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New insight into hydration and aging mechanisms of paper by the line shape analysis of proton NMR spectra

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Summary. — The action of water within biological systems is strictly linked either with their physical chemical properties and with their functions. Cellulose is one of the most studied biopolymers due to its biological importance and its wide use in manufactured products. Among them, paper is mainly constituted by an almost equimolar ratio of cellulose and water. Therefore the study of the behavior of water within pristine and aged paper samples can help to shed light on the degradation mechanisms that irremediably act over time and spoil paper. In this work we present Nuclear Magnetic Resonance (NMR) experiments on modern paper samples made of pure cellulose not aged and artificially aged as well as on ancient paper samples made in 1413 in Perpignan (France). The line shape parameters of the proton NMR spectra were studied as a function of the hydration content. Results indicate that water in aged samples is progressively involved in the hydration of the byproducts of cellulose degradation. This enhances the degradation process itself through the progressive consumption of the cellulose amorphous regions.

1. – Introduction

Water, thanks to its anomalous properties, is the most essential molecule for life [1]. It is key in all biological processes and determines the properties of the systems it interacts with [2,3]. Water is also essential for the production process of paper and it also strongly

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influences its properties during all paper life. In fact, paper is produced from a diluted suspension of cellulose fibres, and water is progressively removed during the production steps [4]. However some water molecules cannot be removed because they make part of the internal structure of paper bridging the hydroxyl groups of different cellobiose units, the monomer of cellulose polymer [5, 6]. The same mechanism is at the base of the protein folding process with the so-called crystallization water being part of the protein structure [3, 7]. The cellulose polymers then constitute the fibres of paper that are kept together by a strong network of inter- and intra-molecular hydrogen bonds (HB) [8]. These kinds of bonds are influenced by a number of factors such as the presence of oxygen and water molecules that promote degradation mechanisms such as the oxidation of the hydroxyl groups of cellulose running through the radical mechanism initiated by active oxygen species especially in acidic or neutral environment [9, 10]. It is noteworthy that oxygen or its active forms, carried by water molecules, can attack directly the hydroxyl groups on C(2), C(3) and C(6) atoms in a glucopyranose unit of cellulose. Furthermore, the process can influence also the C(1) atom involved in the glycosidic bond, leading to the cellulose cleavage and depolymerization [11, 12]. Indeed, the action of water molecules in bulk-like phase is to break some HB bridges and to interpose between two cellulose chains changing the physical properties of paper. However, the complex interaction between water and cellulose chains is not completely understood and many unresolved questions remain. For instance, a very recent study reports that only two of the three available hydroxyl groups on the surface of cellulose fibrils exchange their hydrogen with the surrounding water molecules [13].

At ambient condition, that is 20 °C and 59% of Relative Humidity (RH), the equilibrium condition corresponds to an amount of water of about 8% in weight [5]. During its life, the exposure of paper to humid environments and therefore the presence of liquid water within the fibres, promotes degradation phenomena that indeed depend on water content. Besides, it is remarkable that water molecules can adopt different local structures as a function of the physical-chemical conditions of the hosting material [14].

Nuclear Magnetic Resonance is a technique sensitive to the different environments experienced by the resonant nuclei and allows to discriminate between the same nuclei in different chemical environments [15]. Different NMR approaches were applied in the past to study paper and cellulose-based material [16, 17]. However, due to strong dipolar couplings, high resolution (HR) is easily achievable in solution; however different approaches have been developed to resolve peaks in semi-solid compounds. One of the most used experimental technique is known as Magic Angle Spinning (MAS) that takes advantage of the vanishing of the corresponding Hamiltonian term for an angle of about 54.74° of the sample holder with respect to the direction of the static magnetic field [18, 19]. The HR-MAS technique has been receiving great attention and development thanks to its powerful versatility in different fields, in particular in medicine, biology and even in food science [20-24]. In fact, with a single experiment on few micro-quantities of samples in their intact form (no chemical treatment are needed), it is possible to obtain different and detailed information (both structural and dynamical) on all the components of the studied specimen.

In this paper we study the line shape of the ^1H HR-MAS NMR peaks for paper samples of pure cellulose at different hydration. In particular we consider naturally aged samples (ancient), artificially aged samples and not aged samples as reference. According to the literature we analyze the obtained NMR spectra of paper as the sum of one Lorentzian and one Gaussian function belonging, respectively, to water and cellulose protons [25-27]. Our experimental results are complementary to those obtained by means

of other techniques [28-33] and therefore constitute an additional aid for a deeper insight into hydration and degradation mechanisms of paper.

