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Journal of Magnetic Resonance 170 (2004) 113–120
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

Monitoring degradation in paper: non-invasive analysis by unilateral NMR. Part II

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Received 22 April 2004; revised 15 June 2004
Available online 7 July 2004

Abstract

High quality paper samples have been oxidized with a specific oxidant to reproduce one of the possible causes of the aging of paper. All samples have been characterized by ^{13}C CP–MAS NMR spectroscopy. The artificial aging of paper has been monitored using a standard NMR relaxometer and the results have been compared with the corresponding data obtained using an unilateral NMR relaxometer. Experimental values obtained with both techniques are in agreement, demonstrating that unilateral NMR relaxometric measurements constitute a suitable non-invasive method for assessing the degradation process of cellulose-based materials. The sensitivity of the non-invasive NMR method allows the detection of degradation even at a very early stage. Effects due to the sample volume and to the penetration depth have been investigated.

Keywords: Unilateral NMR relaxometer; Cellulose oxidation; Paper degradation; T_2 relaxation time

1. Introduction

In a previous paper [1], we have shown that it is possible to study the degradation of ancient books using unilateral NMR. The quality of the experimental data was sufficient for discriminating the state of paper preservation in the investigated books. The promising perspectives of this investigation prompted us to perform further experiments on cellulose-based materials to assess the limits and possibilities of the method on artificially aged paper.

Paper is one of the oldest and widely used man-made materials. It is mostly made from cellulose and water with small amounts of organic, inorganic and, possibly, dye additives [2]. While in earlier hand-made and modern high-quality machine papers only cellulose fibers are present [3], in low quality paper the cellulose is embedded in an hemicellulose and lignine matrix. In paper the water component is located in pores. The removal of even a small amount of water from these pores causes an irreversible destruction of the material [4]. In good quality modern paper, the pore size distribution was previously obtained using a well-established NMR method [5–7] which correlates the intensity of the signal of the mobile water component with the temperature. The obtained distribution is strongly asymmetric with a well defined maximum at $\approx$1.4 nm [7]. The average size of the water pools has been confirmed applying NMR techniques suitable for studying the spin diffusion process, i.e., dipolar-filter methods [8,9] and 2D WISE [8]. Both techniques show that the water pools are surrounded by amorphous cellulose, whereas crystalline domains surround amorphous domains which in turn include the water pools [7]. Moreover, dipolar-filter methods allow a rough evaluation of the distance between crystalline domains and the water pools. This distance is about 3 nm. These results agree well with results obtained by transmission electron microscopy (TEM) [10].

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doi:10.1016/j.jmr.2004.06.006

Due to the small average size (≅1.4 nm) of water filled pores, in dry material, the diffusion process of the confined water is negligible. We have confirmed this observation using the Pulsed Field Gradient method. In fact, in dry paper, even when a strong gradient of 1000 G/cm is applied the diffusion coefficient of the water confined in the pores is too small to be measured.

The degradation of paper is a complex phenomenon due to different causes such as the biotic action of fungi and bacteria and/or chemical attack. In chemical terms, the degradation of paper is essentially the conversion of fibrous and highly crystalline cellulose into a largely amorphous degraded material. Such transformation is the result of different, complex processes among which acid hydrolysis is by far the most important. In all cases of paper degradation, a loss of water was previously observed [4] associated with a shortening of the spin–spin relaxation time T_2 of the water confined in the pores. Relaxometric NMR methods have been shown to be valuable in assessing the quality of paper with regard to an early detection of enzymatic attack [11]. The most sensible parameter is the spin-spin relaxation time T_2 of the H_2O component. In fact, after enzymatic attack, a net decrease of T_2 has been reported. Note that the same T_2 shortening is also present in dry, degraded wood [12].

Standard NMR methods are particularly suitable for studying materials and are generally considered as non-invasive. However, they do require some sampling often forbidden when studying rare and precious materials such as old books and *incunabula*. The sampling can be avoided using an unilateral NMR instrument such as the Eureka Mouse[1] (EM10), which is a variant of the NMR-MOUSE[2] [1,13]. These sensors are portable and their use is fully non-invasive, allowing the measurement of a few NMR parameters such as the spin density, the spin–spin and the spin–lattice relaxation times. The sensor can be positioned near intact objects in different positions.

In a previous paper [1], we have indeed demonstrated that unilateral NMR is a suitable instrument to assess the quality of ancient paper made of rags. However, many questions are still open. These are for instance "*Can the relaxation data measured in paper with an unilateral instrument be directly used for assessing the degradation process?*" and "*What is the limit of detection of the degradation process attainable with conventional and unilateral relaxometers?*" To answer these questions a systematic study of one type of artificially aged paper was performed. It is worth noticing that the use of artificially aged paper samples allows a direct comparison of relaxation data obtained by unilateral NMR relaxometry and by measurements in a homogenous field.

