a range of contact-time was established from 0.2 to 8 ms. Proton $T_{1\rho}$ was measured from the decay of all resolved carbons with increasing the contact-time.

Low Field NMR

Low field NMR MARAN ultra 23 was used for the relaxation measurements. Proton spin-lattice relaxation times (T_1) were determined directly by the traditional inversion recovery pulse sequence (recycle delay 180°- τ -90°-acquisition) with 20 data points using a range of τ varying from 0.1 to 5,000 ms, and 5 s of recycle delay. The spin-spin relaxation times (T_2) were also determined using a Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence (recycle delay 90°- τ -180°-acquisition) using τ 100 μs with a recycle delay 5 s. The relaxation values and relative intensities were obtained by fitting the exponential

data with the aid of the WINFIT program. Distributed exponential fittings, as a plot of relaxation amplitude versus relaxation time, were performed by using the software WINDXP software.

RESULTS AND DISCUSSION

Relaxation Measurements

In this work, the amescla natural resin was explored with respect to its molecular mobility using solid state NMR relaxation measurements, in a high and low field NMR spectrometers, because these measurements provide information about various characteristics.

Table 1 shows the proton spin-lattice and spin-spin relaxation times determined for amescla resin measured in a low field NMR spectrometer.

Considering the T_1 values showed in the Table 1, there are at least two domains with different molecular mobility: one related to amorphous phase (low value) and the other one to the rigid domain, probably it is more ordered (high value). Each domain has almost the same proportion in the sample. Four T_2 values were found, the two low values come from the rigid domain, which contains clusters and amorphous domains, and a higher value of T_2 parameter that is of the same intensity proportion than the rigid domain. Comparing the intensity percentage of both domains, they too have almost the same proportion, corroborating the T_1 relaxation data.

The proton $T_{1\rho}$ was measured from the variable contact-time experiment and the values determined from the carbon-13 attenuation during the cross-polarization process are listed in Table 2.

The proton $T_{1\rho}$ relaxation data confirm that the resin is heterogeneous and at least two domains with different molecular mobilities were detected, one related to amorphous phase and the other one derived from the ordered region, which corroborates with proton T_1 parameter.

TABLE 1 Proton Spin-Lattice and Spin-Spin Relaxation Times of Amescla Resin

T_1 (ms)	Intensity (%)	T_2 (ms)	Intensity (%)
		0.3	14
464.4	51	13.0	19
1303.8	49	90.0	24
		437.0	43

TABLE 2 Proton $T_{1\rho}$ Values for the Resolved Carbons of the Amescla Resin, as a Function of Chemical Shifts, Measured by Variable Contact Time

$(\delta^{13}\text{C})$	$T_{1\rho}^{\text{H}}$ (ms)
78.5	8.9
48.2	9.6
40.4	12.6
28.5	15.4
24.4	16.6
17.9	23.8

Thermal Measurements

Thermal gravimetric analysis of amescla resin showed only one stage of degradation (Figure 1). The initial temperature of mass loss is 89°C. The temperature of maximum degradation (peak) was 340.7°C and the final temperature of mass loss was 532°C. This result is in contrast with the thermal analysis of other natural resins, as *Agathis* resin, for example. The profile exhibited by this type of resin showed several stages of degradation. Probably, the main reason for that variation in the TG profile can be due to purification process of amescla resin and/or by the fact that this resin is fresh and it is not as heterogeneous

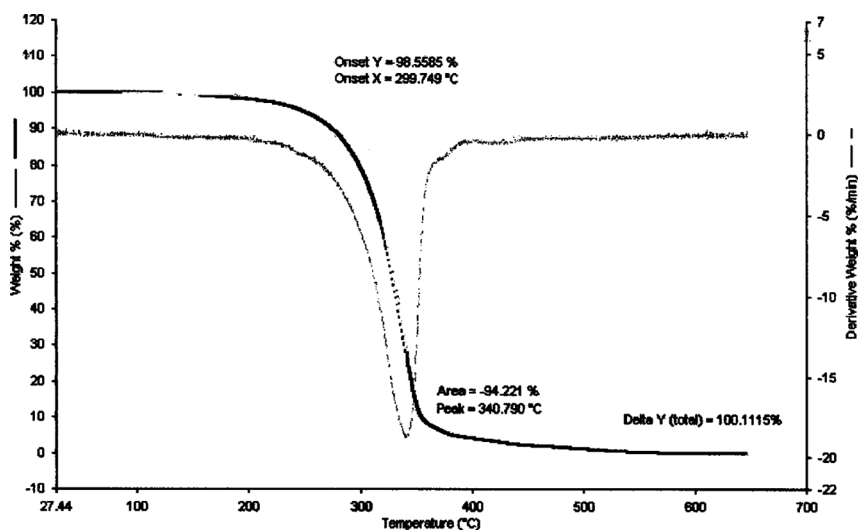


FIGURE 1 TG curve of amescla resin.

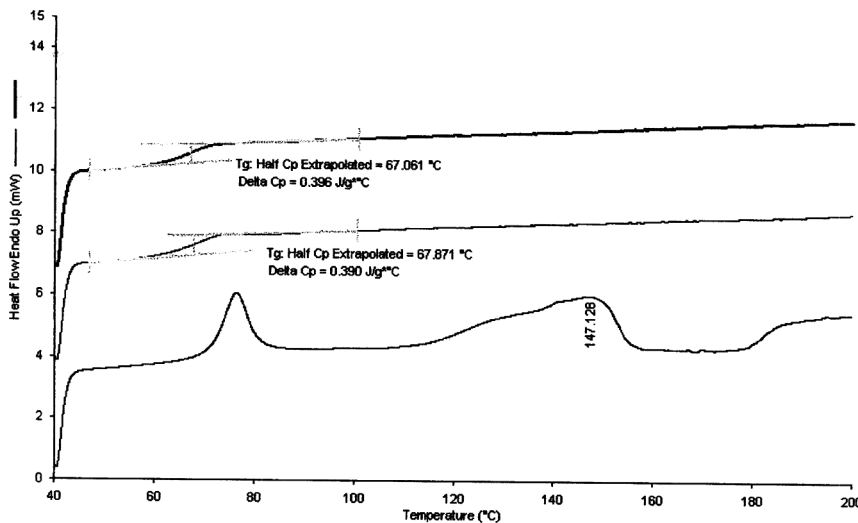


FIGURE 2 DSC curve of amescla resin.

as natural resins in different stages of aging, according to the scale of this measure. This behavior corroborates with the data obtained by the relaxation measurements.

The DSC curve did not show melting temperature (T_m). The curve indicates that the amescla resin is a non-crystalline polymeric material and the glass transition was detected at around 67°C (Figure 2). The DSC result also corroborates the TG and NMR data.

CONCLUSION

The use of NMR relaxation time and thermal measurements gives a correlation of different time scales, allowing the evaluation of the mechanical behavior of the polymeric material under observation.

All results are in concordance and this natural resin can be characterized as an amorphous polymer, in spite of being heterogenous in relation to the distribution of domains with different molecular mobility.

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