2. – Materials and methods

We used the same not aged, artificially and naturally aged samples described elsewhere [34-36]. In particular we consider the P2REF samples (not aged), the P2C9048 samples (artificially aged in a closed chamber at 90 °C and 59% RH for 48 days) and the A1 samples (ancient paper made in 1413 in Perpignan, France). These samples present increasing levels of degradation as expressed by their concentration of chromophores, which are oxidized groups able to absorb ultraviolet and visible photons. While the concentration of chromophores is negligible for P2REF sample, it is 0.8 mmol/100 g of cellulose for P2C9048 and 3.1 mmol/100 g of cellulose for A1 [37, 38]. The desired hydration was obtained by exposing the samples in a closed chamber with 100% RH for several hours at room temperature [35].

^1H NMR spectra were recorded on a Bruker Avance spectrometer operating at 700 MHz (proton Larmor frequency) by means of the High-Resolution Magic Angle Spinning (HR-MAS) technique. We acquired 512 transients of a standard 90 degrees pulse sequence with 16 k points in the time domain and a spectral width of 20 ppm. The duration of the hard pulse was of 7 μs with an attenuation of 3 dB and a repetition time of 20 s. Free induction decays were Fourier transformed and referenced to the trimethylsilyl propionate (TSP) by means of Bruker Xwinnmr 3.5 software packages [35]. The three samples were studied at different water content or hydration, h , given by the ratio between the mass of water and that of the dry cellulose. These values were determined by weighting the samples in dry and hydrated conditions, and by the use of the NMR signal itself. In fact, as mentioned above, the MAS spectra were fitted with a Pseudo-Voigt function of the following form:

$$(1) \quad y = A \left[\mu \frac{2}{\pi} \frac{\omega_L}{4(x - x_c)^2 + w_L^2} + (1 - \mu) \frac{\sqrt{4 \ln 2}}{\sqrt{\pi} w_G} e^{-\frac{4 \ln 2}{w_G^2} (x - x_c)^2} \right],$$

where A is the amplitude, μ is the weight of the two components, x_c is the peak position and w_L and w_G are the corresponding width of the Lorentzian and Gaussian contributions, respectively. By plotting the total sample weight as a function of $A * \mu$ (area of the Lorentzian component ascribed to water), we were able to calculate the mass of dry cellulose by evaluating the y -axis intercept [35].

Figure 1 reports one example of the best fit obtained for the MAS NMR spectra of the hydrated P2C9048 sample with the Pseudo-Voigt function of eq. (1). The four panels show the first four of the five hydration values considered for that sample. In the figure, we use two different y -axis scales for the left and right sides because the width of the peak decreases a lot with increasing hydration. Also, every panel has a different intensity scale that of course increases with hydration. The total fit with the Pseudo-Voigt function is reported as a red line and the two contributions as a green line (Lorentzian) and as a blue line (Gaussian). It is noteworthy that the Gaussian function contributes essentially in an equal way only for the sample with the lowest hydration ($\mu = 0.54$) becoming progressively a negligible background at higher hydration ($\mu = 0.99$ for $h = 20\%$).

We have performed this best-fit procedure for all the three samples, each of them at five different values of h . For each sample (characterized by different aging conditions) we

