Available online at www.sciencedirect.com

Journal of the European Ceramic Society 29 (2009) 1861–1868

www.elsevier.com/locate/jeurceramsoc

Influence of various chemical treatments on the interactions between hemp fibres and a lime matrix

Marianne Le Troëdec, Claire S. Peyratout*, Agnès Smith, Thierry Chotard

Groupe d'Etude des Matériaux Hétérogènes (GEMH, EA 3178), Ecole Nationale Supérieure de Céramique Industrielle,
47 à 73 Avenue Albert Thomas, 87065 Limoges Cedex, France

Received 1 July 2008; received in revised form 18 November 2008; accepted 24 November 2008
Available online 19 January 2009

Abstract

In this paper, results presented concern both the chemical and physical behaviours of hemp fibres in lime-based mineral matrix in order to better understand the role of chemical modifications of cellulosic fibres in the evolution of the macroscopic properties, essentially mechanical ones, of such composite materials. The role of fibres surface treatment has been also studied through various chemical treatments applied on hemp fibres. In a first step, the influence of such treatments on the fibre characteristics has been investigated by several means, such as scanning electron microscopy, thermal analysis, X-ray diffraction and FTIR spectroscopy, in order to evaluate their consequences on the fibre behaviour itself. Secondly, an attempt to characterise the influence of the various chemical treatments of fibres on the mechanical behaviour of hemp reinforced lime-based composites has been completed by a three points bending testing campaign. According to the results, it seems that the modifications induced by specific chemical treatments (EDTA, NaOH) on fibres play a major role in the strengthening of the lime/fibres interface but also in the improvement of the overall stiffness of the composite (with respect to the one reinforced by untreated fibres) most probably related to a specific stiffening process of the fibre itself.

Keywords: Fibres; Composites; Interfaces; Mechanical properties

1. Introduction

Lime-based mortars have been used for centuries as stone binders in ancient buildings. During the 20th century, the use of lime in construction disappeared due to the fast development of Portland cement.[1] Nevertheless, over the past several decades, the need to develop environmental-friendly products has generated new interest in using lime as a building material.

Many studies on lime-based mortar were carried out in order to understand the influence of various parameters, like viscosity, pore structure, capillary porosity and water/lime ratio, in particular on the mechanical properties of resulting mortars.[2–5] To date, no investigation of the incorporation of natural fibres in a lime matrix were reported, although natural fibres were introduced in polymers or cement matrices and are known to improve mechanical properties of mortars.[6–8]

The use of natural fibres and in particular hemp fibres as reinforcing agents in composite materials offers many advantages over glass fibres, such as low density and biodegradability.[6,9,10] However, their incorporation in a polymer or mineral matrix can involve an interface incompatibility between fibres and matrix which may be overcome with fibres chemical pretreatments.[11–13] Each treatment considered in this publication modifies either the chemical nature of the surface of natural fibres, or the surface state (e.g., charge, conformation of polymers). The consequence is probably a modification of the interactions between the mineral matrix and fibres. For example, treatment with sodium hydroxide removes amorphous materials, such as hemicelluloses, lignins and pectins, from the hemp fibres surface, and this in turn would probably increase the crystallinity index of fibres.[13–15]

The adsorption in large quantity of calcium ions on fibres surface can influence the fibre/matrix interface.[16] To check the impact of the calcium adsorption, two approaches were selected. In a first treatment, fibres were treated with acid ethylene-diamine-tetracetic (EDTA) which forms with calcium ions a very stable complex and disturb the complex formed between pectins

---

* Corresponding authors.
E-mail addresses: claire.peyratout@unilim.fr (C.S. Peyratout), agnes.smith@unilim.fr (A. Smith), thierry.chotard@unilim.fr (T. Chotard).

0955-2219/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2008.11.016

and calcium ions.[17] This treatment would prevent the fixing of calcium ions on the surface of fibres. The second treatment consists in modifying the negative charge surface of fibres using a cationic polyelectrolyte, polyethylene imine (PEI), in order to prevent the fixation of calcium ions.[18] Lastly, a lime water solution was used to test the influence of pH in calcium ions adsorption.[19]

The aim of this work is to determine the influence of these different chemical treatments of hemp fibres on the mechanical properties (flexural strength and stiffness) of a composite material including fibres in a lime matrix.