[1] Bruker Biospin produced within the Eureka project Σ!*2214*.

[2] NMR-MOUSE is a registered trademark of Aachen University of Technology (RWTH).

In this work a high quality paper has been oxidized with a specific oxidant to reproduce one of the possible causes of paper aging. The artificial aging of the sheet of paper is then monitored using the unilateral relaxometer, and the results are compared with the corresponding ones obtained using a conventional NMR relaxometer. All paper samples have been also characterized by ^{13}C CP–MAS NMR spectroscopy.

2. Experimental

2.1. Samples

The cellulose substrate was Whatman paper N. 1 filter paper. This type of paper is obtained from cotton "linters" and can be considered as pure cellulose. Its degree of polymerization is 1230. Sodium metaperiodate ($NaIO_4$ 99.8%) was obtained from Sigma–Aldrich and was used without further purification.

2.2. Oxidation reaction

The oxidation of cellulose has been performed with sodium metaperiodate, a specific oxidizing agent. The reaction cleaves the C2–C3 bond and involves the formation of a 2,3-dialdehyde following the mechanism of the Malaprade reaction, without significant side reactions [14–16]. The oxidation reactions have been carried out at 25 °C, on circular dry samples with a diameter of 12 cm. The metaperiodate solution was obtained by dissolving stoichiometric quantities of salt in deionized water. The cellulose samples have been introduced into closed vessels and treated with $NaIO_4$ in the dark and under continuous stirring. At the end of the oxidation reaction the samples were filtered and washed with deionized water up to obtain neutral conditions. The oxidation reactions have been carried out for 2, 24, 48, and 72 h, respectively. Three sets of samples have been prepared using three different concentrations of metaperiodate, namely 0, 0.1, and 0.4 M. Samples soaked in deionized water in the absence of the oxidation reagent were used as a control. All samples have been dried and kept in a sample holder in the dark.

2.3. ^{13}C CP–MAS NMR

The samples were finely cut and packed into 4 mm zirconia rotors and sealed with Kel-f caps. Solid state ^{13}C CP–MAS NMR spectra were carried out at 50.13 MHz on a Bruker ASX-200 spectrometer. The spinning rate was kept at 8 kHz. The 90° pulse width was 3.5 μs, the relaxation delay was 3 s. The cross polarization was achieved with the variable spin-lock sequence RAMP–CP–MAS [17,18]. The RAMP was applied on the ^1H channel, and the center of the ramp

was set to the first matching sideband, taking advantage of a cross-polarization rate faster than that of the matching center band. The contact time τ was 2 ms. The spectra were obtained by acquiring 1024 data points in the time domain and Fourier transformed after a zero-filling to 2048 data points and exponential multiplication with a line broadening of 16 Hz.

2.4. Conventional ^1H NMR relaxometry

^{1}H low resolution NMR measurements were carried out at 18 MHz on a commercial spectrometer Spin Master2000 (SM2000), Stelar Mede Pavia (Italy). The paper samples were introduced into standard 5 mm NMR tubes, and the height of samples was kept well within the NMR coil (5 mm). The 90° pulse was 3.5 μs, and the dead time of the instrument at 18 MHz was about 15 μs. Spin–spin relaxation times T_2 were measured with a Carr–Purcell–Meiboom–Gill (CPMG) sequence [19]. The echo time was 100 μs, and 512 echoes were collected. T_2 values were also measured with the Hahn echo pulse sequence with echo times ranging from 50 to 3000 μs [19].

2.5. Unilateral NMR relaxometry

The measurements were performed with an unilateral NMR relaxometer Eureka Mouse (EM10). The magnetic field is generated using two anti-parallel permanent magnets mounted on an iron yoke with the radio frequency (RF) coil positioned in the gap [1,20]. Two coils were used; one operating at 18.153 MHz with a penetration depth of about 1 mm, the other one operating at 17.3 MHz with a penetration depth of about 3 mm corresponding to a sensitive volume of $1 \times 20 \times 50\,\mathrm{mm}^3$. With both coils we investigated single sheets of paper (≅0.1 mm thickness) and stacks of two, three, four, five, and six sheets (from 0.1 to ≈1 mm thickness). In the case of the 3 mm coil a 2.5 mm thick spacer, free of any ^{1}H NMR signal, was positioned between the coil and the sample. The maximum echo signal, corresponding to a $\pi/2$ pulse, was obtained with a pulse width of 3 μs, and the dead time was less than 15 μs. The spin–spin relaxation times T_2 were measured with the CPMG sequence following the procedure published previously [1,21]. Five hundred and twelve echoes were acquired in each scan with an echo time of 100 μs. T_2 measurements were also performed with the Hahn echo pulse sequence using echo times ranging from 50 to 3000 μs [19].

