J Mater Sci (2007) 42:9336–9342
DOI 10.1007/s10853-007-1903-4

Effect of calcium rich and alkaline solutions on the chemical behaviour of hemp fibres

**David Sedan · Cécile Pagnoux · Thierry Chotard ·
Agnès Smith · Danielle Lejolly · Vincent Gloaguen ·
Pierre Krausz**

Received: 25 July 2006 / Accepted: 31 May 2007 / Published online: 28 July 2007

Abstract Chemical reactivity of hemp fibres placed into a cimentitous matrix was studied by using a lime solution as a simplified cement solution. The hemp fibres contain 56.1 wt.% of cellulose, 20.1 wt.% of pectin, 10.9 wt.% of hemicellulose and 6 wt.% of lignin. These compounds are not solubilised in a basic medium rich in calcium but a part located at the fibre surface should be degraded. This treatment leads also to the decrease of the cristallinity index of the cellulose. Calcium ions adsorb in a large quantity onto the fibre surface due to the high concentration of pectin. The structure of the homogalacturonic part of pectin forms with Ca^{2+} a stable chelate called "egg-box", supporting cation adsorption. The fibres are then covered by $Ca(OH)_2$ nodules after immersion in a lime solution.

Introduction

As a result of the increasing demand for environmentally friendly materials, especially in the building industry, composites of natural fibres and hydraulic binders are potentially interesting. Natural fibres are renewable and low-density materials. They can exhibit high tensile strength and Young's modulus as shown in Table 1 for hemp, ramie, jute or softwood kraft [1]. These mechanical characteristics depend on parameters such as the fibre diameter, the amount of crystalline regions, the degree of crystallinity or polymerisation, the void structure, and whether the fibres come from the plant stem, leaf or seed [1]. Climatic conditions, age and the digestion process influence the chemical composition. Depending on their origin, natural fibres can be grouped into hair, bast or hard fibres. Bast (flax, hemp, jute) and hard fibres (sisal, coir) are commonly used in composites [1–5].

Studies carried out on cement and fibres composites mostly concern their mechanical behaviour [6, 7]. The quality of the interface between the matrix and the natural fibres dictates the mechanical performances. However, there is virtually no fundamental knowledge on the interaction between a cementitous matrix and the fibres. In fact, studies dealing with the effect of an alkaline treatment on fibre properties, concern NaOH solutions but not $Ca(OH)_2$ solutions. This paper presents the chemical behaviour of hemp fibres in a lime solution, which corresponds to a simplified cement solution. The first part concerns the chemical composition of the fibres (mass percentage of each constituent and their molar composition in neutral sugars and acids). Their behaviour in water or lime solutions is then examined.

Experimental

Cortical hemp fibres were supplied by la Chanvrière de l'Aube (Bar-sur-Aube, France). Their density, measured

D. Sedan (✉) · T. Chotard · A. Smith
Groupe d'Etude des Matériaux Hétérogènes, (GEMH, EA 3178), Ecole Nationale Supérieure de Céramique Industrielle, 47-73 avenue Albert Thomas, Limoges cedex 87065, France
e-mail: d_sedan@ensci.fr

C. Pagnoux
Science des Procédés Céramiques et Traitements de Surface, (SPCTS, CNRS UMR 6638), Ecole Nationale Supérieure de Céramique Industrielle, 47-73 avenue Albert Thomas, 87065 Limoges cedex, France

D. Lejolly · V. Gloaguen · P. Krausz
Laboratoire de Chimie des Substances Naturelles, (LCSN, EA 1069), Ecole Nationale Supérieure de Céramique Industrielle, 47-73 avenue Albert Thomas, 87065 Limoges cedex, France

Table 1 Mechanical properties of natural fibres compared to conventional reinforcing [1]

