

IFSTTAR

CONCOURS EXTERNE D'INGENIEUR DE RECHERCHE

N° 2014 – IR – CE - 01

Ingénieur en chimie des matériaux de construction

EPREUVE ECRITE (3 heures)

Veillez respecter l'anonymat dans les réponses. Les candidats peuvent traiter les deux épreuves dans l'ordre de leur choix. Les questions posées dans chaque épreuve sont indépendantes.

EPREUVE 1 - Expertise d'un béton de structure (10 points)

L'expertise d'un béton de structure présentant des signes d'altération est constituée de plusieurs analyses. En particulier, l'analyse chimique élémentaire, la reconnaissance des phases par diffraction des rayons X et l'analyse thermique peuvent être utilisées.

Un béton est un mélange principalement constitué de :

- Eau,
- Granulats (calcaire, quartz, dolomie ...) et sables (plagioclases, feldspaths, matériaux argileux ...),
- Adjuvants,
- Et de ciment.

La solution obtenue après une mise en solution (acide ou fusion) peut être analysée soit par des méthodes dite de paillasse soit par des méthodes instrumentales. Parmi ces dernières, le laboratoire dispose d'une SAA et d'une ICP.

Question 1 : Expliciter ces deux sigles ICP et SAA. Dans ce cas précis, quel instrument à votre préférence pour effectuer cette analyse ? Détailler votre réponse en argumentant sur les avantages et inconvénients de ces deux méthodes instrumentales.

Question 2 : Donner le principe de l'ICP

Question 3 : Donner le principe de la SAA

Les éléments à rechercher sont les suivants : Si, Al, Na, K, Ca, Ti, P, Mg, Fe, S, Cl.

Question 4 : Donner le nom de tous ces éléments.

Question 5 : Lequel de ces éléments ne peut pas être dosé par la SAA ou l'ICP ?

Question 6 : Si un béton a subi une altération par les sels de déneigement, quel est l'élément principal qui va subir une modification de teneur ?

Il existe des ciments contenant du laitier de haut fourneau utilisés dans la formulation des bétons.

Question 7 : Le laitier est un sous-produit de quelle filière industrielle ?

Question 8 : Quel est l'originalité du laitier pour être utilisé en cimenterie :

- | | | |
|------------------------------|-----|-----|
| • Il est cristallisé, | OUI | NON |
| • Il est vitreux ou amorphe. | OUI | NON |

La perte au feu est une composante de l'analyse chimique élémentaire.

Question 9 : Parmi ces trois types d'appareils, le(s)quel(s) permet(tent) d'obtenir ce résultat ?

- | | | |
|----------------------------|-----|-----|
| 1. Etuve ventilée | OUI | NON |
| 2. Four à moufle | OUI | NON |
| 3. Analyseur thermique ATG | OUI | NON |

Question 10 : Un de ces appareils permet d'obtenir une perte au feu détaillée avec quantification des phénomènes ?

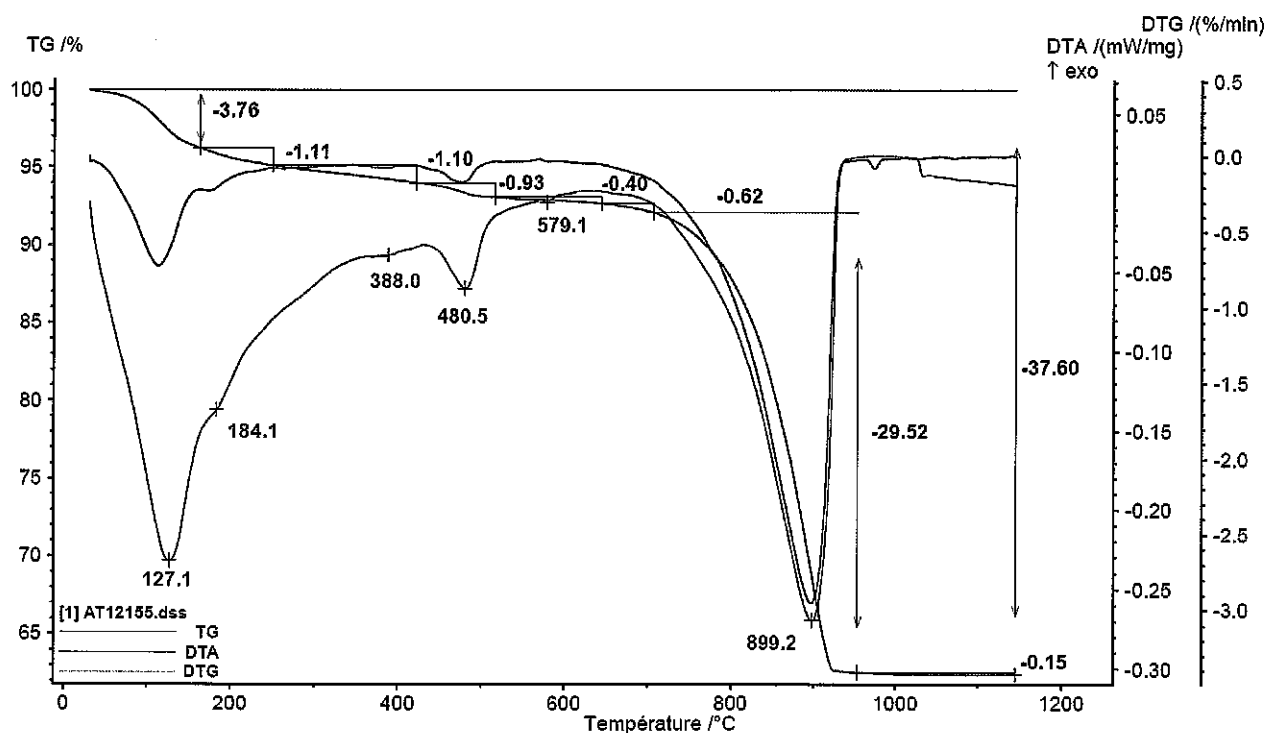
- | | | |
|----------------------------|-----|-----|
| 1. Etuve ventilée | OUI | NON |
| 2. Four à moufle | OUI | NON |
| 3. Analyseur thermique ATG | OUI | NON |

Question 11 : Donner le principe de l'analyse thermogravimétrique

Une ATG / MS (spectrométrie de masse) analyse les gaz issus de la calcination d'un béton. Les masses 44 et 18 sont détectées.