2.6. Analysis of relaxometric NMR data

The echo decays obtained with the CPMG and the Hahn echo sequences are expressed as normalized multi-exponential decays with a continuous distribution $W(T_2)$ of relaxation times T_2

$$y(t_i) = y_i = \int_{T_{2\min}}^{T_{2\max}} W(T_2) \exp\left[\frac{-t}{T_2}\right] \mathrm{d}T_2 \tag{1}$$

or as multi-exponential decays

$$Y = C_0 + \sum_i W_i \exp\left[\frac{-t}{T_{2i}}\right], \tag{2}$$

where i is the number of components, C_0 is the offset value, W_i is the spin density of the i component, and T_{2i} is the spin–spin relaxation time of the i component. With both instruments the error in the reported T_2 values is within 10% of the nominal values.

2.7. Relaxation time distributions of multi-exponential functions

To invert the experimental relaxation curve (1) for a distribution of relaxation times, the decay is approximated by a discrete distribution of relaxation times T_2 [22]. Furthermore, Eq. (2) is rewritten for discrete time values t_i which are equally spaced on the logarithmic scale $q_i = \ln t_i$ i.e.,

$$y(t_i) = y_i \cong W_0 \sum_{k=1}^{M} W_k \exp\left(\frac{-t_i}{T_k}\right).$$

To fit noise-contaminated experimental data, the data are smoothed by introducing a penalty function [23,24]. The final function to minimize in the fit is given by

$$\sum_{i=1}^{N}\left[W_0 + \sum_{k=1}^{M} W_k \exp\left(\frac{-t_i}{T_k}\right) - y_i\right]^2 + c_1 \sum_{k=1}^{M} W_k^2 + c_2 \sum_{k=1}^{M-1} (W_{k+1} - W_k)^2 + c_3 \sum_{k=2}^{M-1} (W_{k-1} - 2W_k + W_{k+1})^2. \tag{3}$$

This fit function has been implemented within a Matlab framework (R. Lamanna, personal communication). In the resultant distribution the abscissa provides the relaxation time values, and the integral corresponds to the normalized spin density.

3. Results and discussion

3.1. ^{13}C CP–MAS NMR spectroscopy

The damage induced on cellulose by the oxidation treatment was characterized by ^{13}C CP–MAS NMR spectroscopy. Fig. 1A shows the ^{13}C CP–MAS spectrum of untreated Whatman paper along with the assignment of the resonances. The "*c*" resonances are from the crystalline domains, while the broad "*a*" resonances are from the amorphous environment [25]. In Figs. 1B, D, F, and H the spectra of Whatman paper after oxidation with 0.1 M $NaIO_4$ for 2, 24, 48, and 72 h are shown, and in Figs. 1C, E, G, and I the spectra of Whatman paper