Fibre	Density ($g\ cm^{-3}$)	Elongation	Tensile strength (MPa)	Young's modulus (Gpa)
Cotton	1.5–1.6	7.0–8.0	287–597	5.5–12.6
Jute	1.3	1.5–1.8	393–773	26.5
Flax	1.5	2.7–3.2	345–1,035	27.6
Hemp		1.6	690	
Rampie		3.6–3.8	400–938	61.4–128
Sisal	1.5	2.0–2.5	511–635	9.4–22.0
Coir	1.2	30	175	4.0–6.0
Viscose (cord)		11.4	593	11
Soft wood kraft	1.5		1,000	40
E-glass	2.5	2.5	2,000–3,500	70
S-glass	2.5	2.8	4,570	86
Aramide (normal)	1.4	3.3–3.7	3,000–3,150	63–67
Carbon (standard)	1.4	1.4–1.8	4,000	230–240

with a pycnometer (Accupic 1330 helium pycnometer, Creil, France) was equal to 1.58 g cm^{-3}. The basic unit consists of cellulose polymeric chains aligned and gathered in microfibrils. They are linked to each other by lignin, pectin and hemicellulose. The quantity of cellulose, hemicellulose, lignin, pectin and fat or waxes contained in hemp was determined after succesive extractions. The procedure was the following: hemp fibres were crushed, sifted at 500 μm and stored for 24 h at room temperature in a dessicator. The dry fibres were treated with ethanol (80 wt.%) for 20 min in reflux, which led to the removal of fats, waxes or small molecules. The residual material was boiled twice in water for 20 min and in a 1 wt.% ammonium oxalate solution (85 °C for 2 h) to extract pectins. The lignins were removed by treating the residue with $NaClO_2$ and CH_3COOH (80 °C for 1 h). The remaining hemicelluloses were solubilised first with a 24 wt.% KOH aqueous solution (25 °C for 24 h) and then a 4.3 wt.% NaOH aqueous solution (25 °C for 24 h). After these extractions, the remaining insoluble material was considered as the cellulosic residue. The mass percentage of each fraction was then calculated. The chemical nature of sugars and acids which composed each fraction was determined by gaseous phase chromatography [8]. Gas chromatography was done with a Perichrom gas chromatograph (Saulx le Chartreux, France) fitted with a flame-ionisation detector. A capillary column (CPSIL-5CB, Chrompack, 0.32 mm × 50 m, Palo Alto, United States) was used with the following cycles: 120–240 °C at 2°C min^{-1}. Nitrogen was the carrier gas at 0.5 atm. The error bar is ±0.5 wt.%.

In order to study the lixiviation of organic products when fibres are in solution, three different environments were examined: water, a calcium chloride solution, which has a slightly acid pH (≈6.0), and a lime-saturated solution ($pH > 12$). For the two calcium solutions, the calcium concentration was identical and equal to 22.10^{-3} mol L^{-1}. The fibre over solution mass ratio was equal to 0.1. The quantities of lixiviated organic molecules, namely neutral sugars and acids, were determined by gaseous phase chromatography. The quantities of lixiviated products were also measured after increasing durations of contact (15 min up to 48 h) between the fibres and the solutions. These experiments were repeated three times. There was no significant evolution of quantities as a function of time. Therefore, all the data reported here correspond to a duration of contact between the fibres and the solutions of 24 h.

The surface composition of the hemp fibres was determined by infrared (IR) measurements. The infrared spectroscopy apparatus was a Perkin–Elmer (Spectrum one, Boston, United States) equipped with a potassium bromide (KBr) beam splitter which allows measurements between 450 cm^{-1} and 5,000 cm^{-1}. Mixtures of 95 wt.% of KBr and 5 wt.% of fibres were pressed for IR measurements.

Hemp fibres dipped in a lime-saturated solution for 48 h were chopped into fine particles and compressed into discs using a cylindrical steel mould (Ø = 16 mm) with an applied pressure of 35 MPa. X-Ray diffraction (XRD—Inel CPS 120-curved diffractometer, Artenay, France) was carried out to assess the influence of alkaline treatment on fibre cristallinity. The diffracted intensity of CuKα radiation (wavelength of 0.1541 nm) was recorded between 5° and 40° (2θ angle range) at 37.5 kV and 28 mA. The cristallinity index (I_C) of the fibre was calculated using Segal's empirical method [9]:

$$I_c = \left(\frac{I_{002} - I_{am}}{I_{002}}\right) \times 100$$

where I_{002} was the maximum intensity of diffraction of the (002) lattice peak at a 2θ angle between 22° and 23°, and I_{am} is the intensity of diffraction of the amorphous material, which is taken at a 2θ angle between 18° and 19° where the intensity is minimal [10].