2. Experimental

2.1. Materials

2.1.1. Fibre treatments

Technical hemp fibres (*Cannabis sativa L.*) were grown by the company Agrofibra (Barcelona, Spain). Their chemical composition was determined using an extraction procedure.[16–20,21] The fibres contain in massic percentage 58.7% of cellulose, 16.8% of pectins, 14.2% of hemicelluloses, 6% of lignins and 4.3% of waxes. 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.

In order to modify the adhesion between fibres and the mineral matrix, fibres were subjected to several surface treatments:

- *Alkalization*: Dried fibres were soaked in 6 vol.% NaOH (Prolabo, Fontenay-sous-Bois, France) solution during 48 h and then neutralized with 1 vol.% acetic acid solution. Fibres were then washed with deionised water until the pH value was 7.
- *EDTA*: Fibres were immerged during 3 h in a solution of EDTA (5 g/l, Sigma–Aldrich, Seeze, Germany) 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 at room temperature.
- *PEI*: Fibres were soaked in a PEI (M.W.: 2000 g mol^{-1}, pH 12, Sigma–Aldrich, Seeze, Germany) solution for 48 h at room temperature, then washed with deionised water.
- *$Ca(OH)_2$*: In order to saturate fibres with calcium ions, fibres were placed for 3 h in a saturated lime solution ($[Ca^{2+}] = 2 \times 10^{-2}$ M, pH 12.7, Merck, Darmstadt, Germany). Following the impregnation, fibres were washed with deionised water.

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

2.1.2. Lime matrix

Natural hydraulic lime (NHL5 formula, Chaux et Enduits de Saint-Astier, Saint-Astier France), was packed upon reception in airtight containers, and was kept during the experiment at constant hygrometry and temperature (20 °C).

2.1.3. Samples elaboration

Prior to paste preparation, the fibres were shortening to about 2 cm long and separated in a laboratory blender (Waring Laboratory, Torrington, USA). The final fibre length ranged between 1 mm and 1 cm. This shortening was necessary to obtain a homogeneous distribution of the fibres in the cement paste. In order to prepare a mix, the pre-cut fibres were introduced in lime, mixed for 2 min in a blender (Perrier Labotest, type 32, France) and water was finally added. In all cases, the Water over Lime mass ratio (W/C) was equal to 0.62.

2.2. Characterisation techniques

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 coverage with a platinum film.

Differential thermal analysis (DTA) measurements on unmodified and modified fibres were performed under dry air nitrogen atmosphere using a Setsys 2400 instrument (SETARAM). Temperature ranged from 25 to 800 °C with a heating rate of 5 °C min^{-1}.

Infrared spectroscopy (FTIR) were performed using a Perkin Elmer spectrometer (Spectrum one, Boston, U.S.A.) using the standard potassium bromide (KBr) pellet technique. A total of 10 scans was taken for each sample between 500 and 4000 cm^{-1}, with a resolution of 4 cm^{-1}. Fibres were chopped roughly to a length of less than 1 mm, mixed with 300 mg of KBr and then pressed into a pellet ($\phi = 16$ mm) for measurements.

The flexural strength of the composite before and after chemical treatments of the fibres were determined using a three-point bending test method (EZ 20 Lloyd Instrument, AMETEK) on 40 mm × 40 mm × 160 mm prisms. The crosshead speed applied was 0.1 mm/min. Each sample was loaded until the core broke and the average over 10 measurements is reported.

3. Results and discussion

3.1. Impact of chemical treatments on fibres

3.1.1. Surface morphology

Scanning electron microscopy provides an excellent technique for examination of surface morphology of natural and treated fibres.[17]

Micrographs of untreated fibres, such as the one presented in Fig. 1a indicates the presence of impurities on surface, mostly waxes and oil. However, after alkali or PEI treatment, as presented in Fig. 1b and d, a surface free of impurities is obtained. Observation of micrographs obtained after the EDTA treatment (Fig. 1c) seemed to separate the fibres. On the contrary, a lime treatment tends to saturate the surface with calcium nodules, as reported by Sedan et al. (Fig. 1e).[19]