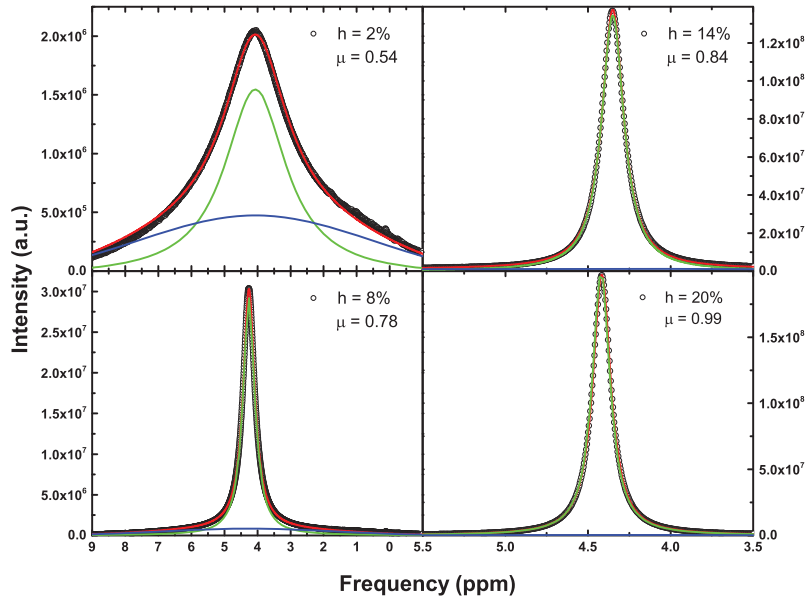


Fig. 1. – The proton HR-MAS NMR spectra of P2C9048 samples at different hydration. We use two x -axes for the left and right sides because the width of the peak changes a lot with h . Besides, every panel has a different intensity scale. The total fit with the Pseudo-Voigt function (red line) and the two components, Lorentzian (green line) and Gaussian (blue line), are reported.

have measured three important parameters characterizing the water proton NMR signal and thus providing information about the physical chemistry properties of water for the different conditions studied. In particular, in the following we discuss the dependence, with respect to the hydration, of the peak position x_c (that is the proton chemical shift), the width of the Lorentzian function ω_L (strictly related to the water mobility and dynamics) and the area of the Lorentzian function A_L , that is the equilibrium magnetization of water molecules.

3. – Results and discussions

It is well known that for water systems, the proton chemical shift reflects the local arrangement of the local hydrogen bonds (HB) geometry which, in turn, depends, in particular, on the number of HBs and also by the intermolecular distances and angles [39, 40]. Therefore, by studying its trend *versus*, in our case, the hydration content, it is possible to enter into the details of the evolution of the water local structure in terms of hydrogen bond formation [41, 42].

The measured peak position of the Pseudo-Voigt function (x_c in eq. (1)) is reported in fig. 2 as a function of hydration for the three studied samples: P2REF (not aged, black squares), P2C9048 (artificially aged, red circles) and A1 (ancient paper, blue triangles). Its behavior is exponential-like and can be modeled by the following function:

$$(2) \quad x_c(h) = (x_0 - x_f) e^{-\frac{h}{h_x}} + x_f,$$

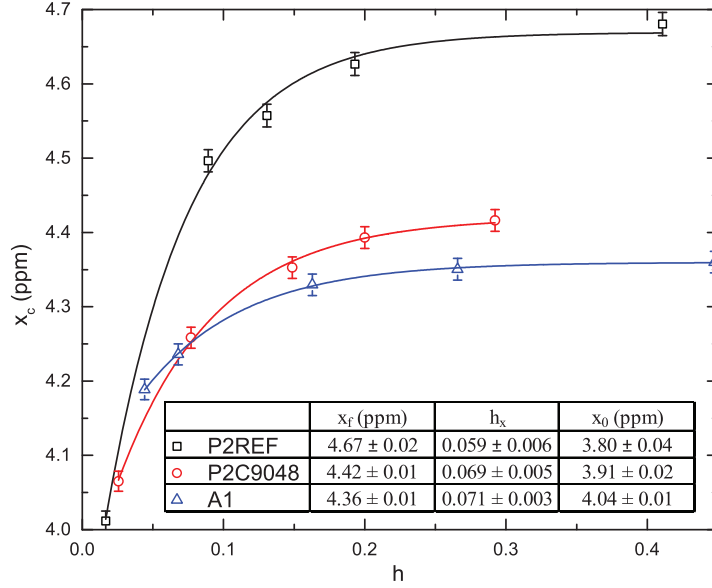


Fig. 2. – The evolution of the chemical shift of the NMR peak with hydration content. The value is referenced to the signal of the tetramethylsilane at 0.00 ppm. Black squares, red circles and blue triangles correspond to P2REF, P2C9048 and A1 samples, respectively. Lines are best fit by using eq. (2) and the corresponding obtained parameters are reported in the inset.

where x_f is the asymptotic value, x_0 is the intercept with the y -axis for $h = 0$ and h_x represents the characteristic value of the chemical shift variation due to the hydration mechanism for the considered sample. It also represents the value at which x_c attains $1/e$ of its asymptotic value. In fig. 2 (inset) we report the values (together with the standard deviation) of these three parameters obtained by a best-fit procedure by eq. (2) (solid lines).