To measure the quantities of calcium ions that could be adsorbed on the hemp fibres, two routes were investigated: fibres mixed with a lime-saturated solution ($pH > 12.0$) and fibres mixed with a calcium chloride solution (pH 6). In these two situations, the calcium concentration was identical (22.10^{-3} mol L^{-1}) and the water over fibre mass ratio was the same (0.05). The time of contact was 45 min. The solutions were extracted by centrifugation and their calcium concentration was determined by the Inductive Coupled Plasma (ICP) technique (Iris Plasma Spectrometer-Thermo Jarrel Ash brand, Waltham, United States).

Scanning Electron Microscopy (SEM) was carried out with a Cambridge Stereoscan S260 apparatus, equiped with an Energy Dispersive Spectroscopy (EDS) analysis. Characterisation was done on cortical fibres soaked in a lime solution (water over fibres mass ratio: 100). After drying on a blotting paper, these fibres were glued directly on a sample holder and coated with a carbon film.

Results and discussion

The hemp fibres contain 56.1 wt.% of cellulose, 20.1 wt.% of pectin, 10.9 wt.% of hemicellulose and 6 wt.% of lignin (Table 2). These values are in accordance with literature data on natural fibres analysis [11]. For each fraction which represents more than 10 wt.% (cellulose, pectin and hemicellulose), its composition was determined by gas chromatography. The results are given in Table 3. The cumulative mass content is also given in this table. It turns out that the main neutral sugar is glucose. It is well known that cellulose is composed essentially by glucose units [1]; consequently in this study glucose is considered as the main compound of the cellulosic residue. Among the two acids that are present, the most abundant is galacturonic acid, which is the main constituent of pectin [1].

Table 4 presents the weight content of neutral sugars and acids that lixiviate once fibres have been immersed for 24 h in water, in a lime-saturated solution or in a calcium chloride solution. In water, for 1 g of fibres, only 11.4 mg of sugars lixiviate. It is low compared to the initial sugar content (870 mg). The same comment can be made for the acids: 10.3 mg lixiviate while the initial content is 130 mg. In a calcium chloride solution, there are only 17.5 mg of sugars and 0.6 mg of acids that lixiviate. Again, the dissolution is low. In a lime solution, only 17.5 mg of sugar and 0.6 mg of acids are present. Comparison between infra-red spectrum of non-treated fibres and of fibres treated in a lime-saturated solution shows that there is an absorption in non treated fibres at 1,740 cm^{-1} which no longer exists in treated fibres (Fig. 1). It is reported in the literature that hemicellulose contains groups that adsorb around 1,740 cm^{-1} in the carbonyl region [12, 13]. This value is

Table 2 Chemical analysis of hemp (wt.%)

	Waxes, fats, proteins	Pectins	Lignins	Hemicellulose	Cellulosic residue
Weight percentage	7.9	20.1	6	10.9	56.1

Table 3 Weight content of each neutral sugar and acid (calculated for fractions greater than 10 wt.%, namely pectin, hemicellulose and cellulosic residue)

	Pectin g (10^{-3})	Hemicellulose g (10^{-3})	Cumulated weight (including the Cellulosic residue) g (10^{-3})	Mass of each fraction contained in 1 g of matter g (10^{-3})
Glucose	21.5	19.3	601.8	691
Xylose	6.5	41.6	48.1	55
Rhamnose	25.1	9.4	34.5	40
Galactose	22.1	10.0	32.1	37
Mannose	11.0	11.8	22.8	26
Arabinose	12.7	3.7	16.4	19
Fucose	0.5	1.3	1.8	2
Galacturonic acid	90.7	10.0	100.7	116
Glucuronic acid	10.9	1.9	12.8	14
Total	201.0	109.0	871	1,000

Table 4 Mass of neutral sugars and acids (calculated for 1 g of hemp fibres) lixiviated after 24 h in water, in a lime-saturated solution, or in a calcium chloride solution

	Glucose	Fucose	Xylose	Rhamnose	Galactose	Mannose	Arabinose	Glucuronic acid	Galacturonic acid	Total sugar	Total acid
Sugars and acids lixiviated in water (g (10^{-3}))	2.7	1.7	0.9	2.5	0.8	2.7	0.1	1.1	9.2	11.4	10.3
Sugars and acids lixiviated in a lime solution (g (10^{-3}))	12.1	0	0.7	0.8	1.3	1.3	1.3	0.2	0.4	17.5	0.6
Sugars and acids lixiviated in a $CaCl_2$ solution (g (10^{-3}))	10.3	1.7	0.6	2.4	5.2	0.7	1.1	2.6	3.3	22	5.9