Question 12 : Quels sont les deux gaz pouvant répondre à ces deux masses ? Quels phénomènes chimiques donnent naissance à ces deux gaz ? (Utiliser le tableau périodique donné en page 4).

Les résultats d'un essai d'analyse ATG effectué sur un béton sont donnés ci-dessous.



Question 13 : En vous servant des données ci-dessous (identification des phases par les pics ATD), pouvez vous identifier certains pics ATD de cette figure ?

Question 14 : Calculer la teneur en portlandite ($\text{Ca}(\text{OH})_2$) et en calcaire (ou appelé calcite : CaCO_3) du béton concernée par cette analyse ?

Données à utiliser : **Tableau périodique des éléments :** H = 1, C = 12, O = 16, Cl = 35.5,
Ca = 40, Na = 23, K = 39, P = 31, Al = 27, Fe = 56, S = 32.

Identification des phases par les pics ATD :

110-130 °C : C-S-H et ettringite

175 – 190 °C : monocarboaluminate de calcium hydraté

460 – 510 °C : portlandite

575 – 579 : quartz

850 – 920 °C : calcite

L'expertise d'un béton de structure se fait également par diffractométrie des rayons X.

Questions 15 : Concernant l'utilisation des appareils émettant des rayons X, existe-t-il une réglementation ?

OUI NON

Questions 16 : Si OUI, quels sont les équipements de protection individuelle obligatoires ?

Le laboratoire chargé de ces analyses est certifié ISO 9001-2008 et accrédité par le COFRAC.

Question 17 : Que définit la norme ISO 9001-2008 ?

Question 18 : Citer trois documents obligatoires pour les laboratoires certifiés ISO 9001-2008 ?

Question 19 : Que signifie le sigle COFRAC ?

Question 20 : Quelle est la mission du COFRAC ?

EPREUVE 2 - Exploitation des données d'un article scientifique (10 points)

Les chercheurs du laboratoire Comportement Physico-Chimique et Durabilité des Matériaux s'intéressent depuis plusieurs années à l'étude de la durabilité de matériaux contenant des particules végétales pour des applications dans le domaine de la construction.

Vous disposez d'un article (Le Troedec *et al.*, Composites: Part A 39 (2008) 514-522) qui présente l'influence de traitements chimiques sur la composition et la structure de fibres de chanvre ("hemp fibres" en anglais).

Grâce aux informations contenues dans cet article, répondez aux questions suivantes :

Question 1 : D'après l'introduction, quelles sont les molécules contenues dans les fibres de chanvre et quelle est leur microstructure ?

Question 2 : Pour les différents traitements effectués sur les fibres, quelles modifications peut-on attendre sur ces particules végétales ?

Question 3 : Quelles sont les techniques expérimentales utilisées pour caractériser les fibres de chanvre dans cet article? Quelles caractéristiques des fibres permettent-elles d'obtenir ?

Question 4 : D'après les observations par microscopie électronique à balayage, quel est l'effet des différents traitements sur la surface des fibres ?

Question 5 : D'après les résultats d'analyse thermique différentielle, quelles réactions peut-on observer pour les fibres de chanvres non traitées ?

Question 6 : A quels composés peut-on attribuer les principaux pics observés par DRX ?

Question 7 : D'après l'analyse par DRX, quel est l'influence des traitements des fibres sur leur taux de cristallinité ?

Question 8 : D'après l'analyse infra-rouge, quelle est la principale modification du spectre des fibres de chanvre observée après certains traitements ?



Influence of various chemical treatments on the composition and structure of hemp fibres

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Abstract

The impact of several chemical treatments, including NaOH, polyethyleneimine, ethylenediaminetetraacetic acid, $\text{Ca}(\text{OH})_2$ and CaCl_2 onto the composition and structure of hemp fibres was evaluated using differential thermal analysis, scanning electron microscopy, X-ray diffraction and Fourier transform infrared spectroscopy. Comparison of results obtained with the last two techniques allows us to quantify the impact of the chemical treatments onto the crystallinity index.

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Keywords: A. Natural fibres; D. Surface analysis; E. Surface treatment

1. Introduction

Fueled by environmental impact considerations, the need to redirect agricultural production from the sole food industry to other applications and the need to find alternative, more energy saving materials, there are renewed scientific as well as industrial interests in traditional construction materials, such as lime-based mortars and their mixture with cellulosic fibres, such as hemp fibres bundles. The use of natural fibres and in particular hemp (*Cannabis Sativa* L.) fibre bundles as reinforcing agents in composite materials offers many advantages, such as a low density and an enhanced biodegradability, over glass fibres [1–3]. The technical fibre used for the experiments consists of elementary fibres glued together by an inter-phase consisting mainly of pectins and hemicelluloses,

which are a mixture of different lower molecular weight branched polysaccharides. However, the major disadvantage of cellulosic fibres is a high moisture sensitivity, which can cause the chemical degradation of the structure of fibres as well as dimensional variations of the fibres according to the percentage of moisture. This last effect has an impact on the quality of the mechanical interaction between hemp fibres and matrix. Thus, their incorporation in a polymer or mineral matrix implies the overcoming of interface incompatibilities by means of fibres chemical pre-treatments [4,5]. The objective of this publication is to study the impact of several fibre pre-treatments onto the physico-chemical properties of cellulosic fibres. Each considered treatment modifies either the chemical nature of the surface of natural fibres, or the surface state, like the charge or the conformation of polymers.