Note that all the three parameters depend monotonically on the state of degradation of the sample expressed by their increasing level of oxidation. In particular oxidation is related to the development of acidic degradation byproducts such as carboxylic acids [11, 34]. Note that increasing degradation provokes a slower hydration process, as evident from the decreasing values of x_f and the increasing values of h_x as a function of sample's degradation. In addition, the increasing presence of acidic byproducts as a function of degradation [34] provokes an increasing upfield shift of the water chemical shift. On the other hand, this can be also related to the increasing oxidation of cellulose polymers as degradation proceeds, that decreases the number of available hydroxyl groups and promotes the repulsion of new additional water molecules by means of hydrophobic interactions [35].

Furthermore, the increase in x_c on increasing hydration reflects the enhancement in the local order of the water molecules due to the formation of more ordered hydrogen-bonded structures [43]. Hence, our results evidence that as degradation proceeds, the formation of the ordered hydrogen-bonded structures is progressively prevented by the higher presence of degradation byproducts in hydrated water.

As already seen in fig. 1, the width of the Lorentzian function (ω_L) decreases with increasing hydration whereas that of the Gaussian (ω_G) increases becoming essentially a

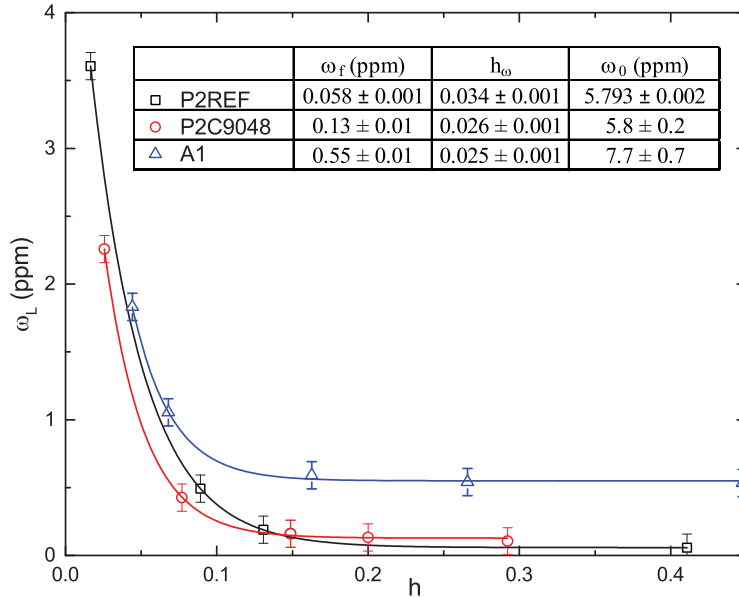


Fig. 3. – The width of the Lorentzian component of ^1H HR-MAS NMR spectra of hydrated paper. Symbols and colours are the same as those used in fig. 2. In the inset we report the parameters obtained by the best fit with eq. (3).

flat and almost negligible background. Indeed, for our purpose we have considered only the behavior of $\omega_L(h)$. In particular, as shown in fig. 3, its dependence on the hydration can be described by the same exponential function used to perform the best fit of the x_c data (eq. (1)) rewritten in terms of ω_L

$$(3) \quad \omega_L(h) = (\omega_0 - \omega_f) e^{-\frac{h}{h_\omega}} + \omega_f,$$

where indeed ω_f is the asymptotic value, ω_0 is the intercept with the y -axis for $h = 0$ and h_ω represents the characteristic value of the Lorentzian width variation due to the hydration mechanism for the considered sample. Note that, more liquid and disordered is a system, smaller is the width of its NMR signal because weaker is the intensity of the corresponding spin-spin interaction [44].

It is noteworthy that ω_f increases with degradation especially for the ancient sample A1. This confirms that even at high hydration, water molecules interact with byproducts produced by oxidative and hydrolytic degradation reactions that prevent water from building its characteristic extended network of HBs. Furthermore, even for this parameter, the decreasing number of available hydroxyl groups promotes the repulsion of new additional water molecules by means of hydrophobic interactions. On the other hand, when paper is not aged (P2REF case) the value of the water Lorentzian width at the highest hydration resembles that of the bulk liquid as well as the chemical shift value for liquid bulk water (≈ 4.7 ppm) as shown in fig. 2.