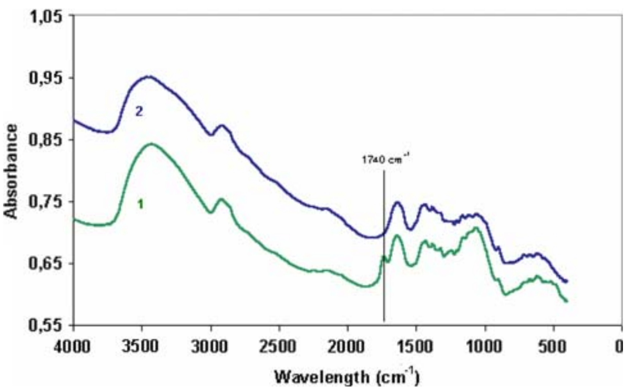


Fig. 1 ATR-FTIR spectra of untreated (1) and $Ca(OH)_2$ treated (2) hemp fibres

assigned to the C=O stretching vibration of the carboxyl and acetyl groups in the xylan component of hemicelluloses. Therefore, other studies shows that the same absorptions bands around 1,740 cm^{-1} correspond to isolated carbonyl group (COOR), indicating ester containing compounds commonly found in membrane lipid and cell wall pectin [14]. In a sodium hydroxide solution, which is alkaline as a lime-saturated solution, hemicellulose and pectin can be converted into sugars and acids. By analogy, a treatment with a lime solution could convert these compounds. However, given the initial composition of hemicellulose and pectin (Table 3), one could expect to find larger quantities of lixiviated sugars and acids than what is measured experimentally (Table 4). It is possible that the produced sugars and acids are degraded, which could explain why a small quantity of neutral sugars and acids was found in the analysed solutions. Lastly, an alkaline treatment can also dissolve compounds located at the fibre surface like waxes, pectins, hemicelluloses [15, 16].

Table 4 shows that galacturonic acid, which is the main component of pectin, is less soluble in a lime solution than in water. It means that either pectin dissolution is inhibited or it forms with calcium a solid product that has not been collected during centrifugation. Pectin extracted from the protocol described in the experimental section was mixed in a lime-saturated solution (solution over pectin mass ratio equal to 20) for 24 h. A gel was formed. The calcium concentration, in the extracted supernatant, dropped to 43.10^{-5} mol L^{-1}. It shows that pectin can react with calcium ions in an alkaline environment, and it could also explain the vanishing of the absorption peak at 1,740 cm^{-1} for treated fibres. Indeed, because of the pH value of the $Ca(OH)_2$ solution (pH > 12) a saponification reaction will

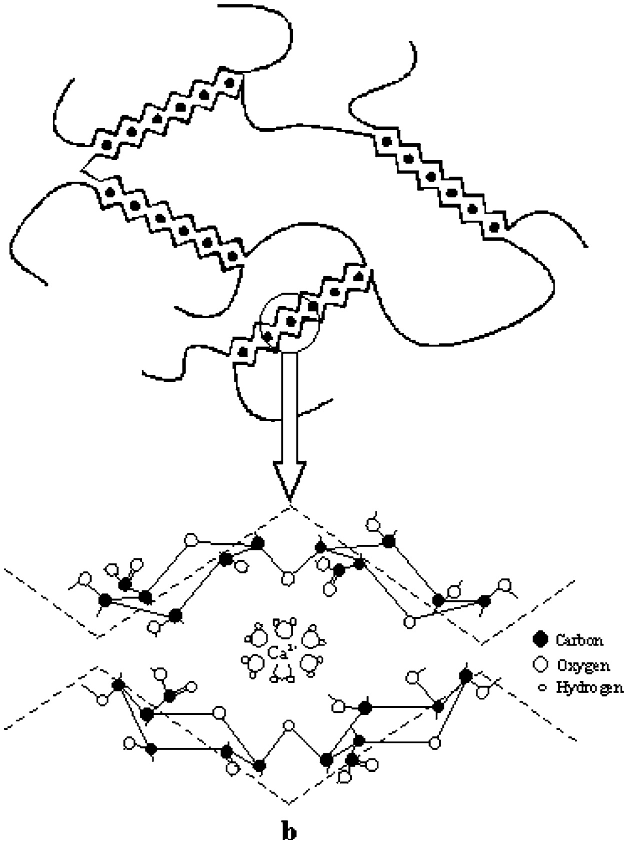


Fig. 2 Six fold hydrated calcium can bind with the surrounding electronegative oxygen atoms on the two adjacent pectin chains to form a “egg box structure” (**b**)

