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NMR study of paper

Maurizio Paci,*[a] Carlo Federici,[b] Donatella Capitani,[c] Nicoletta Perenze[c] & Anna Laura Segre[c]

[a]*Department of Chemical Science and Technology, University of Rome Tor Vergata, 00 137 Rome, Italy*
[b]*Istituto Centrale per la Patologia del Libro, Via Milano 76, 00184, Rome, Italy*
[c]*Istituto Strutturistica Chimica and NMR Service, CNR, Area della Ricerca di Roma, Mailbox 10, 00016 Monterotondo Stazione, Rome, Italy*

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High quality antique sheets of paper have been characterized by ^{1}H NMR relaxations and ^{13}C CP MAS spectra. Paper can be regarded as a bicomponent material made of cellulose and water plus a small amount of organic and inorganic impurities. Semicrystalline fibrous cellulose, rich in water, is present in the I_α and I_β forms. The amorphous cellulose, with a low water content, contains a higher amount of paramagnetic impurities and it is characterized by quite short ^{1}H spin-lattice relaxations and by ^{13}C resonances with noticeable chemical shifts. *Ad hoc* tailored pulse sequences are able to produce ^{13}C CP MAS spectra in which only the amorphous content of paper is clearly observed. It is shown that water is fully bound to the cellulose lattice. It also seems reasonable to formulate the hypothesis that a larger concentration of paramagnetic ions is located in the amorphous fraction of highly degraded paper compared with paper in good condition.

INTRODUCTION

Paper is one of the most common and widespread materials; it is also one of the oldest and sometimes precious man-made materials. Paper is mostly made by cellulose and water with small amounts of organic or inorganic additives or impurities. The aim of this research was to characterize the material 'paper' in terms of a cellulose–water bicomponent material.

Apart from a few contemporary standards, all the studied samples were unprinted sheets of well-documented historical origin, spanning between the 15th and 18th centuries. This choice has many advantages, the main one being that these samples are high quality paper made of rags, compared with modern paper made of wood-pulp. Another advantage for the study of paper degradation is the possibility of obtaining paper in a good state of preservation, or in poor condition, or even completely destroyed, from the same source, i.e. an old book.

Characterization (McBrierty & Packer, 1993) on solid paper was performed as follows: pulsed low resolution NMR relaxation measurements, high resolution proton NMR line width and T_1 measurements at 200 MHz, ^{13}C NMR spectroscopy with CP-MAS at 100 MHz of *ad hoc* tailored pulse sequences were also employed.

EXPERIMENTAL

Materials

Samples of old sheets of paper from different European areas were used. There were differences between samples of the same period and also between those of the same book.

The samples for pulsed low resolution NMR and the 200 MHz measurements, which were all of the same weight, were conditioned in a controlled atmosphere. The samples were sealed in standard 5 mm diameter NMR tubes. The height of the sample was always kept less than 0·5 cm; i.e. the sample was well contained within the receiver coil both at 200 and at 57 MHz. The samples for the ^{13}C CP MAS NMR were prepared either by carefully rolling up paper foil within the KelF rotor for paper samples in a good state of preservation or pressed in the same rotor in the case of destroyed paper samples.

Proton NMR

All pulsed low-resolution ^{1}H NMR measurements were performed at 57 MHz on a commercial Spinmaster spectrometer (made by STELAR). The dead time of this instrument is 8 μs, the 90° pulse is 5·0 ± 0·1 μs, the temperature was maintained at 296 K ± 0·1 K. In order to minimize experimental errors a continuous attenua-

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*To whom correspondence should be addressed.

tor was introduced between the transmitter output and the receiver input; in this way it was possible to subject each sample to 90 and 180° pulses in a standard 5 mm diameter NMR tube and with a height well within the coil.

Spin-lattice relaxation times T_1 were measured with the Aperiodic Pulse Sequence (saturation recovery method) with phase detection (APS) (Fukushima & Roeder, 1981). A few measurements were also performed using an inversion recovery method in order to confirm the APS data.

In each T_1 determination at least 128 delays (τ values) were used in a multiscan–multiblock procedure. Each block has a 128 word size corresponding to 128 ms in the time domain. Thus each point corresponds to a 1 μs increment. The full procedure was repeated 16 times (16 scans) in order to ensure a good signal to noise ratio. After the dead time (7–8 μs) the first 13 points of each block were averaged and used for the determination of T_1 of the cellulose component.

Following the first 56 points of each block 64 points were averaged and used for the determination of T_1 the spin lattice relaxation time of the water protons. This procedure can be applied when the two overlapping signals are well separated in the time domain (Capitani *et al.*, 1992; Segre *et al.*, 1992; McBrierty & Packer, 1993).