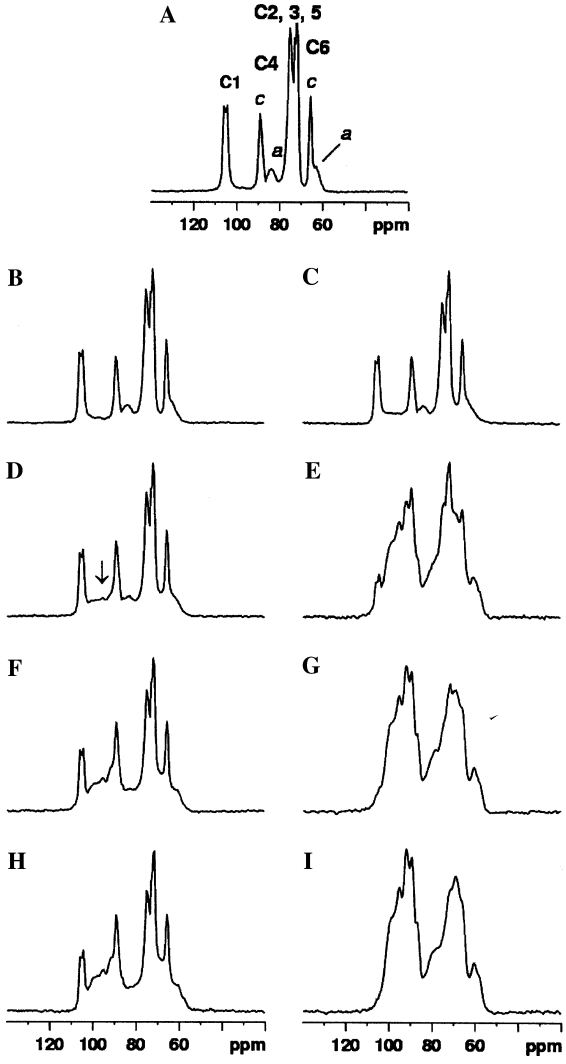

Fig. 1. ^{13}C CP–MAS NMR spectra at 50.13 MHz of untreated Whatman paper (A); Whatman paper oxidized with 0.1 M $NaIO_4$ for 2 h (B), 24 h (D), 48 h (F), and 72 h (H); Whatman paper oxidized with 0.4 M $NaIO_4$ for 2 h (C), 24 h (E), 48 h (G), and 72 h (I). Details of the assignment of the resonances C1–C6 are given in [25]. The arrow shows the characteristic resonances of cellulose oligomers [26].

after oxidation with 0.4 M $NaIO_4$ for 2, 24, 48, and 72 h are shown.

The spectra of the samples oxidized for 24, 48, and 72 h show a general broadening of all resonances as well as the appearance of new resonances in 90–100 ppm range which are due to cellulose oligomers [26]. At a high degree of oxidation the crystalline cellulose structure is seriously affected with a net increase of the amorphous component (Figs. 1E, G, and I). It is worth noticing that the spectrum of the sample oxidized for 2 h with 0.1 M $NaIO_4$ does not show any degradation of the cellulose matrix (Fig. 1B). Moreover, this sample does not show any sign of degradation by visual inspection. The spectrum of the sample oxidized for 2 h with 0.4 M $NaIO_4$ shows the presence of a very small amount of oligomers (Fig. 1C). This sample shows few yellowish spots on the surface.

3.2. NMR relaxometry

3.2.1. Measurements on single-sheet layers

In the past few years NMR relaxometric methods have been proved to be valuable in assessing paper quality [27]. The spin–spin relaxation time T_2 is very sensitive to the degree of paper degradation due to aging as well as to the enzymatic attack [11,12]. In fact, in all degraded samples, a net shortening of T_2 has been reported.

In Fig. 2A we report T_2 data obtained using a conventional relaxometer and applying a CPMG sequence on oxidized and control paper sheets. Circles refer to

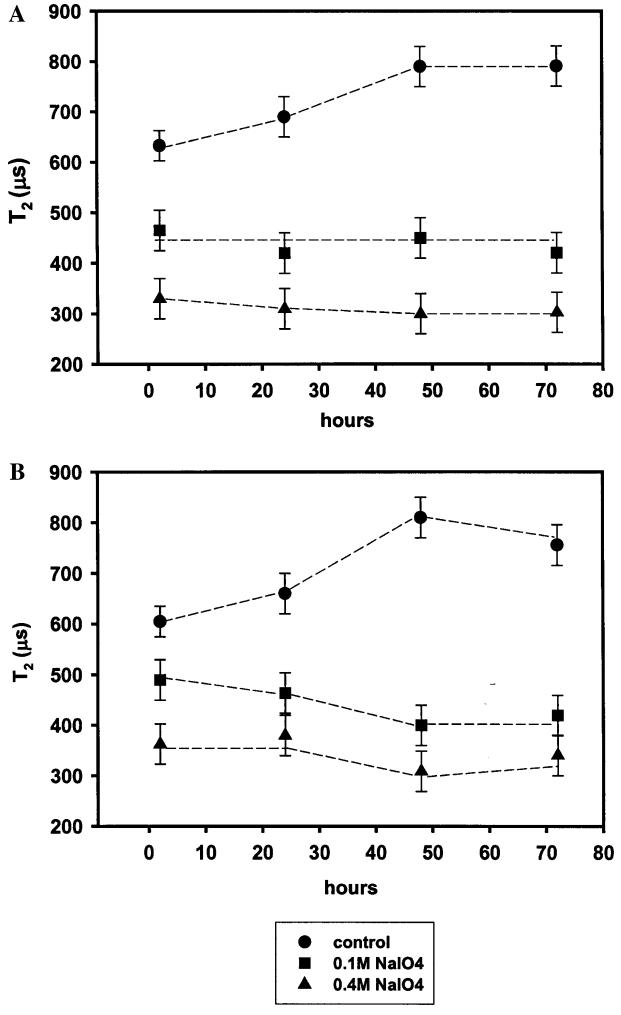

Fig. 2. CPMG T_2 values obtained with (A) the standard relaxometer, (B) the unilateral relaxometer. T_2 values are plotted vs. the number of hours of the oxidation treatment. (●) untreated Whatman paper; (■) Whatman paper oxidized with 0.1 M $NaIO_4$; and (▲) Whatman paper oxidized with 0.4 M $NaIO_4$. The increase in T_2 values of control samples is due to the prolonged soaking. This procedure is exactly the one followed in conservation treatments procedures.