For example, alkalisation of natural fibres with sodium hydroxide is already known to remove amorphous materials, such as hemicelluloses, lignins and pectins, from the surface of fibre bundles [6–8].

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The adsorption in large quantity of calcium ions on the fibres surface can influence the fibre/matrix interface [9]. To check the impact of the calcium adsorption, several approaches were selected. In one experiment, the fibres were treated with acid ethylenediaminetetracetic (EDTA), which forms with calcium ions a very stable complex and weakens the gel structure formed by pectins and calcium ions [10]. This treatment would prevent the fixing of calcium ions at the surface of fibres. We also investigated the combination of alkalisation and EDTA treatments.

A second treatment consists in modifying the surface charge of hemp fibres. In this approach, the surface charge of negative cellulose is modified by the reaction with the cationic polyelectrolyte, polyethylene imine (PEI). This step should prevent the further fixation of calcium ions [11]. Degradation of cellulose treated with amino compounds, like PEI, is partly caused by the reaction of cellulosic carbonyl groups with amino groups to form imines [12].

Lastly, treatment of hemp fibre bundles with lime water (pH 12.7) and a calcium chloride solution (pH 6.0) were compared to monitor the influence of pH on calcium ions adsorption [13].

2. Experimental

Technical hemp fibres (*Cannabis Sativa* L.) were a gift from the company Agrofibra (Barcelona, Spain). The fibres composition indicated in Table 1 was determined according to a previously published extraction procedure [9].

Ethylene diaminetetraacetic acid (EDTA), polyethyleneimine (PEI) (Sigma–Aldrich, Seeze, Germany) and NaOH (Prolabo, Fontenay-sous-Bois, France) were used without further purification.

3. Fibre surface treatments

Prior to treatment and in order to ensure a constant humidity content, fibres were dried at 40 °C for 24 h in a drying oven.

- **Alkalization.** Dried fibre bundles were soaked in 1.6 M NaOH (pH 14) solution during 48 h and then neutralized with 1% vol. acetic acid. Fibres were then washed with deionised water until the pH value was 7. The alkalisation conditions are relatively mild, in order to leave the cellulosic part of the fibre bundles unscathed and to prevent conversion of cellulose I [8,25].
- **EDTA.** Fibres were immersed during 3 h in a solution of EDTA (5 g/l) which pH was adjusted to 11 with caustic

soda. In order to ensure removal of excess EDTA, fibres were then washed with deionised water for 2 h [17].

- **PEI.** Fibres were soaked in a PEI (MW = 2000 g mol⁻¹) solution for 48 h, then washed with deionised water.
- **Ca(OH)₂.** In order to saturate fibres with calcium ions, fibres were placed for 48 h in a saturated lime solution ([Ca²⁺] = 2.10⁻² M, pH 12.7). Following the impregnation, fibres were washed with deionised water.
- **CaCl₂.** Fibres were immersed during 48 h in a solution of CaCl₂ (2.2.10⁻² M, pH 6) and then washed with deionised water.
- **Alkali and EDTA treatments.** Fibres were first soaked in 6% NaOH solution and after neutralization and washing, they were placed in EDTA solution during 3 h.

After all treatments, fibres were dried at 40 °C for 24 h.

4. Fibre characterization

A Scanning Electron Microscope (SEM) (Cambridge stereoscan S260) was used to examine the effects of chemical modifications upon the fibre surface. Samples are obtained by cutting small pieces of fibres and sticking them on a carbon adhesive, before being covered with platinum film.

Differential thermal analysis measurements were performed under dry atmosphere using a Setsys 2400 instrument (SETARAM). Temperature ranged from 25 °C to 800 °C with a heating rate of 5 °C min⁻¹.

Cellulose exists under several polymorphic states, the most well-known and studied one being cellulose I, or native cellulose, which is the crystalline form detectable by X-ray diffraction. The other states are amorphous. In order to assess the influence of the treatments on fibre crystallinity, XRD experiments were carried out using a home-made diffractometer deriving from the Debye–Scherrer geometry [14]. The primary beam is supplied by a sealed tube operating at 37.5 kV/28 mA associated with a curved quartz monochromator selecting the CuKα₁ radiation. The flat samples are irradiated under a constant incidence angle and the diffracted beams are collected by a curved position sensitive detector (Inel CPS 120). This set-up has been described in more details previously [15].

In order to elaborate XRD flat samples, fibres were cut with a knife crusher to about 500 µm and pressed into a pellet using a cylindrical steel mould (φ = 16 mm) with an applied pressure of 35 MPa in a laboratory press. Preliminary XRD experiments, realized under different incidence angles have shown that using this elaboration procedure, the polycrystalline samples are randomly oriented.

The crystallinity index (CI), which is a measurement of the amount of crystalline cellulose with respect to the global amount of amorphous materials, was evaluated using Segal empirical method [16] and an internal standard method [17] described thereafter.

Table 1
Chemical composition of hemp fibres

Fibres of hemp	% mass	Cellulose residues	Pectins	Hemicelluloses	Lignins	Waxes, oils
		58.7	16.8	14.2	6	4.3

Method 1: Segal method

The CI has frequently been determined by means of the empirical Segal equation [16]:

$$CI(\%) = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the maximum intensity of the 002 lattice reflection of the cellulose I and I_{am} is the maximum intensity of X-ray scattering broad band due to the amorphous part of the sample.