The last parameter we have achieved by the analysis of the NMR spectra is the area of the Lorentzian function obtained by multiplying the parameters A and μ of eq. (1) ($A_L = A \cdot \mu$). $A_L(h)$ is reported in fig. 4 and, even in this case, its behavior can be well

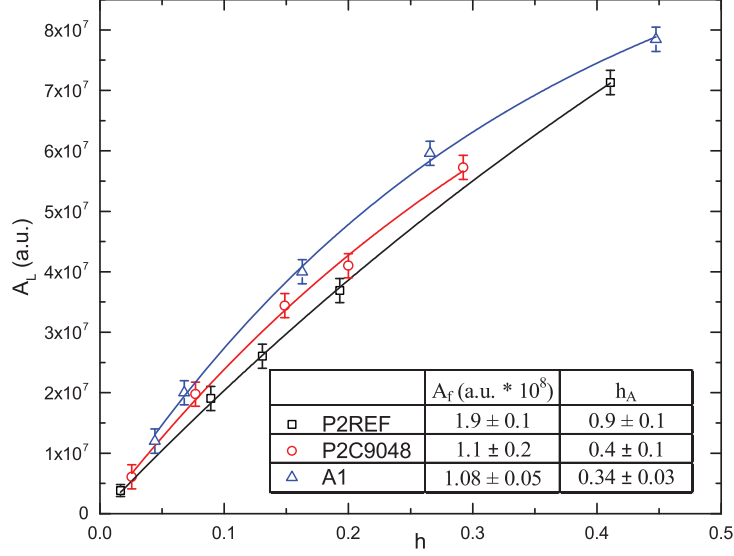


Fig. 4. – The area of the Lorentzian function (A_L) obtained by multiplying the parameters A and μ of eq. (1) ($A_L = A \cdot \mu$). Symbols and colours are the same as those used in figs. 1 and 2. In the inset we report the parameters obtained by the best fit with eq. (4).

fitted by an exponential function where, of course, its value must be zero for the totally dry sample. Hence, we use the following equation to best fit the data:

$$(4) \quad A_L(h) = A_f \left(1 - e^{-\frac{h}{h_A}} \right),$$

where A_f is the limit value for $h \rightarrow \infty$ and h_A represents the characteristic value of the Lorentzian area variation due to the hydration mechanism for the considered sample.

Note that the behavior of $A_L(h)$ is almost linear for the not aged sample (P2REF) with h_A assuming the value of 0.9 while becoming less than half for the aged samples. This is the indication that the not aged sample weakly influences the water behavior being it an almost inert host. On the contrary, for aged samples, the amphiphilic character of the different byproducts and cellulose surfaces determines the complex dependence on hydration.

Note that, by means of proper pulse sequences, we were able to get more detailed insights about the dynamics of water molecules by well separating the different relaxing contributions [35]. In particular, we were able to discriminate and study the different contributions around the hydration level corresponding to ambient conditions. This is of particular importance because for $h \lesssim 8\%$ paper behaves like an hydrophilic material whereas for $h \gtrsim 8\%$ it shows hydrophobic behavior [35]. In a very recent paper it has been studied, by means of molecular dynamics simulations, how water mediates the interaction between hydrophilic and hydrophobic surfaces [45]. The authors find that the most important parameter that determines the hydration properties is the polarity of the surface that indeed changes as a function of the water layers covering it.

In this work we provide additional information concerning the water local structure mainly by means of the observed chemical shift and the area of the NMR signal

corresponding to water molecules. In particular, our new data confirm that for $h \lesssim 8\%$ cellulose attracts water molecules mainly through its hydroxyl groups. However, for $h \gtrsim 8\%$ hydroxyl groups of cellulose are no longer available for hydrogen bonding with water molecules. In such a case the hydrophobic repulsion by glucopyranose ring moieties on the additional water molecules becomes important and water interaction with degradation byproducts are favored.

4. – Conclusions

In this work we have studied the proton HR-MAS NMR spectra of modern paper samples made of pure cellulose not aged (P2REF) and artificially aged (P2C9048) as well as an ancient paper sample made in 1413 in Perpignan, France (A1). In particular we consider artificially aged samples kept at 90 °C and 59% RH for 48 days and not aged samples as reference. We analyze the ^1H HR-MAS NMR peak by means of a Pseudo-Voigt function, in which the Lorentzian contribution belongs to the water signal and the Gaussian contribution to that of cellulose.