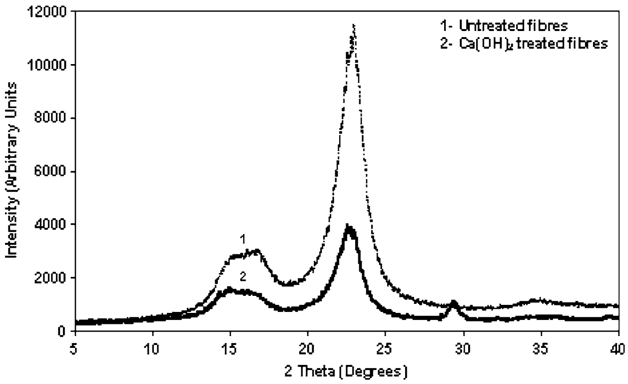


Fig. 3 X-ray diffraction patterns of untreated (1) and $Ca(OH)_2$ treated (2) hemp fibres

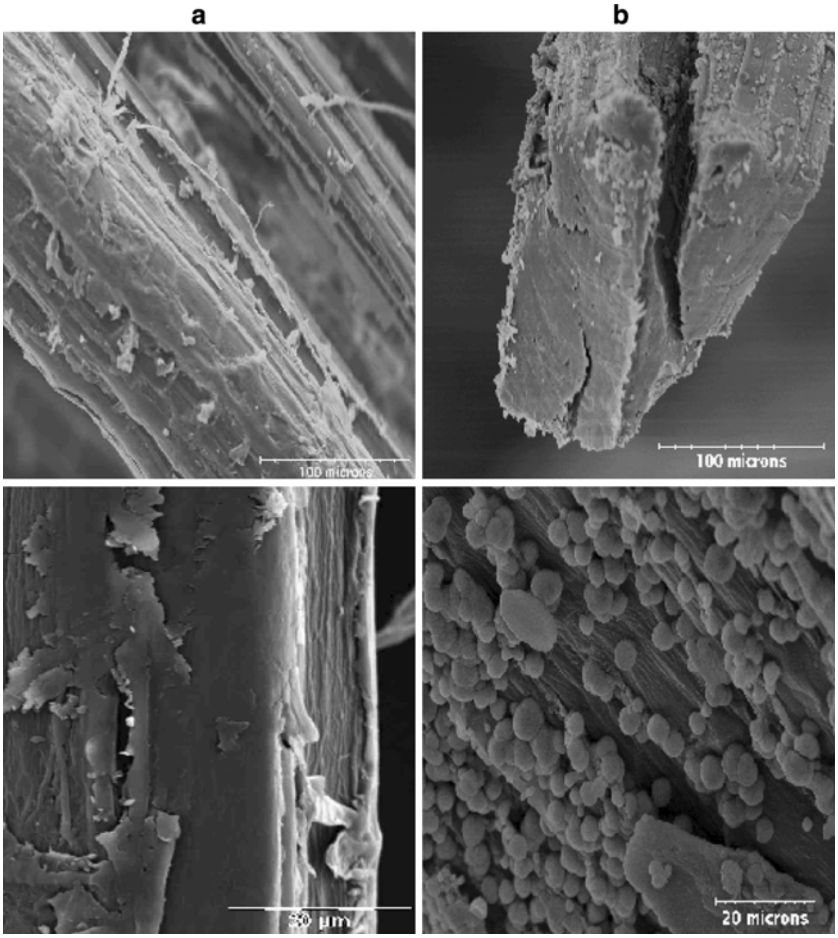
Table 5 Crystallinity index of $Ca(OH)_2$ treated and untreated hemp fibres

	$I_{0.02}$ ($2\theta = 22.5°$)	I_{am} ($2\theta = 18.1°$)	Crystalliniy index (%)
$Ca(OH)_2$ treated hemp	3,980	868	78.2 ± 1
Untreated hemp	10,386	1,907	81.2 ± 0.5

occur at the level of the ester groups contained in compounds fibres. Consequently, carboxyl function will be released and will react with Ca^{2+} contained in the lime-saturated solution. This ester breaking will be in accordance with the previous I.R. observations. Nevertheless, when two pectidic chains portions are in a calcium environment, they can trap calcium ions as shown on Fig. 2. Six fold hydrated calcium can bind with the surrounding electronegative oxygen atoms on the two adjacent polymeric chains. When this fixation is repeated between two chains, a very stable "egg box" structure is formed (Fig. 2), which leads to gel formation [11].