samples used as a control, squares refer to samples oxidized with 0.1 M $NaIO_4$, and triangles refer to samples oxidized with 0.4 M $NaIO_4$. All T_2 values are reported with the corresponding fit errors. Note that the T_2 values measured in oxidized samples are definitely shorter than the values measured in the corresponding samples used as a control. The increase in T_2 values of the control samples is due to the prolonged soaking. This procedure is exactly the one followed in conservation treatment procedures. Moreover, the T_2 values measured in samples oxidized with 0.4 M $NaIO_4$ are always shorter than the corresponding values measured in samples oxidized with $NaIO_4$ 0.1 M. In addition to that, a net shortening of T_2 is also observed in the sample oxidized for 2 h with 0.1 M $NaIO_4$. As stated above, this sample does not show any visual degradation, and a degradation of its cellulose matrix was not detectable using ^{13}C CP–MAS NMR spectroscopy (Fig. 1B). Therefore, relaxometric data confirm our previous observation [11] that T_2 is a very sensitive parameter well suited to the characterization of any degradation process in paper even at its very early stage.

Even though the amount of sample required for performing the conventional relaxometric measurements is rather low (≈20 mg), the NMR method applied in the standard way cannot be considered as non-invasive. In fact, cutting samples from objects of cultural heritage must be strictly avoided. The advantage of using an unilateral NMR instrument is that the magnetic field is applied to the sample from one side only. The probe can measure the spin density, T_1 and T_2 relaxation times in a fully non-destructive way, i.e., fully preserving the integrity of the object under investigation.

In Fig. 2B we report T_2 values measured with the unilateral relaxometer using the CPMG pulse sequence. The T_2 values are reported vs. the time of oxidation. Circles refer to samples used as a control, squares refer to samples oxidized with $NaIO_4$ 0.1 M, and triangles refer to samples oxidized with 0.4 M $NaIO_4$. All T_2 values are reported with the corresponding fit errors.

The two sets of T_2 data, obtained with both instruments, are equal within the error, meaning that even in a strongly inhomogeneous field T_2 relaxation values are perfectly reliable, as clearly shown in Fig. 3, where T_2 values obtained with the unilateral instrument (empty symbols) are reported along with the corresponding values obtained within a homogeneous field (filled symbols). Note that in the presence of degradation, a definite T_2 shortening is observed. Even in a very early state of degradation, when other methods are insensitive, a small but definite T_2 shortening can be measured.

It must be pointed out that using the CPMG sequence only the mobile water component is observed, whereas the rigid cellulose component is disregarded. As previously shown [11], the paper degradation is associated with a reduction of the T_2 value of the confined

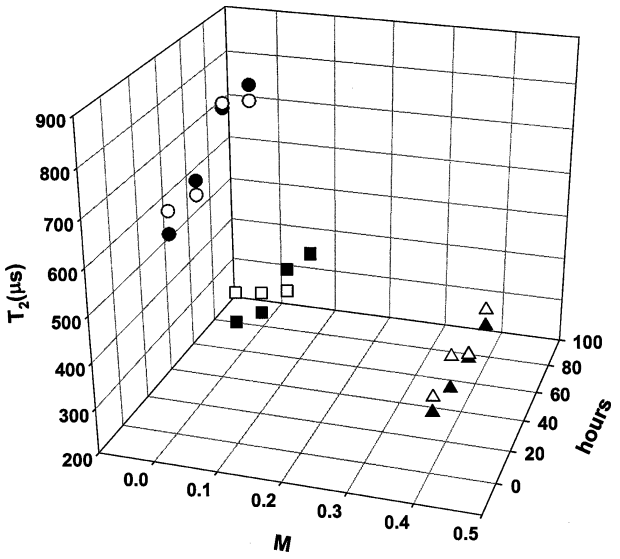

Fig. 3. CPMG T_2 values reported vs. the concentration of $NaIO_4$ and the time of oxidation. Empty symbols indicate measurements performed with the unilateral relaxometer whereas filled symbols indicate measurements performed with the standard relaxometer; circles refer to control samples, squares refer to samples oxidized with 0.1 M $NaIO_4$, and triangles refer to samples oxidized with 0.4 M $NaIO_4$.

water. Therefore, the T_2 value of the water confined in the pores can be considered as a degradation index. A possible rationalization of this conclusion is that the confined water acts as a sort of adhesive which glues the amorphous cellulose together through a network of hydrogen bonds.