High-resolution NMR spectra

High-resolution NMR spectra were also run at 200·13 MHz on a Bruker AC-200 Spectrometer on the same samples as above, without spinning and at a temperature of 298 K. Typical free induction decay (FID) used 1024 data points in the time domain and before the Fourier transformation the size was increased to 8 K by zero filling.

Line widths were measured at the half height of experimental peaks. Areas were calculated setting the absolute intensity of sample number one to equal 1 and keeping it fixed for all the other samples. The frequency range of integration was always five times that of the corresponding line width. T_1 values were measured by the inversion recovery method with a relaxation delay longer than five times that of the longer T_1 value.

Data analysis

Inversion recovery and Aperiodic Pulse Saturation (APS) experiments lead to an equation of the type $M = S_iA_i\exp(\text{-t}/T_i) + A_0(i = 1, \ldots, N)$ where N is the number of different T_i relaxations having weight A_i, while A_o is the value of the magnetization M after a single 90° pulse. This equation was fitted with a computer program 'Stefit' included in the Spinmaster software. This method employs a 'Simplex' algorithm. Fitting was performed by minimizing the mean square deviation. The experimental points were compared with the calculated ones and their compatibility was tested to a 68% confidence level according to the 'F' distribution. The number of sign changes of the ordered experimental points was tested with respect to the calculated function. Deviation of the number of sign changes compared with binomial distribution function to within a 68% confidence level was accepted.

^{13}C NMR

^{13}C CP MAS experiments were performed on a Bruker AM 400 instrument operating at 100·53 MHz. The MAS rotor was spun at 3500–4200 Hz depending on the samples. Cross polarization (CP) was obtained by a spin lock of 1–1·5 ms duration, the number of scans varied from 2546 to 2048. FIDS were transformed with an exponential multiplication of 16–32 Hz. Resolution enhanced spectra were obtained by Gaussian Lorentian transformation with the typical $\text{Lb} = -1$ and $\text{Gb} = 0{\cdot}1$.

The pulse sequences applied in order to discriminate different relaxation components as presented in the Results and Discussion were as follows. That reported in (a) (see Results and Discussion below) was that proposed by Torchia (Torchia, 1978). This is able to discriminate between different ^{13}C NMR longitudinal relaxation properties. The (b) and (c) pulse sequences were mainly formulated in order to discriminate the effect of proton relaxation properties on the ^{13}C NMR spectrum.

In particular, in (b) a DEFT pulse sequence (Becker *et al.*, 1969) on proton magnetization prior to the CP MAS experiment was able to discriminate the ^{13}C resonances dipolarly coupled to long and fast relaxing proton resonances. In fact:

90-τ- 180-τ–90 (^{1}H) spin lock (CP)
————————————(CP)——AQ (^{13}C).

This preparatory sequence acts on proton resonances depending on the value of the delay τ. At short τ values it is able to selectively realign the magnetization of the slow relaxing component of the proton spins along the z-axis. In this way the slow relaxing component of the proton magnetization becomes inactive for the CP transfer to carbon resonances. In contrast, the last 90° pulse aligns on the x, y plane the magnetization of only the short relaxing proton component ready for the polarization transfer to the dipolarly coupled ^{13}C resonances. Sequence (c) on other hand selects between ^{13}C resonances dipolarly coupled to protons which undergo either fast or slow transverse relaxation.

90(^{1}H)-τ- spin lock (CP)
——————(CP)——AQ (^{13}C).

In fact, the inserted delay τ allows the preceding proton magnetization in the x, y plane to undergo a transverse relaxation. In this way after a sufficient long τ delay only the slow proton relaxing component is able to give a cross polarization to the carbon resonances.

RESULTS AND DISCUSSION

Cellulose, the major component of paper, is always present as a semicrystalline polymer. A variable mixture of different polymorphous forms always exists (VanderHart & Atalla, 1984), accompanied by a variable amount of the amorphous fraction. The structure of some of the polymorphous forms has been recently defined by electron diffraction data (Sugiyama *et al.*, 1991). Most of the previous studies, and in particular the fundamental ones showing that a complex polymorphism is present in cellulose, have been made by ^{13}C CP MAS techniques. The existence in material originating from algae (Torri *et al.*, 1993), and spectroscopically well characterized by ^{13}C NMR CP-MAS. We present here an NMR study of paper using both ^{1}H NMR pulsed relaxation methods as well as ^{13}C CP MAS techniques.

Low-resolution pulsed NMR

In Fig. 1A, a decay of nuclear magnetization ^{1}H NMR (FID) at 57 MHz is shown. In the time domain, a fast decaying component, owing to cellulose protons, is clearly observable, while the slow decaying component due to the more mobile protons of water is barely observable. On Fourier transformation of the time domain into the frequency domain (Fig. 1B), the cellulose component appears broad and noisy, while the water component appears as a sharp peak at the top of the broad one.