In the case of natural hemp fibres, the two peaks characteristics of diffraction planes (110) and (1 $\bar{1}$ 0) are distinct, which indicate a high proportion of cellulose I . Indeed, the crystallinity index according to Segal is equal to 80% for untreated fibres. In a first approximation, the Segal method is a fast technique to estimate the crystallinity index and allows comparative measurements. However, the use of Eq. (1) requires that the Bragg reflection and the broad peak due to the X-ray scattering by the amorphous part are well separated. In fact, diffuse scattering due to the amorphous part and the Bragg (002) reflection of the cellulose are partially superimposed. Moreover, the Segal method is based on the sole measurement of the maximum of the peak intensity. Thus, this approach completely neglects the shape of the scattered and diffracted intensities. Since quantitative XRD measurements have to be based on the evaluation of the integrated intensities, a more convenient method based both on the measurement of the integrated intensities and on the use of standard samples is commonly used in the field of the characterization of inorganic materials [14]. It was already applied to the characterization of cellulose-containing samples a few years ago [17]. Our samples were characterized following this approach, described below.

Method 2: Internal standard method

According to the kinematic theory of the X-ray diffraction, the integrated intensity of the diffraction peak is directly proportional to the volumic quantity of the corresponding phase presents in the homogeneous mixture. For a given (hkl) reflection and taking into account the diffractometer configuration, the diffracted integrated intensity of the (hkl) peak is written:

$$I_{hkl} = I_0 \frac{e^4}{m^2 c^4} \left(\frac{1 + \cos^2(2\beta) \cos^2(2\theta_{hkl})}{1 + \cos^2(2\beta)} \right) \times \left(\frac{1}{16\pi R \sin^2(\theta_{hkl}) \cos(\theta_{hkl})} \right) \left(\frac{\lambda^3 n_{hkl} |F_{hkl}|^2}{V_c^2} \right) AD\Omega \quad (2)$$

where

I_0 is the intensity of the primary beam
 e , m and c are, respectively, the charge and the mass of the electron and the velocity of the light
 θ_{hkl} is the Bragg angle of the hkl reflection
 β_{hkl} is the Bragg angle of the monochromator reflection
 R is the distance between the sample and the detector

λ is the wavelength of incident X-rays

n_{hkl} is the multiplicity factor

$|F_{hkl}|^2$ is the square of the modulus of the structure factor

V_c is the volume of the elementary cell

A is the mean mass absorption coefficient of the sample

D is the Debye factor

Ω volume of the diffracting phase

According to the Eq. (2) and considering a material containing two crystalline phases, the ratio of the integrated intensity of one diffraction peak for each phase gives a direct estimation of the volume ratio of the two phases. In the present case, the situation is more complicated. In fact the samples are containing only one crystalline phase (cellulose I), the residual part is amorphous. The intensity of the diffuse scattering part due to the amorphous phase is not corresponding to the Eq. (2). One way to overcome this problem is to introduce in all the samples a constant amount of a standard crystallized material. The amount of the crystallized phase under interest is then determined with respect to the amount of standard material introduced.

Following this approach, we have introduced in all our samples (treated and untreated fibres) 30% wt of a $Ca(OH)_2$ powder. The amount of cellulose was then determined by measuring the ratio between the integrated intensity of the (002) cellulose peak and the (110) $Ca(OH)_2$ peak, occurring at 2θ close to 50° . The last step consists in determining the relationship between this ratio and the amount of cellulose. For this purpose, we prepared various samples containing microcrystalline cellulose (Avicel) and different amounts (between 0 and 50 wt%) of $Ca(OH)_2$ and we realized for each of those samples an XRD pattern (see Fig. 1a). Measuring the integrated intensity of both the (002) cellulose peak and the (110) $Ca(OH)_2$ peak, we were able to plot the value of the ratio of those intensities as a function of the amount of $Ca(OH)_2$. This abacus is reported in Fig. 1b. The experiments were run the same day the samples were prepared in order to limit the transformation of lime into calcium carbonate and to prevent eventual calcium loading by the fibres, both effects which could complicate the analysis.

FTIR measurements were performed using a Perkin-Elmer spectrometer (Spectrum one, Boston, USA) using the standard KBr pellet technique. A total of 10 scans was taken for each sample between 400 cm^{-1} and 4000 cm^{-1} , with a resolution of 4 cm^{-1} . Fibres were chopped roughly to a length of less than 1 mm and mixed with 300 mg of KBr and then pressed into a pellet ($\phi = 16\text{ mm}$) for FTIR measurement.

5. Results and discussion

5.1. Hemp fibres surface morphology

Fig. 2 presents the micrographs of hemp fibres obtained by scanning electron microscopy after various chemical