Our measurements show that, on a single paper sheet, the measurements performed with the unilateral instrument agree well with the corresponding ones performed with a conventional relaxometer, without any apparent effect of B_0 or B_1 inhomogeneity [28]. Therefore, the unilateral instrumentation is suitable for studying natural and induced aging in cellulose-based materials. According to our results, since in the dry material the diffusion process of water confined into paper is negligible, we may directly link unilateral NMR measurements on cellulose-based materials to the corresponding measurements performed in homogeneous field without any need of corrections [29].

3.2.2. T_2 distributions obtained by inversion of relaxation functions

From our previous work on the size of the water filled pores in the paper, we are aware that a continuous distribution of pores appears to account for a single T_2 value. Hence, even in the presence of just one single exponential decay, the relaxation time obtained should be denoted as an average value from a distribution of relaxation times. The echo envelopes obtained with a CPMG sequence have been inverted to a distribution of relaxation times. The resultant distributions are centered

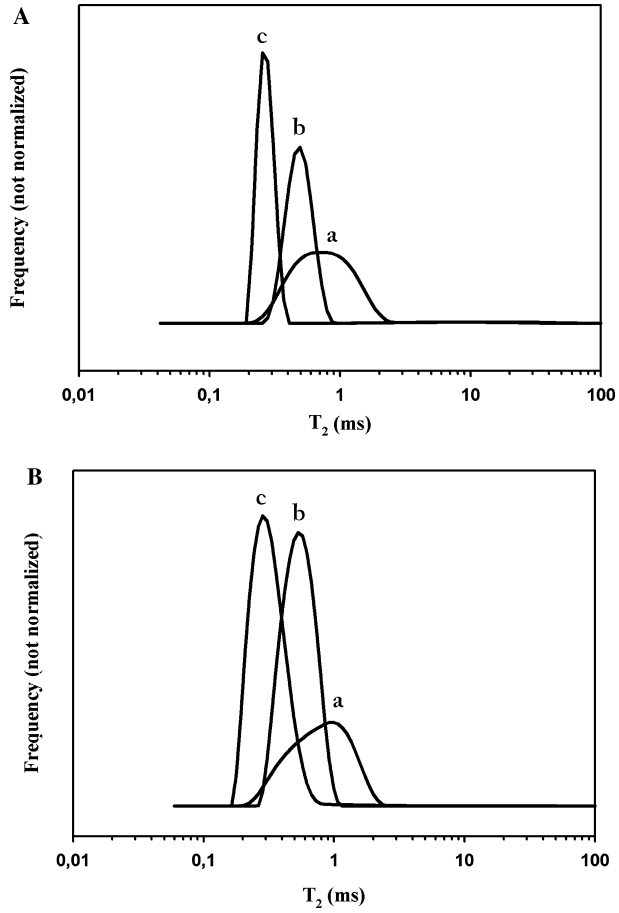

Fig. 4. T_2 distributions obtained by inverting CPMG relaxation decays. (a) Untreated Whatman paper; (b) Whatman paper oxidized for 48 h with 0.1 M $NaIO_4$; and (c) Whatman paper oxidized for 48 h with 0.4 M $NaIO_4$. (A) The distributions obtained with the standard relaxometer are shown, whereas in (B) the distributions obtained with the unilateral relaxometer are shown.

at a given position corresponding to the relaxation time and with an area corresponding to the signal amplitude. In this way a quick and easy representation of relaxation is obtained. The distributions obtained with the standard NMR relaxometer are shown in Fig. 4A, and those obtained with the unilateral instrument are shown in Fig. 4B. In both cases, the center of the distribution shifts down to shorter T_2 values as the degradation of the sample increases. The discrimination of samples appears to be best when using the relaxation time distribution compared to using relaxation times as such.

3.2.3. Effect of the thickness of the paper on T_2 values

In untreated paper, T_2 measurements with the CPMG sequence were performed as a function of the thickness of the paper using the unilateral instrument. A thickness ranging between 0.1 and 1 mm was obtained by stacking up to six sheets of paper. The resultant T_2 values range between 520 and 600 ms (Fig. 5), and agree within the experimental error. Therefore, measurements performed

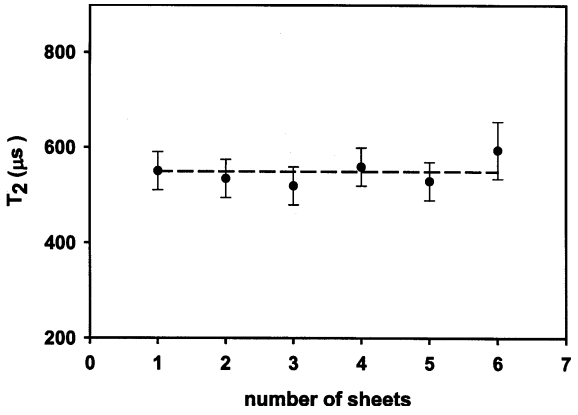

Fig. 5. CPMG T_2 values measured with the unilateral relaxometer as a function of the thickness of the paper. We obtained a thickness ranging between 0.1 and 1 mm by stacking up to six sheets of paper.

with the unilateral probe having 1 mm of penetration depth are not affected by the thickness of the sample.