Taking the first few points of the FID (Segre *et al.*, 1992), T_1 measurements can be easily performed on the cellulose components. If the first points of the FID are neglected, i.e. considering the data when the fast relaxing component is fully decayed, the T_1 measurement of the slow relaxing component, i.e. water, is rather easy. The procedure used is reported in detail in Methods. A Fourier transformation on the same experimental data leads to the same measure in the frequency domain; however, in the frequency domain only the sharp water component can be measured reliably.

In all the samples examined, both the water and the cellulose signals exhibit multiple T_1 relaxation; thus, both for the cellulose and the water signals, T_1 measurements show the presence of three components (see Fig. 2A and 2B). The existence of a fast, intermediate and slow NMR relaxing component, respectively, is, in general, to be attributed to the solid states with either a different aggregation state or dipolar interaction regime.

For all the samples studied, the T_1 values of the long relaxing component of cellulose are shown in Fig. 3A, plotted against the corresponding long T_1 value of the water component. All these values, without any correction, are well correlated around the $y = x$ line; a correlation coefficient larger than 98% has been found between the two sets of data, the slope of the line is 1·09 ± 0·06. This finding indicates that a spin diffusion mechanism exists (Abragam, 1978). There is very efficient transfer of magnetization from the cellulose to the

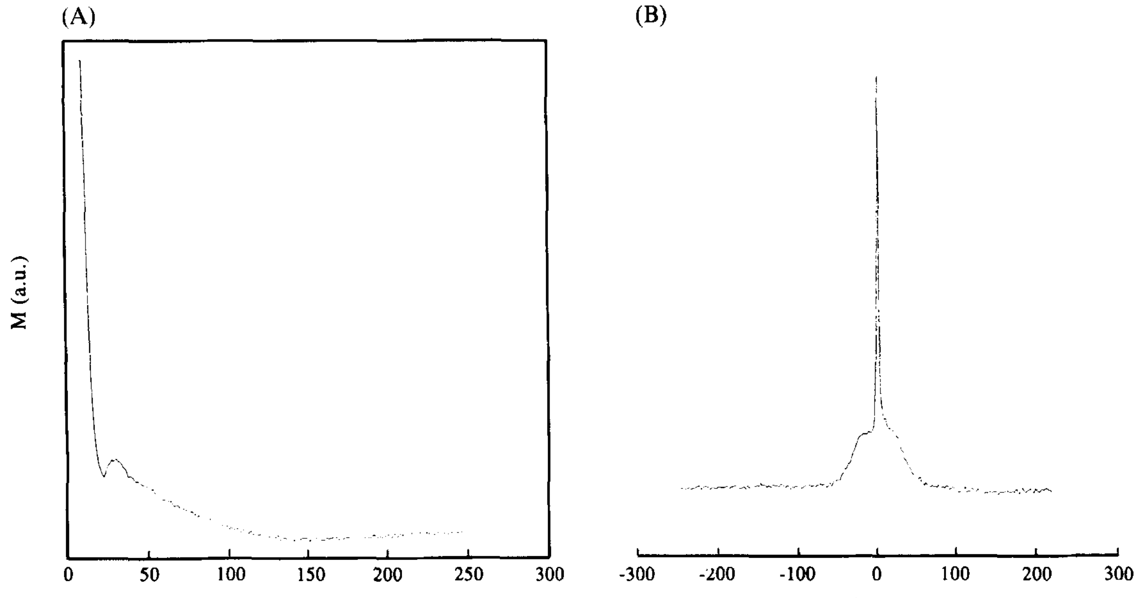

Fig. 1. (A) Free induction decay in the time domain of a piece of antique paper at an NMR frequency of 57 MHz. The fast decaying component is due to cellulose. (B) The same data after Fourier transformation. The sharp resonance is due to water protons, while the broad one (~30 kHz) is due to cellulose.

