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ELECTRONIC SUPPLEMENTARY INFORMATION

The role of water in the degradation process of paper seen by ^{1}H HR-MAS NMR spectroscopy

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The thermodynamical properties of water are essential in determining the corresponding properties of every biosystem interacting with. Indeed, the comprehension of hydration mechanisms is fundamental for the understanding and the control of paper degradation pathways induced by natural or artificial aging. In fact, the interactions between water and cellulose at the accessible sites within the fibres' complex structure are responsible for the rupture of hydrogen bonds and the consequent swelling of the cellulose fibres and consumption of the amorphous regions. In this paper we study the hydration process of cellulose in naturally and artificially aged paper samples by measuring the proton spin-lattice (T_1) and spin-spin (T_2) relaxation times of the macroscopic magnetization through Nuclear Magnetic Resonance (NMR) experiments. The observed behaviour of T_1 and T_2 is quite complex and strictly dependent on the water content of paper samples. This has been interpreted as due to the occurrence of different mechanisms regulating the water-cellulose interaction within the fibres. Furthermore, we have measured T_1 as a function of the artificial aging time comparing the results with those measured on three paper samples dated back to the 15^{th} century. We found that the evolution of T_1 in model papers artificially aged is correlated with that of ancient paper providing therefore a way for estimating the degradation of cellulosic materials in terms of an equivalent time of artificial aging. These results provide fundamental information for industrial applications and for the preservation and restoration of cultural heritage materials based on cellulose such as ancient paper or textiles.

^{1}H HR-MAS technique applied to paper

The Nuclear Magnetic Resonance (NMR) spectroscopy is certainly one of the most suited experimental technique allowing the investigation of the microscopic details behind the interaction between cellulosic materials and water. Indeed many studies in literature report different kind of NMR analyses aimed to shed light on the details of the role of water within cellulosic fibres [1–9]. However, due to strong dipolar coupling the classical NMR approaches used to have an high resolution for molecules in solutions cannot be applied to solid systems such as paper samples. Therefore, different approaches to investigate solid systems by means of NMR spectroscopy were developed in order to reduce or even neglect those mechanisms that provoke intense line broadening. One of the most promising NMR technique that can be used to probe the ^{1}H nucleus on semi-solid systems is known as ^{1}H High Resolution Magic Angle Spinning (^{1}H HR-MAS). Indeed this methodology allows the achievement of highly resolved spectra on micro quantities of semi-solid compounds [10,11] that do not need complex extraction procedures. For this reason ^{1}H HR-MAS is extremely used for studying biological samples (cells, tissues, organs, foodstuffs, etc.) in their physiological or normal conditions [12–16].

Note that the ^{1}H HR-MAS technique can be considered a hybrid approach between classical solution and solid-state NMR. In fact, from one side it uses the classical solution NMR experiments including bidimensional pulse sequences and, from the other side, it takes advantage of the magic angle spinning strategy typical of the solid-state NMR. Hence, ^{1}H HR-MAS can be distinguished by CP-MAS (Cross Polarization Magic Angle Spinning) experiments on true solids because it involves direct polarization transfer (between ^{1}H and heteronuclei, ^{13}C or ^{15}N) instead of cross-polarization [11,17,18].

The two main line-broadening mechanisms (apart from the occurrence of anisotropic interactions) that are important in acquiring spectra of a solid or semi-solid sample are indeed dipolar coupling and heterogeneous isotropic susceptibility [11,19]. In fact, for an external homogeneous field in the absence of a radio frequency field, the spin Hamiltonian may be written as

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$$H(r) = H_0 + H_{DD}(r) + H_{sus}(r) \quad (1)$$

in which $H_0 = \sum_j \gamma^j B_0 I_z^j$ represents the interaction of spins with the external static magnetic field B_0, γ is the gyromagnetic ratio, I is the spin angular momentum and the summation is over all the spins in the sample. The other two terms in the equation come respectively from the dipolar coupling and the heterogeneous susceptibility and are both position dependent. In fact, the local magnetic field created by dipolar coupling and by heterogeneous susceptibility varies from position to position and so the resonance frequency varies as well. This provokes a frequency distribution for each resonance frequency that depends on the intensity of the two effects and causes the line-broadening of NMR peaks.