3.2.4. Effect of the depth of penetration of the probe on T_2 values

Another effect which must be taken into account is that in any unilateral measurement the sensitive volume depends on the penetration depth of the probe. It was therefore necessary to test the effect of the volume on the measured T_2 values. T_2 values measured with the CPMG sequence obtained with a probe having a penetration depth of 1 mm and the corresponding ones obtained with a probe having a penetration depth of 3 mm were then compared. The thickness of the sample was about 1 mm resulting from six stacked sheets. The results are given in Fig. 6. The T_2 values refer to a sample used as a control (●), to a sample oxidized for 2 h with 0.1 M $NaIO_4$ (■) and to a sample oxidized for 2 h with 0.4 M $NaIO_4$ (▲). As shown in Fig. 6, T_2 values measured with

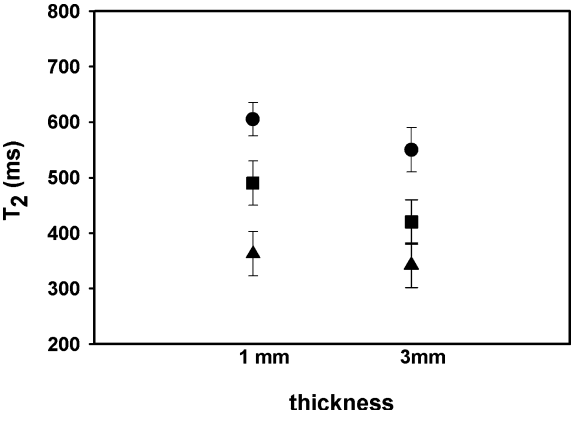

Fig. 6. CPMG T_2 values measured with the unilateral relaxometer using the probe with a penetration depth of 1 mm and using the probe with a penetration depth of 3 mm. Untreated Whatman paper (●); Whatman paper oxidized with 0.1 M $NaIO_4$ (■); and Whatman paper oxidized with 0.1 M $NaIO_4$ (▲).

the probe with 3 mm penetration depth, are only slightly shorter than the corresponding ones obtained with the probe having a penetration depth of 1 mm. All T_2 values obtained with both probes are well within the experimental error of the corresponding values obtained in a homogeneous field. Therefore, the measured T_2 values do not depend on the applied field gradient strength and on the depth.

3.2.5. T_2 measurements performed with the Hahn echo sequence

T_2 measurements were also performed on a few oxidized 1 mm thick samples with the Hahn echo sequence. Using this sequence it is possible to measure the T_2 value of the cellulose matrix as well as the T_2 values of the mobile water component. In Fig. 7 the decay obtained after applying the Hahn echo sequence is reported: the decay obtained with the standard relaxometer is shown in the top whereas the decay obtained with the unilateral relaxometer is shown in the bottom. Regardless of the treatment, a very short T_2 component of about 30 ± 10 μs is measured in all samples using both a conventional and an unilateral relaxometer. This short component is insensitive to the oxidation process. Whereas the long relaxing T_2 component is clearly affected by the oxidation,

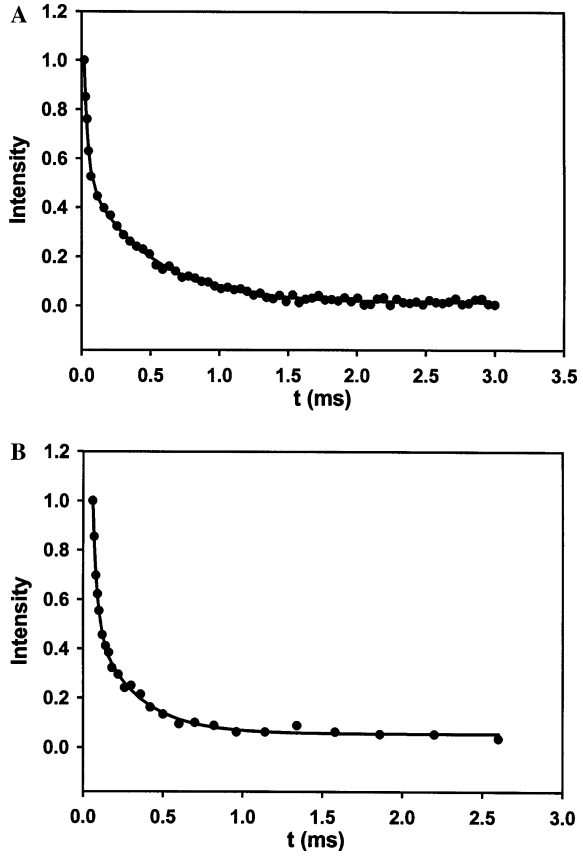

Fig. 7. T_2 decay obtained after applying the sequence for measuring the Hahn Echo: (A) data obtained with the standard relaxometer; (B) data obtained with the unilateral relaxometer.