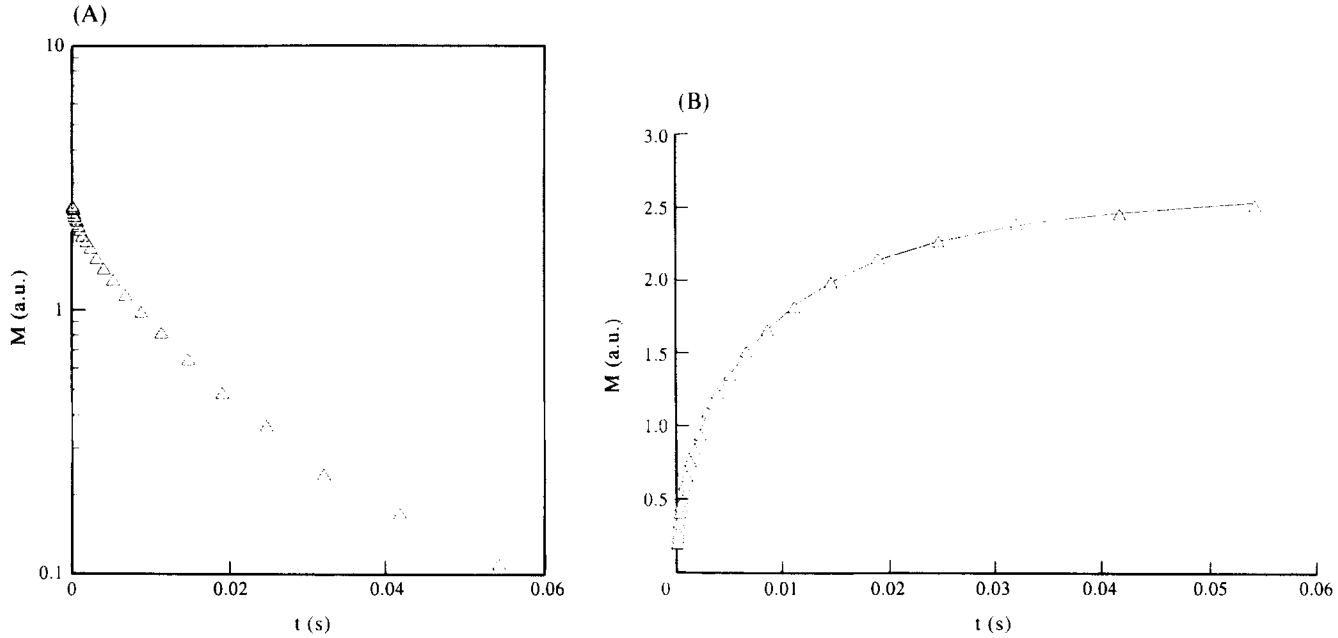

Fig. 2. ^{1}H NMR aperiodic saturation recovery experiment obtained as reported in Methods, on the cellulose component. (A) For the sake of clarity a multi-exponential decay is shown in a semilogarithmic representation. (B) The same experiment. The full line represents the best fit calculated curve.

water and vice versa. From an inspection of Fig. 3A another important piece of information can be derived. By measuring the slowest T_1 component of the water (an easy measurement), the corresponding T_1 value of cellulose is obtained. Finally, the almost perfect linear correlation of these T_1 values shows that water is present in a form strongly bound to the cellulose and, as a consequence, that the amount of free water, if any, is negligible.

By plotting the intermediate T_1 value of water protons vs the corresponding intermediate value of those of cellulose, it can be seen that all points lie in the upper part of the $y = x$ line (Fig. 3B). The correlation coefficient of the two sets of data is rather high, 62%,