In particular, the dipolar coupling can be intramolecular or intermolecular and depends on the magnitude and orientation of magnetic moments ($\mu = \gamma\hbar I$) of coupled spins and also on the distance and orientation of the vector describing their relative positions. However, in the secular approximation, based on the energy levels difference which depends on whether the spin system is homonuclear or heteronuclear[11,19], both the Hamiltonian contributions for dipolar coupling and susceptibility heterogeneity depend on the same term:

$$3\cos^2\theta_{ij} - 1 \quad (2)$$

where θ_{ij} is the angle between the unit vector from spin i to spin j and the direction of the static magnetic field. This term vanishes for $\theta_{ij} \sim 54.74^\circ$ therefore, by tilting samples at this magic angle and by spinning at a rate greater than or equal to the magnitude of the anisotropic interaction (few thousands of Hertz), high-resolution spectra can be achieved for semi-solids samples.

In figure 1 we report the picture of the component (stator) of the HR-MAS probehead (left side) that induces the spinning of the sample holder (rotor) at the magic angle (right side) by means of a piston and of high pressure nitrogen insisting on the wings of the rotor cap.

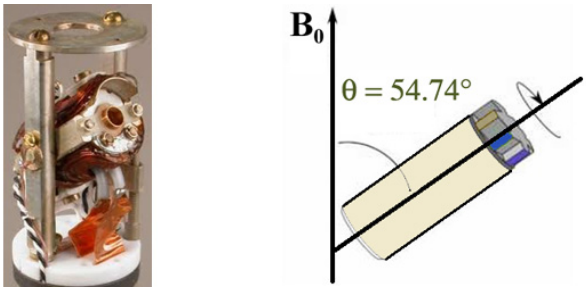

Fig. 1 Details of the stator of the Bruker HR-MAS probehead (left) and of the magic angle configuration (right). Figure adapted from ref. 17.

Our ^{1}H HR-MAS experiments were performed at atmospheric pressure and ambient temperature by using a Bruker Avance spectrometer operating at 700 MHz, ^1H resonance frequency. We used a 4 mm-diameter zirconia rotor with a total volume of about $80\mu l$ and a Kel-F® rotor cap. Small rectangular pieces of papers, 0.7×1.8 cm^2 in size and of about 10 mg in weight, at different hydration were rolled up, placed in the rotor (figure 2), sealed with the rotor cap and spun at 7000 Hz at the magic angle.

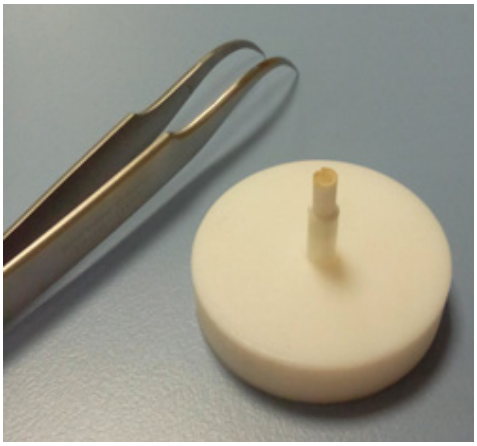

Fig. 2 Picture of the HR-MAS rotor with a paper sample rolled inside it.

We recall here that artificial aging was performed on samples made of pure cellulose within a climatic chamber at a relative humidity (RH) of 59% and temperature of 90°C for 6, 12, 24, 36 and 48 days. Furthermore, the hydration procedures consisted of keeping the samples in an oven at 105°C for 4 hours reaching a moisture content of about 2% that we identify as the "quasi-dry" state of the samples. Then, the dry samples were hydrated in a closed chamber at RH=100% until reaching the desired moisture content evaluated by weighting the samples and verified by means of the integrated area of NMR signal (see the main text for the details). In our study we have considered values for moisture content of approximately 2%, 8%, 14%, 20% and 40%, being the moisture content or hydration, h, defined as the ratio between the mass of water and that of the completely dry sample (see the main text for the details).

Finally we want to highlight that in the last years the NMR approaches using MAS technique have been subjected to intense development[20,21] and have been applied to very different investigation fields[22,23].

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