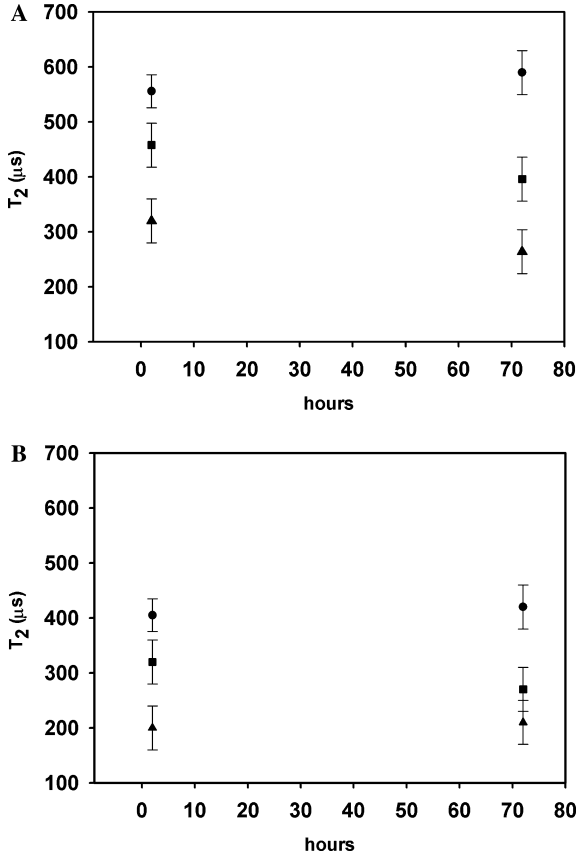

Fig. 8. T_2 values obtained with the Hahn echo sequence: (A) standard relaxometer; (B) unilateral relaxometer. The T_2 values are reported vs. hours of oxidation treatment. (●) untreated Whatman paper; (■) Whatman paper oxidized with 0.1 M $NaIO_4$; and (▲) Whatman paper oxidized with 0.4 M $NaIO_4$.

see Fig. 8A for the data obtained with the standard relaxometer, and Fig. 8B for the data obtained with the unilateral instrument. A T_2 shortening is always observed in oxidized samples with respect the corresponding T_2 value measured in the control samples. However, the previous agreement between the two sets of data is partially lost and all measurements performed in the inhomogeneous field are shorter than the corresponding ones performed with the standard relaxometer. This effect is clearly due to the lack of compensation of inhomogeneity effects in a simple Hahn echo when compared to the CPMG sequence [30]. It must be noted, however, that T_2 values measured with both pulse sequences are sensitive to the degradation of paper even when the degradation occurs at a very early stage.

4. Conclusion

The aging of paper has been mimicked by an oxidation reaction. The damage induced by oxidizing the cellulose fibers of Whatman paper has been followed with ^{13}C CP–MAS NMR spectroscopy and by

measurements of the transverse relaxation in homogeneous and inhomogeneous fields. In dry material, even at an early stage, the degradation of paper is characterized by a shortening of the spin–spin relaxation time of the confined water. This can be observed with a conventional, minimal-invasive NMR relaxation measurements as well as with non-invasive measurements with unilateral NMR instruments. Experimental values obtained with ^{1}H NMR relaxometric techniques, both standard as well as unilateral, are in good agreement. Therefore, unilateral NMR relaxometric measurements constitute a suitable, fully non-invasive method for assessing the degradation state of cellulose-based materials such as precious old books and *incunabula*.

In dry paper effects due to the sample volume and to the penetration depth have been found to be negligible.

It is worth of noticing that in the absence of diffusion the measured spin–spin relaxation times do not depend on the applied field gradient strength. As a consequence, unilateral NMR relaxometric measurements on cellulose based materials are nicely consistent with the same measurements performed in homogeneous field. Measurements on wood, stones, ceramics, paintings, bricks, and all materials containing confined water are in progress.

Acknowledgments

Thanks are due to Dr. R. Lamanna of Enea (Trisaia) for the software providing the data inversion. Thanks are also due to Dr. Fabio Tedoldi and Roberto Melzi of Bruker Biospin Milano. This work was carried out as a part of the Eureka project Σ!*2214—Eurocare Mouse*. We acknowledge the support of Prof. A. Guarino.

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