An alkaline treatment, carried out with NaOH solutions, is also well known to increase the cristallinity index of the hemp fibres [9, 13, 17]. This index is linked to the arrangement of cellulosic chains. This increase of the crystallinity index of hemp fibres and consequently of the cellulosic chains is due to the removal of amorphous constituents from the fibres such as lignin, hemicelluloses, pectins and amorphous cellulose. The X-ray spectra of untreated fibres and $Ca(OH)_2$ treated hemp fibres are shown in Fig. 3. The major crystalline peak observed around $2\theta = 22.5°$ on each pattern corresponds to the (002)

Fig. 4 SEM micrographs of cortical fibres before (**a**) and after immersion for 24 h in a lime-saturated solution (**b**)



crystallographic plane for cellulose. The 14.8° and 16.4° reflections correspond to the $(10\bar{1})$ and (101) crystallographic planes. The cristallinity index of the treated and untreated hemp samples are given in Table 5. It shows that a treatment in lime solution decreases by 3% the crystallinity index of the hemp fibres. When the amount of crystalline cellulose is high, as in the case of hemp fibres, the two diffraction peaks around 14.8° and 16.4° can be observed. On the contrary, when the fibre contains large amounts of amorphous materials (such as pectins, hemicelluloses, lignin and amorphous cellulose), these two peaks appear as one broad peak. We can observe in Fig. 3 that these two peaks are more defined for the untreated fibres than for the fibres treated in a lime-saturated solution. It is in accordance with a decrease of the cristallinity index (Table 5). A reverse effect is reported in the literature for an alkaline treatment but with NaOH solutions, where an increase of 10% in cristallinity is observed [17]. The conversion of cellulose I to cellulose II could partly explain the decrease of the cristallinity index of $Ca(OH)_2$ treated fibres. However, this conversion is not systematic as it mentioned in several studies [18, 19]. Indeed, the effect of alkali on a cellulose fibre is a swelling reaction, during which the natural crystalline structure of the cellulose relaxes. The type of alkali and its concentration will influence the degree of swelling, and hence the degree of lattice transformation into cellulose II. A new peak on the X-ray diffractogram appears at $2\theta = 29.4°$ after the $Ca(OH)_2$ treatment. This peak corresponds to $CaCO_3$ (Calcite). Consequently, the effects of NaOH and $Ca(OH)_2$ treatments are not identical. They both permit to remove amorphous materials from the fibre (waxes, fats, hemicelluloses...) [17], but NaOH treatment increases the cristallinity index of the fibres whereas $Ca(OH)_2$ treatment decreases slightly this index.

Figure 4 shows micrographs of cortical fibres before (a) and after immersion for 24 h in a lime-saturated solution (b). In this second situation, nodules are sitting on the hemp fibres. A comparative EDS analysis between areas covered with nodules and nodule free domains shows that the nodules are calcium rich compared to a nodule free region (Fig. 5). This suggests that the fibres can trap calcium. We can observe that hemp fibres contain potassium, due to the use of fertilizers for their cultivation. Potassium is fixed in hemp stem during fibres growth. After immersion for 45 min (water over fibre mass ratio equal to 0.05), the calcium concentration supernatant decreases to 14.10^{-3} mol L^{-1} with a corresponding pH of 12.2. The solubility product of calcium hydroxide is not obtained ($Ks = 5.5{*}10^{-6}$) [20]. Larger quantities of calcium hydroxide in the initial solution would be necessary to saturate the fibres. However, when hemp fibres are immersed in $CaCl_2$ solution (pH ≈ 6), calcium ions are not adsorbed on fibres surface. It shows that calcium adsorption is pH dependent and it only occurs in alkaline medium.