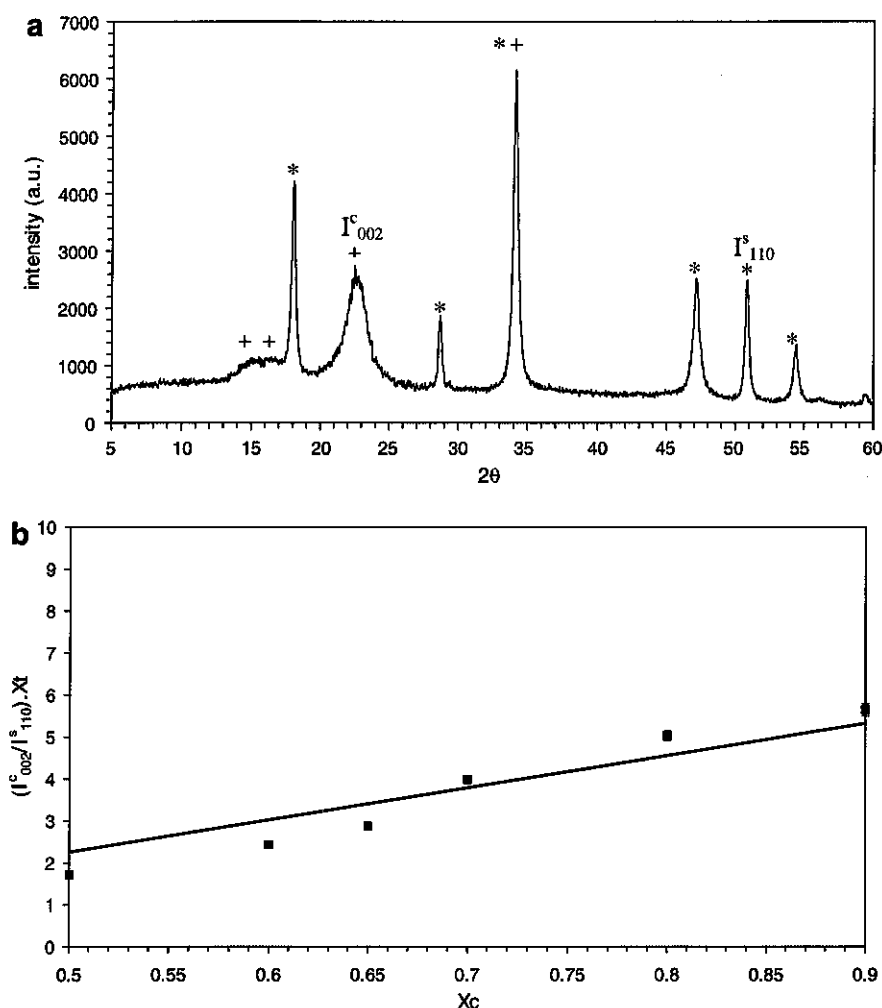


Fig. 1. (a) X-ray diffraction pattern of 50% w. standard (*) and 50% w. cellulose (+). (b) Calibration curve for quantitative analysis using internal standard method through X-ray diffraction (x_i represents the weight fraction of component i).

treatments. Treatment with NaOH at pH 14 removes waxes and oils from the surface of the fibres and thus increases the overall rugosity of the surface. The same result is obtained with a treatment with PEI. However, impregnation of the fibres with a calcium hydroxide solution at the same pH leads to the deposition of calcium containing nodules at the surface of the hemp fibres, as reported by Sedan et al. [9]. Immersion of the fibres in a neutral calcium chloride suspension in the same conditions do not lead to any notable modifications of the hemp fibres surfaces. Atomic emission analysis of the calcium containing solutions showed that almost no calcium ions were adsorbed when the fibres were immersed in a calcium chloride solution. Thus, we can conclude that an alkaline environment (pH > 12) as well as the presence of calcium ions are necessary to induce the adsorption of calcium containing species at the surface of hemp fibres. Treatment with EDTA, a strong calcium chelant, seems to promote hemp fibres separation. Indeed, it was previously reported that EDTA complexes calcium ions present in pectin aggre-

gates, and this in turn induces the separation of fibres [18]. Thus, surface observations point out that calcium ions, especially at high pH, play a role towards fibre surface morphology.

5.2. Thermal analysis of fibres

Independently of chemical treatments, differential thermal analysis (DTA) curves show a first endothermic peak between temperature of 50 and 175 °C, which is caused by the evaporation of weakly bound water molecules.

The DTA curve of untreated natural fibres, presented in Fig. 3, presents three exothermic reactions: a first peak located between 320 and 370 °C is attributed to the thermal depolymerisation of hemicelluloses and pectins. A signal between 390 and 420 °C is attributed to the cellulose decomposition. Finally, a last peak at higher temperatures represents decomposition of lignin residues [22].

All treatments influence in the same fashion the peak characteristic of the degradation of hemicellulose and

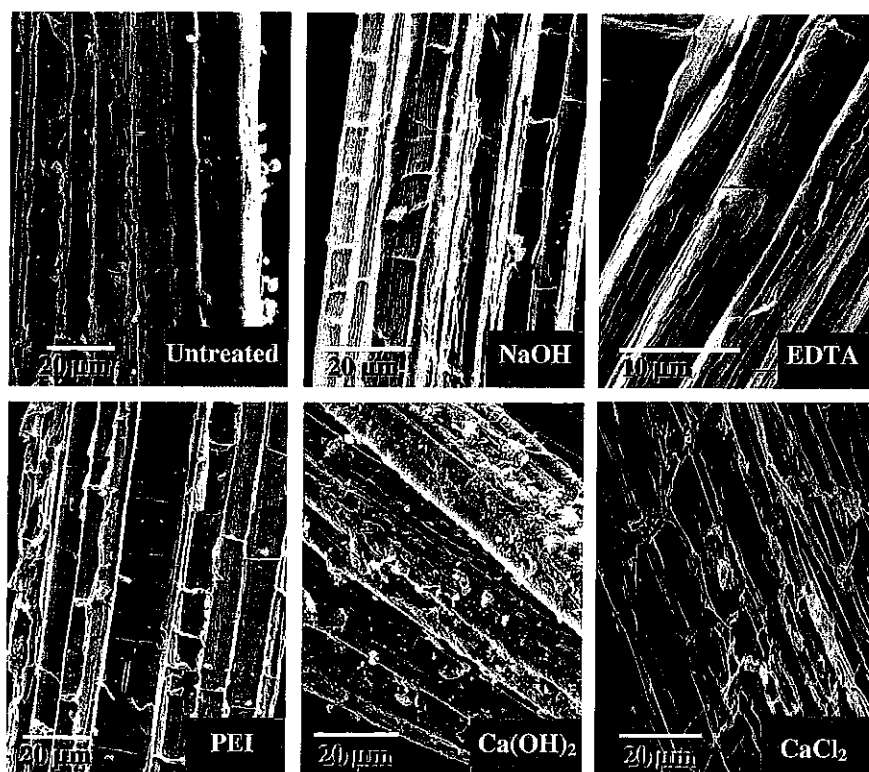


Fig. 2. Scanning electron microscopy images of untreated and treated hemp fibre bundles.

pectins : it is somewhat shifted at a higher temperature, but with a sharp signal obtained with $\text{Ca}(\text{OH})_2$ and CaCl_2 at 335°C ($+15^\circ\text{C}$). This shift and sharp signal was also observed for pure pectin treated with $\text{Ca}(\text{OH})_2$ (data not shown) and reflects a strong interaction between calcium ions and pectin molecules. In contrast, NaOH , EDTA and PEI treatments lead to a broadening of the signal and a slighter shift at higher temperature. Thus, all treatment removes well the vast majority of amorphous materials, leaving more organized and thus heat-resistant molecules behind.