We find that the behavior of the three parameters characterizing the Lorentzian contribution of water protons (x_c , ω_L and A_L) has an exponential dependence on the hydration with a characteristic value that depends on aging time. In particular, we find that the asymptotic value of the chemical shift (x_f) at high hydration is lower for aged samples. This is due to the presence of byproducts, most of them acidic, that provokes an upfield shift of the water chemical shift. On the other hand, the parameter characterizing the hydration process as seen by the chemical shift (h_x) is higher for aged samples indicating a slower hydration process. The oxidation processes, that decrease the number of available hydroxyl groups of cellulose and promote the repulsion of new additional water molecules by means of hydrophobic interactions, are mainly involved in these trends, especially at higher hydration conditions. Finally, the increase in x_c with hydration confirms that the addition of water molecules provokes an enhanced local order due to the formation of hydrogen-bonded structures, more evident in the not aged sample.

For what concerns the width of the Lorentzian function, our data show that water mobility decreases with degradation especially for the ancient sample A1 because water molecules, due to the interaction with the degradation byproducts, are not able to build the characteristic extended network of HBs. On the contrary, not aged samples (P2REF case) show a value for ω_L at the highest hydration resembling that of bulk liquid water.

Finally the hydration dependence of the area of the Lorentzian function A_L , that is the equilibrium magnetization of water molecules, presents an almost linear behavior only for the not aged P2REF sample, with the characteristic h_A value equal to 0.9. Instead, h_A equals 0.34 for the ancient A1 sample. This indicates an almost inert character for P2REF and a more complex hydration mechanism for P2C9048 and even more for A1. Again, the reason is that the aged samples have their amorphous regions progressively consumed, with the subsequent production of different byproducts whose amphiphilic attribute determines the complex dependence on hydration.

In conclusion our main result is the observation by proton HR-MAS NMR of a precise structural and dynamical trends *versus* hydration content and aging time of paper samples. The parameters characterizing the proton NMR signal of water molecules are strictly related to and allow the understanding of the microscopic mechanisms at the origin of hydration and aging processes. The influence of the degradation byproducts and cellulose oxidation on the properties of water molecules revealed by NMR could be used for non-destructive diagnostic of ancient materials made with cellulose.