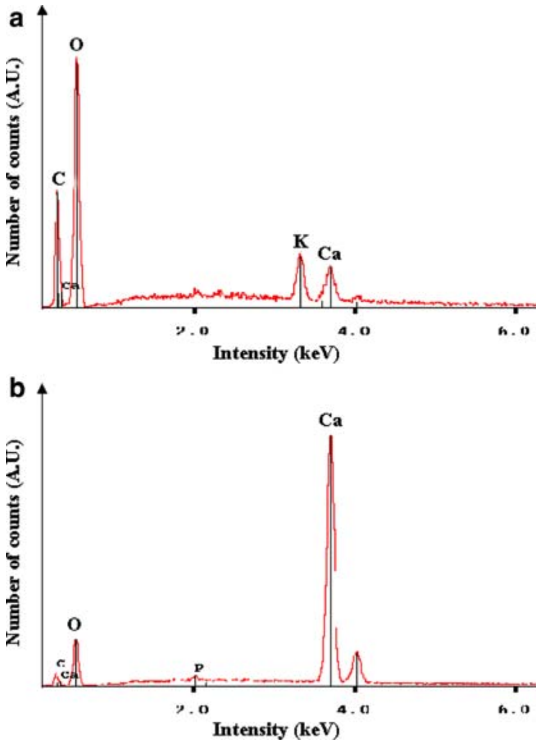


Fig. 5 EDS analysis between areas covered with nodules (**a**) and nodule free domains (**b**)

Conclusion

Before realizing “eco-friendly” composites in the system hemp fibres/cement matrix, the behaviour, in an alkaline and rich calcium media, of hemp fibres was studied. The natural fibres are rich in cellulose and pectin and exhibit a good stability in aqueous media such as pure water, lime saturated or calcium chloride solutions. Quantities of sugars or uronic acids release by the fibres are too little to have an effect on the chemical properties of the solutions. Only a few amount of hemicellulose located at the fibre surface should be degraded. The fibre cristallinity is not affected by the treatment. Hemp fibres in $Ca(OH)_2$ solution can trap large quantities of calcium, but this adsorption phenomena is not observed when fibres are immersed in a $CaCl_2$ solution. Calcium adsorption is pH dependant and only occurs in alkaline medium. So, pectin contained in fibres can react with calcium ions in an alkaline environment and form a very stable “egg box” structure. These surface modifications could play a major role in the bonding between cement and natural fibres in cement-based composites and consequently have a strong impact on their mechanical properties.

References

1. Gassan J, Bledzki AK (1999) Prog Polym Sci 24:221
2. Gassan J (2002) Compos Part A 33(3):369
3. Mishra S, Tripathy SS, Misra M, Mohanty MK, Nayak NK (2002) J Reinf Plast Comp 21(1):55
4. O'Donnell A, Dweib MA, Wool RP (2004) Compos Sci Technol 64:1135
5. Hepworth DG, Holson RN, Bruce DM, Farrent JW (2000) Compos Part A 31:1279
6. Zhu WH, Tobias BC, Coutts RSP, Langfors G (1994) Cement Concrete Comp 16(1):3
7. Tolêdo Filho Romildo D, Ghavami K, England GL, Scrivener K (2003) Cement Concrete Comp 25:185
8. Moine C (2005) In: Extraction, caractérisation structurale et valorisation d'une famille d'hémicelluloses du bois. Obtention de matériaux plastiques par modification des xylanes. PhD, Limoges University
9. Tserki V, Zafeiropoulos NE, Simon F, Panayiotou C (2005) Compos Part A 36:1110
10. Roncero MB et al (2005) Bioresource Technol 96:21
11. Garcia-Jaldon C, Dupeyre D, Vignon MR (1998) Biomass Bioenerg 14:251
12. Valadez-Gonzales A, Cervantes-Uc JM, Olayo R, Herrera-Franco PJ (1999) Compos Part B 30:309
13. Herrera-Franco PJ, Valadez-Gonzales A (2005) Compos Part B 36(8):597
14. Yang J, Yen HE (2002) Plant Physiol 130:1032
15. Barkakaty BC (1976) J Appl Polym Sci 20:2921
16. Cazaurang MN, Peraza S, Cruz-Ramos CA (1990) Cellulose Chem Technol 24:629
17. Pickering KL, Beckermann GW, Alam SN, Foreman NJ (2007) Composites Part A 38:401
18. Ouajai S, Shanks RA (2005) Polym Degrad Stab 89(2):327
19. Fengel D, Wegener G (1983) Derivatives of cellulose, wood: chemistry, ultrastructure, reactions. de Gruyter, Berlin, p 66
20. Depovere P (1992) In: Chimie Générale. Mc Quarrie/Rock, 3éme édn, De Boeck Université