The influence onto the degradation of cellulose of the various chemical treatments is more contrasted. $\text{Ca}(\text{OH})_2$ and EDTA treatments lead to a decrease of the cellulose degradation temperature, with a more pronounced effect with calcium hydroxide. This result indicates that cellulose is degraded by these two treatments.

NaOH treatment increases slightly the cellulose degradation temperature to 410°C . This comes from the fact that amorphous cellulose is more easily degraded with the alkaline treatment than the crystallized form. Thus, more crystallized and heat resistant cellulose molecules are left behind after treatment. The cellulose peak is also much weaker and broader (it reaches 450°C) with CaCl_2 and PEI treatments.

Treatments with EDTA and lime water decrease the initial temperature of decomposition of cellulose of 10 and 20°C , respectively, whereas treatments with PEI , caustic soda and CaCl_2 make the celluloses compounds more sta-

ble. Indeed, PEI treatment seems to act like a protection on the surface of fibres and prevent the degradation of cellulose. Successive treatment with NaOH and EDTA results in a combination of the effects of the two individual treatments onto the thermal analysis curves.

5.3. X-ray diffraction

Fig. 4 shows the diffractogram obtained for untreated, NaOH and $\text{Ca}(\text{OH})_2$ treated fibres. It presents a major diffraction peak for 2θ ranging between 22° and 23° , which corresponds to the (002) crystallographic planes of cellulose I. The peak at 2θ close to 50° is corresponding to the (110) peak of the standard sample $\text{Ca}(\text{OH})_2$. There are no overlapping peaks between the cellulose and lime diffractograms in the range of study.

Table 2 presents the crystallinity index obtained by two calculation methods. Although the calculated crystallinity index value differs between the two methods, they both produce similar trends. The discrepancy between the calculated values comes from the relative inaccuracy of the Segal method, which relies only onto the ratio of the peaks height. Hemp fibres treated with $\text{Ca}(\text{OH})_2$ and CaCl_2 do not exhibit any peak for the angle value of 2θ close to 50° (see Fig. 4c and d). Therefore, the peak area ratio are representative of the percentage of crystalline cellulose.

These values show that treatments with EDTA , PEI and NaOH increase the crystallinity index. Indeed, EDTA treatment allows the formation of a very stable complex

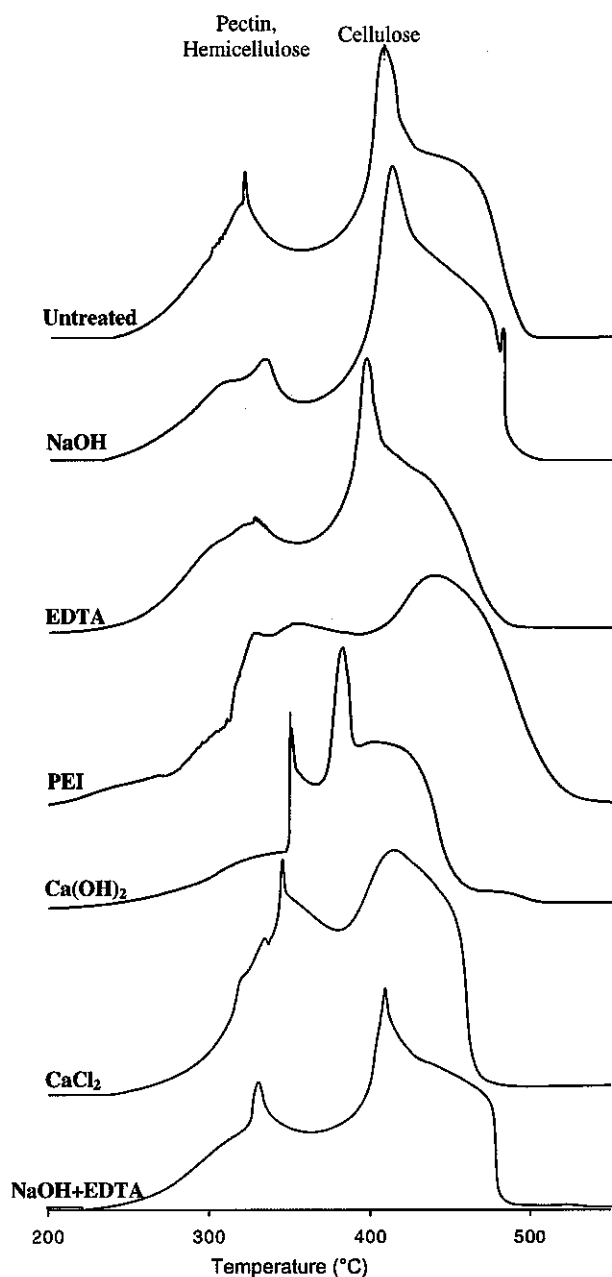
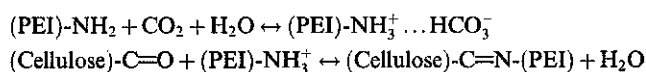


Fig. 3. Comparison of the differential thermal analysis of untreated and treated hemp fibre bundles.

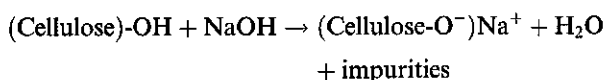
between calcium ions trapped mostly in the pectins and the chelant. This complex formation disturbs the pectin/calcium complex and causes the degradation of pectin. This amorphous molecule is thus degraded and the crystallinity of the hemp fibre bundles is increased.

At pH 12, PEI amine groups react with cellulose carbonyl groups to form amine bicarbonate salts according to the following reactions [19]:



This reaction is probably at the origin of the crystallinity index increase.