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REFERENCES

- [1] MALLAMACE F., CORSARO C., MALLAMACE D., VASI C. and STANLEY H. E., *Faraday Discuss.*, **167** (2013) 95.
- [2] BAGCHI B., *Water in Biological and Chemical Processes: From Structure and Dynamics to Function*, edited by SAYKALLY R., ZEWAİL A. and KING D. (Cambridge University Press, New York, USA) 2013.
- [3] BELLISSENT-FUNEL M.-C. *et al.*, *Chem. Rev.*, **116** (2016) 7673.
- [4] HUNTER D., *Papermaking: The History and Technique of an Ancient Craft* (Dover Publications, New York, 1978).
- [5] BRÜCKLE I., *Structure and Properties of Dry and Wet Paper*, in *Paper and Water: A Guide for Conservators*, edited by BANIK G. and BRÜCKLE I. (Elsevier, Amsterdam, The Netherlands) 2011, pp. 81–105.
- [6] KLEMM D., PHILIPP B., HEINZE T., HEINZE U. and WAGENKNECHT W., *Comprehensive Cellulose Chemistry; Volume I: Fundamentals and Analytical Methods* (WILEY-VCH Verlag GmbH, Weinheim, Germany) 1998.
- [7] MALLAMACE F., BAGLIONI P., CORSARO C., SPOOREN J., STANLEY H. E. and CHEN S.-H., *Riv. Nuovo Cimento*, **34** (2011) 253.
- [8] MISSORI M. *et al.*, *Phys. Rev. Lett.*, **97** (2006) 238001.
- [9] KOLAR J., *Restaurator*, **18** (1997) 163.
- [10] ALI M., EMSLEY A. M., HERMAN H. and HEYWOOD R. J., *Polymer*, **42** (2001) 2893.
- [11] LOJEWSKI T. *et al.*, *Carbohydr. Polym.*, **82** (2010) 370.
- [12] DI LAZZARO P. *et al.*, *J. Cult. Herit.*, **17** (2016) 14.
- [13] LINDH E. L., BERGENSTRÄHLE-WOHLERT M., TERENCEZ C., LENNART SALMÈN and ISTVÀN FURÒ, *Carbohydr. Res.*, **434** (2016) 136.
- [14] CERVENY S., MALLAMACE F., SWENSON J., VOGEL M. and XU L., *Chem. Rev.*, **116** (2016) 7608.
- [15] ABRAGAM A., *The Principles of Nuclear Magnetism* (Clarendon, Oxford) 1961.
- [16] CAPITANI D., PROIETTI N., ZIARELLI F. and SEGRE A. L., *Macromolecules*, **35** (2002) 5536.
- [17] FEDERICI C. *et al.*, *Sci. Tech. Cult. Herit.*, **5** (1996) 37.
- [18] ANDREW E. R., *Progr. Nucl. Magn. Res. Spectrosc.*, **8** (1971) 1.
- [19] FITCH W. L., DETRE G. and HOLMES C. P., *J. Org. Chem.*, **59** (1994) 7955.
- [20] MOESTUE S., SITTER B., BATHEN T. F., TESSEM M.-B. and GRIBBESTAD S. I., *Curr. Top. Med. Chem.*, **11** (2011) 2.
- [21] TORRE A., TRISCHITTA F., CORSARO C., MALLAMACE D. and FAGGIO C., *Cell. Biochem. Funct.*, **31** (2013) 489.
- [22] BECKONERT O. *et al.*, *Nat. Protoc.*, **5** (2010) 1019.
- [23] CORSARO C. *et al.*, *J. Anal. Methods Chem.*, **2015** (2015) 175696.
- [24] CÍCERO N. *et al.*, *Nat. Product Res.*, **29** (2015) 1894.
- [25] Blicharska B. and KLUZA M., *Colloids Surf. A: Physicochem. Eng. Aspects*, **115** (1996) 137.
- [26] CAPITANI D. *et al.*, *Tappi J.*, **79** (1996) 113.
- [27] TOPGAARD D. and SÖDERMAN O., *Cellulose*, **9** (2002) 139.
- [28] SOUGUIR Z. and DUPONT A.-L., *Biomacromolecules*, **9** (2008) 2546.

- [29] LOJEWSKI T. *et al.*, *Appl. Phys. A*, **100** (2010) 873.
- [30] BOGOLITSYNA A. *et al.*, *J. Chromatogr. A*, **1218** (2011) 8561.
- [31] MISSORI M., *Nuovo Cimento C*, **39** (2016) 293.
- [32] MISSORI M., RIGHINI M. and DUPONT A.-L., *Opt. Commun.*, **263** (2006) 289.
- [33] MISSORI M., RIGHINI M. and SELCI S., *Opt. Commun.*, **231** (2004) 99.
- [34] CORSARO C. *et al.*, *Sci. Rep.*, **3** (2013) 2896.
- [35] CORSARO C. *et al.*, submitted to *Phys. Chem. Chem. Phys.* (2016).
- [36] MOSCA CONTE A. *et al.*, *Phys. Rev. Lett.*, **108** (2012) 158301.
- [37] MISSORI M. *et al.*, *Phys. Rev. B*, **89** (2014) 054201.
- [38] MOSCA CONTE A. *et al.*, *Appl. Phys. Lett.*, **104** (2014) 224101.
- [39] MATUBAYASI M., WAKAI C. and NAKAHARA M., *Phys. Rev. Lett.*, **78** (1997) 2573.
- [40] MODIG K., PFROMMER B. G. and HALLE B., *Phys. Rev. Lett.*, **90** (2003) 075502.
- [41] SEBASTIANI D. and PARRINELLO M., *Chem. Phys. Chem.*, **3** (2002) 675.
- [42] MALLAMACE F. *et al.*, *Proc. Natl. Acad. Sci. U.S.A.*, **105** (2008) 12725.
- [43] DE SPIRITO M. *et al.*, *Phys. Rev. E*, **77** (2008) 041801.
- [44] CORSARO C. *et al.*, *J. Phys. Chem. B*, **112** (2008) 10449.
- [45] KANDUČ M., SCHLAICH A., SCHNECK E. and NETZ R. R., *Langmuir*, **32** (2016) 8767.