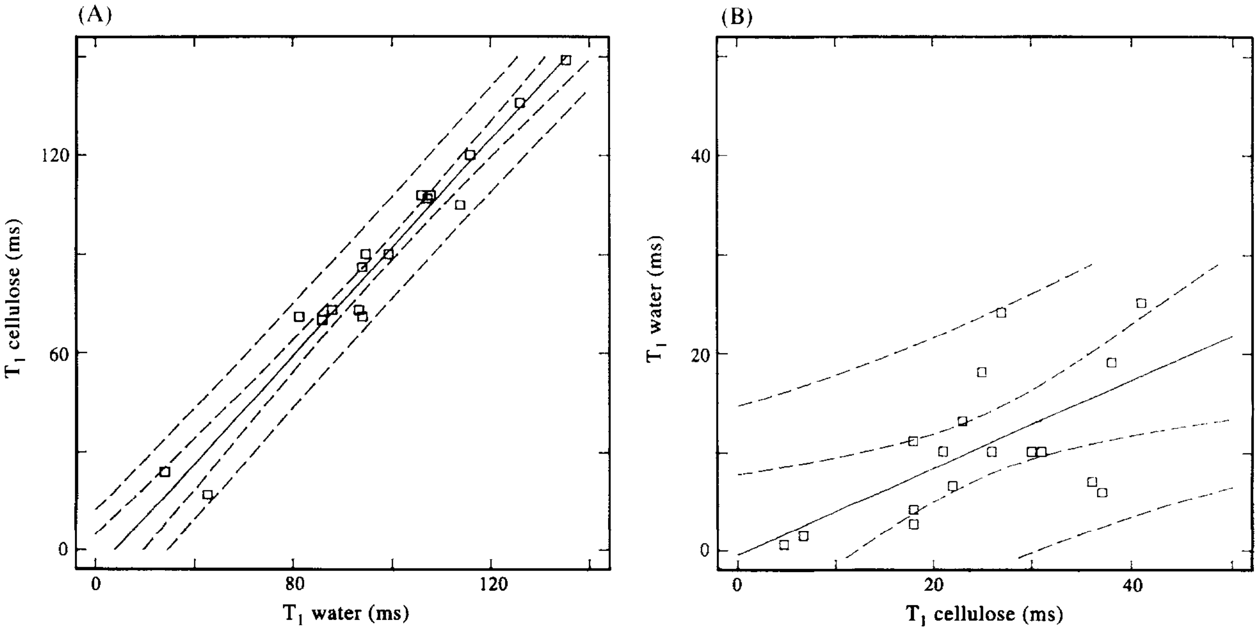

Fig. 3. ^{1}H NMR T_1 relaxation. (A) The T_1 of the long relaxation component of cellulose vs water. (B) The T_1 of intermediate relaxing component of water vs cellulose. The full lines are calculated from a linear regression analysis showing two pairs of dotted lines representing the 98% confidence and prediction limits.

with an error much larger than in the previous case. The slope of the best fitted straight line is 0·45 ± 0·14. This kind of correlation indicates that an imperfect spin diffusion process occurs between the water and the cellulose.

Thus either the spin diffusion process is inefficient because these components and their relaxations are compartmentalized into different domains or, more likely, very effective relaxation reagents of a different nature, probably paramagnetic species, are present in one of the two components. In fact the former seems less probable due to a high correlation present between the two relaxation values. Another possible explanation of this effect is that the total amount of water is not enough to be fully efficient in the spin diffusion process. The water component is correlated by spin diffusion to the cellulose component; however, the whole process is rather inefficient due to the low water/cellulose ratio.

Thus the short T_1 values (Table 1) indicate the presence of a relaxation mechanism mainly dominated by paramagnetic impurities. The presence of these impurities has been verified by EPR spectra; small amounts of Fe^{3+}, Cu^{2+}, Mn^{2+} and other paramagnetic species have been observed in all the paper samples.

The fastest T_1 component, both for cellulose and for water, has a short value with a rather high error; this high error is probably due to the very crude approximation involved in assuming that only one T_1 component is present with a very short relaxation value. In any case, the fastest T_1 relaxing component might be reasonably attributed to cellulose and water in proximity to a paramagnetic centre.

High-resolution NMR spectra

The sharpness of the water peak indicates the possibility of performing ^{1}H NMR measurements on a conventional high resolution NMR spectrometer. An inversion recovery experiment performed on this signal at 200 MHz, shows the presence of three components (data not shown) whose values agree well with the corresponding ones at 57 MHz (Table 1).

Owing to the efficiency of the spin diffusion process previously found, simply by measuring the spin-lattice relaxation of water on a conventional high-resolution spectrometer it is possible to attain the spin-lattice relaxation on the slow relaxing component of cellulose.

A comparative measure of the total water amount was also made on paper showing different degradation. Table 1 shows that the water content is correlated in some way to the degradation state of the paper. In all the sheets of paper which appear in a good state of preservation or showed only slight deterioration the amount of water is the same within 10% of the amount present in sample 1. This sample was taken as a standard of high quality and good preservation. In all samples which appear in a very bad state of preservation (strong degradation), a net loss of water can be measured, the net loss being more than 10% and up to 25%.

Moreover, by comparing the proton line width of paper belonging to the same source, but showing a different state of degradation, a definite enlargement of the water line width can be observed, as reported in Table 1. This enlargement may be due to a higher paramagnetic concentration in the 'amorphous' part of the paper compared to its semicrystalline counterpart. Moreover the loss of water is also associated with a net degradation increase, which in turn may be associated with an increase in the amorphous fraction. It also seems reasonable to formulate the hypothesis that a larger concentration of paramagnetic ions is located in the amorphous fraction of paper. It is noteworthy that in semicrystalline polymers it is well known that impurities tend to concentrate in the amorphous fraction.

^{13}C NMR spectroscopy in the solid state

For ^{13}C CP MAS NMR spectroscopy our attention was concentrated on sample 1 as a source of paper with a high polymerization index, long fibres and a high 'crystalline' fraction, and on sample 4 as a source of amorphous cellulose with lower water content; ^{13}C CP MAS NMR spectra were performed on these samples. The ^{13}C NMR spectrum of a destroyed piece of paper (sample 4) is shown in Fig. 4. The observed resonances are attributed to the carbons of the carbohydrate moiety according to literature data (Horii *et al.*, 1987; Isogai *et al.*, 1989; Debzy *et al.*, 1991). As previously shown the sharp resonances must be attributed to the long fibre components of the cellulose, whilst the broad ones are due to the amorphous components (Cael *et al.*, 1985; Debzy *et al.*, 1991; Torri *et al.*, 1993). The chemical shift of these broad resonances (C1 and C4 carbons, respectively) corresponds well to previously published spectra of amorphous cellulose components (VanderHart & Atalla, 1984).