Alkali treatment hydrolyses the amorphous parts of cellulose present in fibres and after treatment the material contains more crystalline cellulose. The reaction between cellulose and caustic soda is:



Na^+ ions come to fit in the unit cell of cellulose, increasing the cell parameter [20].

However, $\text{Ca}(\text{OH})_2$ and CaCl_2 treatments have little impact on the crystallinity index.

5.4. Infrared spectroscopy

FTIR allows the measurement of variations of hemp fibre composition after chemical treatments. Table 3 summarizes the major bands observed in the FTIR spectrum of hemp fibres and their assignments to chemical group vibrations and molecules. Infrared spectra of hemp fibres without and with chemical treatment are displayed in Fig. 5. One of the most visible difference between the spectra is the modification of the signal at 1732 cm^{-1} , characteristic of the stretching of unconjugated CO groups present in hemicelluloses. This peak has fully disappeared after treatment with NaOH and is very weak after PEI and $\text{Ca}(\text{OH})_2$ treatments. Indeed, treatments with lime water, PEI and NaOH, are known to remove hemicelluloses [6–8,11]. The observation of the peak located at 1505 cm^{-1} after all treatments seems to indicate that none of the chemical treatment is successful in completely removing lignin from hemp fibre bundles. With caustic soda treatment, the intensity of the peak characteristic of waxes and oils present at 2850 cm^{-1} decreases whereas the intensity of the peak characteristic of polysaccharides hydroxyl bonds and located near 3300 cm^{-1} increase.

The intensity of the peak at $1650\text{--}1630\text{ cm}^{-1}$, which corresponds to water absorbed in cellulose, increases slightly after treatment with caustic soda. Indeed, NaOH react with hydroxyl groups present on cellulose to form water molecules.

Some authors differentiate the peaks associated to pectins [21]:

- esterified pectins have three characteristic peaks at 1748, 1445 and 1234 cm^{-1} . These three weak peaks are difficult to dissociate from the signals relative to others.
- calcium pectates result in the presence of a signal at 1615 cm^{-1} and a broad band in 1425 cm^{-1} . The first peak is very difficult to dissociate from the water signal. As for the peak at 1425 cm^{-1} , it is also characteristic of the CH bonds present in all organic molecules. In order to analyse the percentage of calcium pectates, it would be necessary to first completely remove the water molecules from hemp fibres.

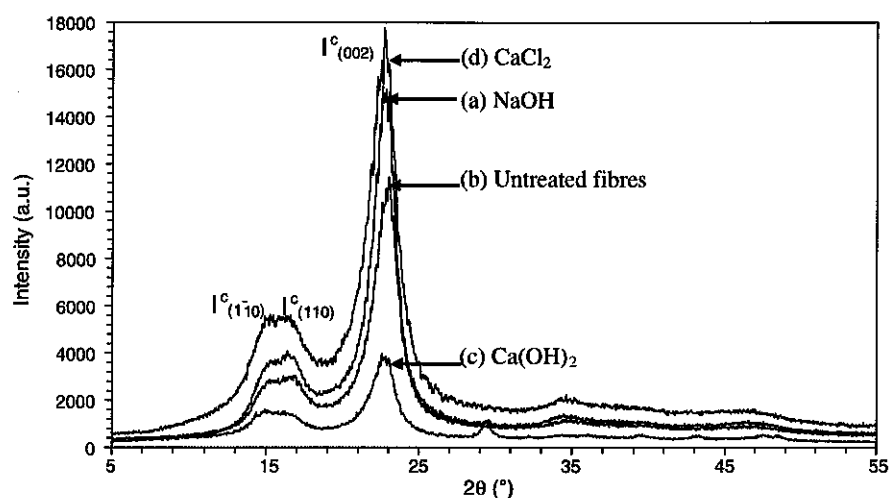


Fig. 4. X-ray diffractograms of untreated (b), alkali (a), $\text{Ca}(\text{OH})_2$ (c) and CaCl_2 (d) treated hemp fibres.

Table 2

Crystallinity index of untreated and treated hemp fibres obtain by X-ray diffraction (panel a); crystallinity of untreated and treated hemp fibres measured using FTIR spectroscopy (panel b).

Chemical treatment	Degree of crystallinity (XRD)		
	Internal standard method	Segal	
<i>Panel a</i>			
Untreated fibres	55	80	
NaOH	80	86	
EDTA	72	83	
PEI	75	81	
Ca(OH) ₂	51	78	
CaCl ₂	54	65	
NaOH + EDTA	76	80	
Chemical treatment	Absorbance ratio (FTIR)		
	1427/896 cm ⁻¹	1373/2885 cm ⁻¹	1373/667 cm ⁻¹
<i>Panel b</i>			
Untreated fibres	1.82	0.19	0.38
NaOH	1.82	0.20	0.50
EDTA	1.15	0.18	0.38
PEI	0.88	0.20	0.32
Ca(OH) ₂	0.53	0.20	0.29
CaCl ₂	0.67	0.19	0.34
NaOH + EDTA	0.74	0.21	0.40

CaCl_2 treatment has little effect on the chemical composition of fibres, whereas $\text{Ca}(\text{OH})_2$ treatment involves a fixation of calcium ions, which allow us to conclude that calcium ions are fixed only in alkali conditions.

Intensities of some bands in IR spectra have been found to be sensitive to variations in cellulose crystallinity [22]. Such variations may be determined by calculating the ratio of the intensity of IR bands sensitive and insensitive to variation of crystallinity. Several author already tackled the evaluation of crystallinity through variations in IR band ratios. The ratios of peaks at 1427 and 896 cm^{-1} , and 1373 and 2900 cm^{-1} have been used to measure relative cellulose crystallinity [23,24]. However, although vibrations at 896 cm^{-1} can be unambiguously attributed to vibrations belonging to polysaccharides, the peak at 1427 cm^{-1} receives contributions from almost all species present in hemp fibres. Thus, it can be difficult to correlate the 1427/896 ratio with the crystallinity index obtained with X-ray diffraction analysis. In the same way, the ratio of bands at 1373 and 2900 cm^{-1} are characteristics of polysaccharides in general, and thus correlate weakly with an increase in cellulose I percentage. Richter et al. proposed

Table 3

Infrared main transitions for hemp fibre bundles

Wavenumber (cm^{-1})	Vibration	Source
3300	O–H linked shearing	Polysaccharides
2885	C–H symmetrical stretching	Polysaccharides
2850	CH_2 symmetrical stretching	Wax
1732	C=O unconjugated stretching	Xylans (Hemicelluloses)
1650–1630	OH (water)	Water
1505	C=C aromatic symmetrical stretching	Lignin
1425	CH_2 symmetric bending C=C stretching in aromatic groups	Pectins, lignins, hemicelluloses, calcium pectates
1370	In-the-plane CH bending	Polysaccharides
1335	C–O aromatic ring	Cellulose
1240	C–O aryl group	Lignin
1162	C–O–C asymmetrical stretching	Cellulose, hemicellulose
895	Glycosidic bonds symmetric ring-stretching mode	Polysaccharides
670	C–OH out-of-plane bending	Cellulose

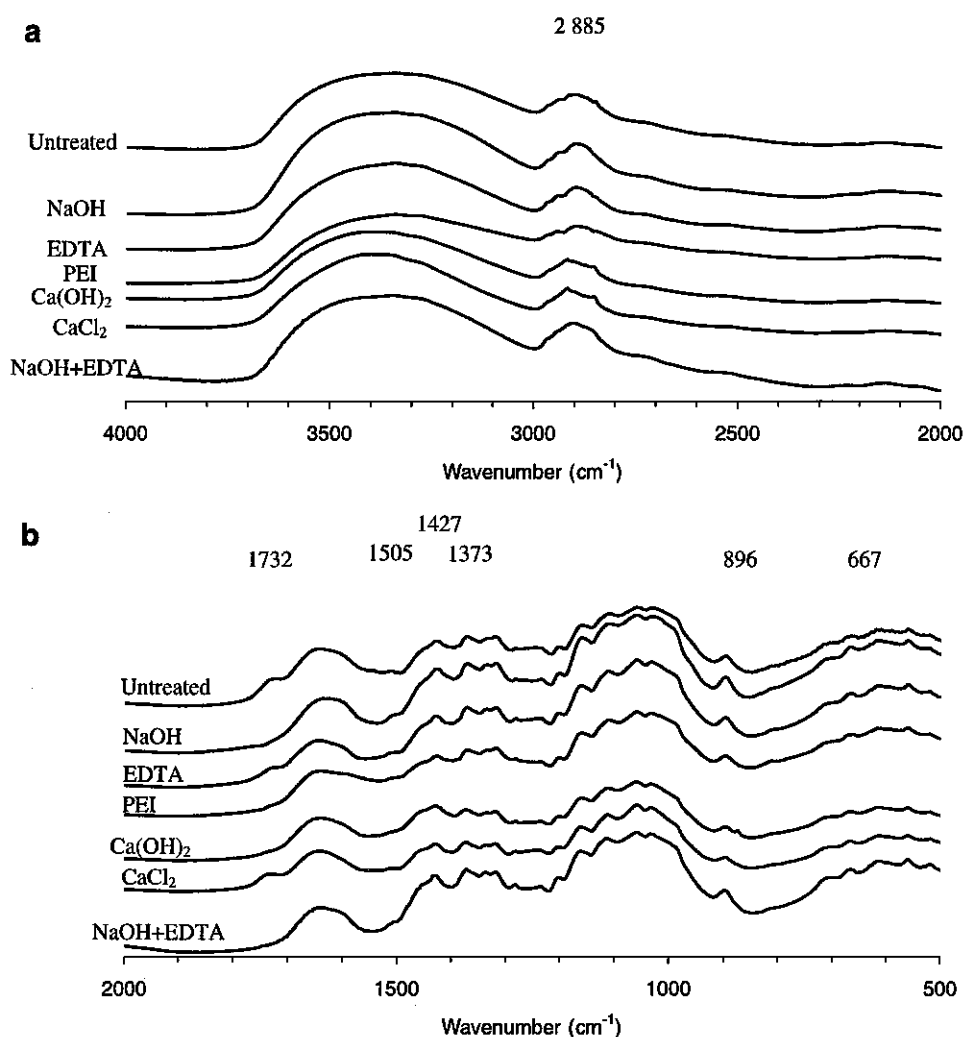


Fig. 5. FTIR spectra of untreated and treated hemp fibres bundles: (a) 4000–2000 cm^{-1} ; (b) 2000–400 cm^{-1} .

the ratio of the peaks areas at 1373 and 670 cm^{-1} as IR index for the lattice transformation cellulose I to cellulose II. Table 3 presents the correlation between the crystallinity index value calculated from XRD data and FTIR measurements. These results show that best correlation is obtained when the ratio of the band at 1373 and 667 cm^{-1} is taken into account.

6. Conclusion

Based on measurements of cellulosic fibres properties with scanning electron microscopy, differential thermal analysis, X-ray diffraction and FTIR after several chemical treatments, we observed that each considered treatment has a direct action onto the fibre surface:

- Treatment with 6% NaOH cleans fibres by removing the amorphous compounds, and increases the crystallinity index of fibre bundles.

- EDTA treatment separates fibres and complex calcium ions associated with pectins.
- PEI treatment exhibits an intermediate behaviour for all studied properties.
- Lime water treatment involves a fixation of calcium ions at the surface of fibres whereas a calcium chloride treatment does not. This result shows that pH plays a role on the fixation of calcium onto the hemp fibre bundles.

Experiments are now under way to estimate the impact of these chemical treatments onto the mechanical properties of the resulting composite materials obtained from mixtures of lime and hemp fibre bundles.

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