In the enlarged spectrum, resolution enhanced, as shown in Fig. 4, the shape of the resonance of C1 at 106 ppm clearly indicates the presence of amounts of the microcrystalline forms of type Iα and Iβ (Axelson, 1986; Isogai *et al.*, 1989; Debzy *et al.*, 1991). The resolution enhancement procedure strongly decreases the broad lines of the amorphous fraction.

The presence of heterogeneity in all samples (at least two different forms of polymorphous fibres plus a high amorphous content) and the information obtained from the previously shown relaxation studies, leads to the hypothesis that a selection of the relaxation times might be useful in order to unravel the spectra of the components. Thus we attempted to reveal differences in samples 1 and 4 by different experimental procedures as follows:

(a) in the ^{13}C relaxation applying the pulse sequence proposed by Torchia (Torchia, 1978);

Table 1. Spin lattice T_1 relaxation times of ancient paper samples

	Sample	Line width (Hz)	T_1 (200 MHz) (water) (ms)	T_1 (57 MHz) (cellulose) (ms)	T_1 (57 MHz) (water) (ms)
1	15th century (north Italy) good	2014	130±5 40±2 3·48±0·07	149±6 41±3 3·5±0·7	143±4 26±1 2·0±0·1
2	15th century (north Italy) deteriorated	2014	124±2 28±1 3·00±0·05	73±2 18±2 2·0±0·3	80±5 12±1 1·9±0·1
3	15th century (north Italy) good	1307	220±2 53±1 3·70±0·04	120±4 30±2 2·0±0·3	114±5 11±1 2·2±0·2
4	15th century (Italy or Germany) destroyed	1816	108±7 40±1 2·07±0·04	70±11 23±2 1·4±0·7	69±7 14±2 1·7±0·3
5	15th century (north Italy) destroyed	1683	138±10 56±5 4·1±0·1	90±5 37±2 2·7±0·2	82±6 5·8±0·5 1·7±0·2
6	18th century (Sardegna) destroyed	3759	30±1 9·8±0·6 0·9±0·2	24±3 6·7±0·5 0·84±0·06	21±1 2·3±0·3 0·51±0·07
7	18th century (Sardegna) destroyed	3682	26±1 8·9±0·4 0·99±0·07	17·2±0·4 4·7±0·3 0·42±0·05	34±1 1·4±0·3 0·42±0·02
8	15th century (Italy) very poor	1414	127±4 34±1 3·37±0·02	71±2 18±1 1·79±0·03	62±7 3·2±0·4 2·0±0·2
9	15th century (Italy) poor	1403	98±3 9·3±0·5 2·38±0·04	71±2 18±1 1·37±0·03	81±4 4·7±0·3 1·08±0·02
10	15th century (Italy) good	1120	167±4 56±1 4·68±0·04	90±2 21±1 2·4±0·1	89±3 11·0±0·6 2·12±0·07
11	15th century (France) very poor	1704	146±3 38·3±0·8 2·86±0·02	73±4 22±2 1·6±0·3	72±1 7·55±0·02 3·09±0·01
12	15th century (France) very good	1557	280±9 88±3 3·9±0·1	107±2 27±1 2·9±0·3	101±3 30±2 2·89±0·05
13	15th century (France) destroyed	1857	177±3 56±1 2·92±0·03	86±3 25±2 2·0±0·2	81±6 19±2 2·5±0·2
14	15th century (France) very good	1683	227±3 49±4 3·76±0·07	105±2 31±2 2·9±0·4	111±3 11·0±0·6 2·1±0·1
15	16th century (Germany) very good	1215	169±2 33±3 6·09±0·07	108±3 26±2 3·4±0·3	99±5 10±1 3·2±0·3
16	15th century (Germany) some deterioration	1195	106±2 13±1 4·27±0·06	108±5 36±2 2·6±0·1	102±4 8±2 1·7±0·4
17	15th century (Germany) very good	1180	209±4 42±6 6·1±0·1	136±4 38±2 3·9±0·3	129±3 20±1 3·4±0·1

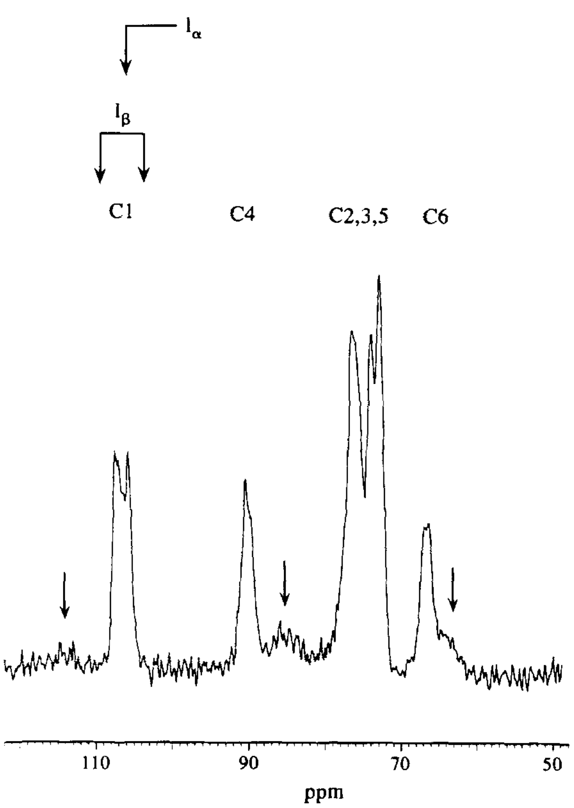

Fig. 4. ^{13}C CP MAS at 100 MHz of sample 4. A resolution enhancement function (LB = −1, GB = 0·1) has been applied to the FID before the Fourier transformation on 8 K points. Carbon resonance assignment is reported. I$_\alpha$ and I$_\beta$ refer to the polymorph phases of cellulose (VanderHart & Atalla, 1984). Arrows indicate characteristic broad resonances of amorphous cellulose components (VanderHart & Atalla, 1984).

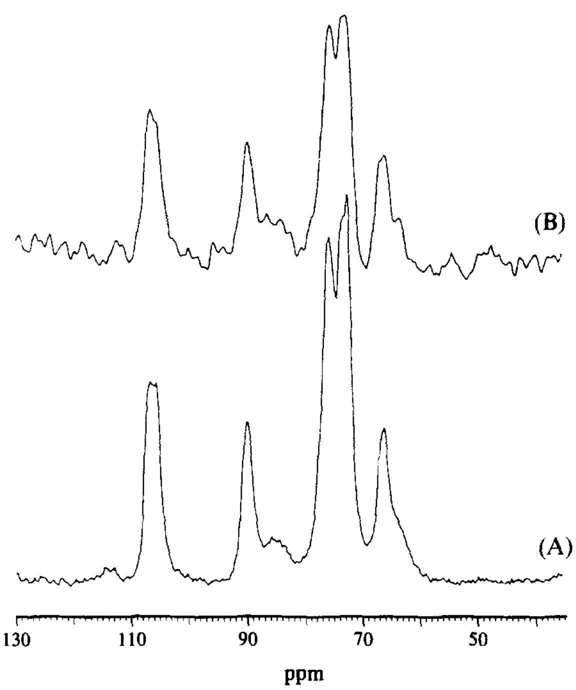

Fig. 5. ^{113}C CP MAS spectrum obtained with pulse sequence (b) reported in Methods which includes a DEFT preparatory pulse sequence prior to the CP spin-lock in order to select the different longitudinal relaxation of proton resonances. Measurements were performed on sample 4. Delay applied: spectrum (A) $\tau = 2{\cdot}2$ s; (B) $\tau = 0{\cdot}65$ ms. The spectrum in B is amplified 4 times.

(b) monitoring the effects on the ^{13}C NMR spectrum of the proton T_1 relaxation selection obtained including a preparatory DEFT sequence in the standard CP MAS procedure as reported in Methods; and

(c) monitoring the effects on the ^{13}C NMR spectrum of the proton T_2 relaxation selection including an additional delay which allows the fast component of the transverse relaxation occurring in the standard CP MAS procedure as also reported in Methods.

The attempt to monitor different ^{13}C NMR longitudinal relaxations, as in (a) did not give significant results for the two samples under study. For (b) we attempted to correlate different ^{13}C NMR spectra of the two solid phases to the different T_1 relaxations of the proton resonances. In fact the DEFT sequence is able to separate in the CP MAS ^{13}C NMR spectrum the resonances which are dipolarly coupled to slow relaxing protons from those coupled to the fast relaxing ones depending on the τ value as shown in Methods. The spectra obtained are reported in Fig. 5A and B. When τ is long enough to allow a full T_1 recovery of both the fast and slow relaxing proton components a 'normal' ^{13}C spectrum is obtained (see Fig. 5A). With a delay of 0·65 ms (Fig. 5B) which allows the recovery of only the slow relaxing proton component the ratio between the intensity of the resonances changes significantly. Nevertheless, it was impossible to adjust this delay to a value to obtain a full suppression of one of the two components in the ^{13}C spectrum.

The reason for the incomplete suppression is probably the presence of a very fast relaxing component due to the proximity to paramagnetic centres. Even if the efficiency of the spin diffusion process is different in different domains of the material, it still acts as an equilibrator which destroys the differences in the transfer of polarization from ^{1}H to ^{13}C.

Method (c) was directed toward the selection of different proton transverse relaxation times (T_2) prior to CP MAS measurement applying the pulse sequence (c) as reported in Methods. Resonances due to 'crystalline' components, of long, well-packed fibres, characterized by low internal mobility give a good cross polarization with a higher number of spin–spin interactions rather than the corresponding amorphous fractions. Short fibres, badly packed, rich in paramagnetic ions, dephase more efficiently thus decreasing, and eventually eliminating the cross polarization from protons to carbon (Axelson, 1986; Jelinsky & Melchior, 1987). The results obtained on a destroyed sheet of paper (sample 4) are reported in Fig. 6A, B and C, respectively.

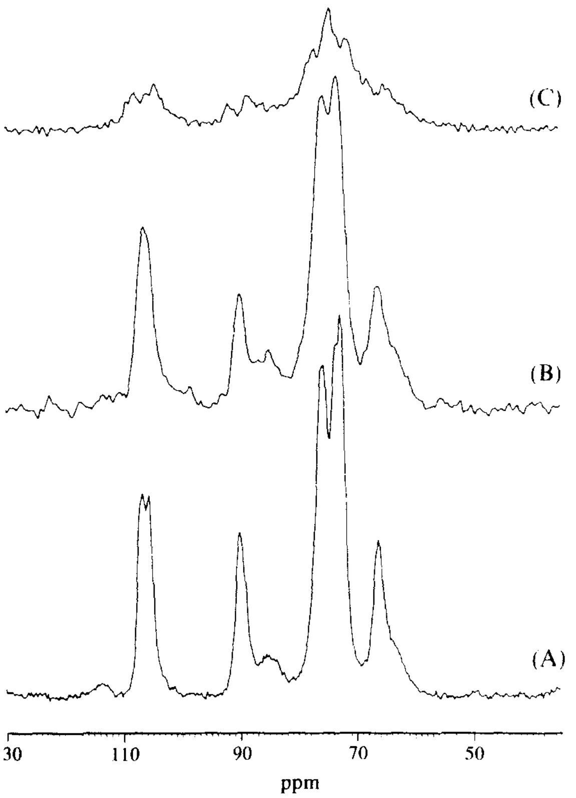

Fig. 6. ^{13}C CP MAS of the same sample 4 obtained with the pulse sequence (c) reported in Methods. Spectrum (A) $\tau = 43$ μs; (B) $\tau = 0$; (C) difference B − A. The T_2 selection of the proton resonances depending on the efficiency of transverse relaxation is discussed in the text. Spectra in B and C are vertically amplified 2 times.

In the case of destroyed paper, the different intensities of resonances obtained in the A and B spectra where delays of 43 and 0 μs were applied, respectively, is clearly visible. The spectrum difference between spectra A and B, reported in Fig. 6C, clearly shows the resonances due to the amorphous components. In contrast, the same experiment performed on the well preserved example does not show any difference (spectra not shown).

CONCLUSIONS

These observations are part of an investigation on the physico-chemical properties of paper considered as a material composed of water and cellulose. An internal heterogeneity appears evident, due to the presence of different polymorphs of cellulose and to the presence of amorphous material, characterized by a different amount of water. Paramagnetic impurities are found in different parts of the material acting as a relaxation reagent. The presence of amorphous components where paramagnetic impurities preferentially localize, was clearly indicated by the results of the magnetic relaxation experiments.

The ^{13}C CP MAS experiments clearly showed that no difference in longitudinal ^{13}C NMR resonances was observed. The selection based on the proton T_1 values in order to obtain different ^{13}C spectra, was only partly successful probably due to the presence of paramagnetic ions not only in the amorphous but also in the fibrous part of paper, as shown by proton relaxation. Selection of different components of proton transverse relaxation markedly influenced the cross polarization of dipolarly coupled carbons and, thus, the intensity of the ^{13}C NMR resonances. These results, taken together, gave an insight into the structure of amorphous cellulose. This structure should be poor in water content, rich in paramagnetic impurities and with a twisted conformation with respect to the long fibres common in cellulose I_α and I_β. This is well demonstrated by the strong chemical shift differences of resonances of carbons 1, 4 and 6 of the cellulose ring. This investigation has been performed on high quality sheets of paper. We plan to extend the NMR analysis to samples of modern origin.

This work is aimed at fixing protocol for paper evaluation, in order to establish the state of degradation and the restoration procedure required.

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