3.1.2. Thermal analysis of fibres

Thermal analysis was performed to determine the moisture content and the amount of volatile components present in fibres

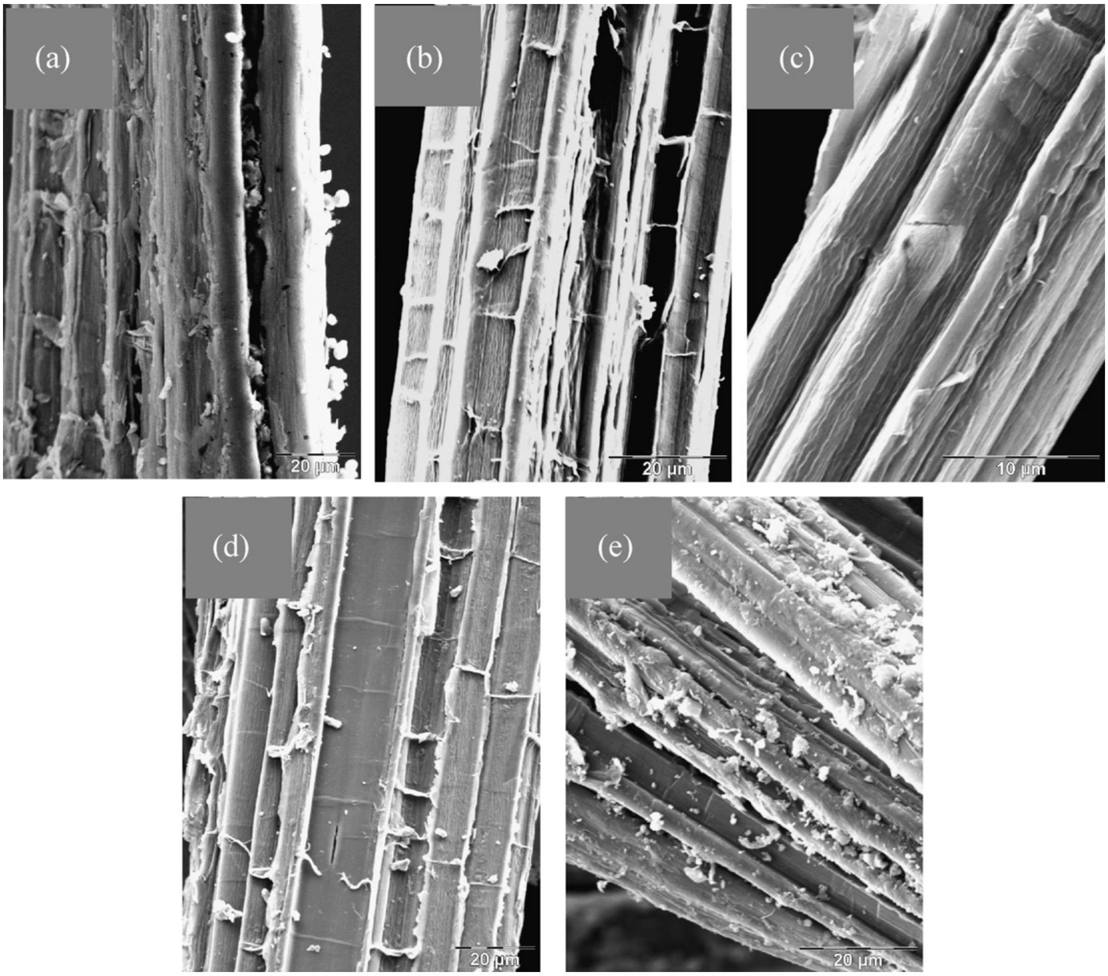

Fig. 1. SEM images of (a) untreated, (b) NaOH, (c) EDTA, (d) PEI and (e) $Ca(OH)_2$ treated hemp fibres.

under inert atmosphere and in air, and to see if surface modifications had an impact on the thermal properties of the fibres.

When measurements were conducted in air, independently of chemical treatments, differential thermal analysis curves show a first endothermic peak between temperature of 50 and 175 °C, which is caused by the evaporation of adsorbed moisture and physisorbed water. The content of water was evaluated with DTA to 7% mass. Since the fibres were dried prior to use at a temperature of 40 °C, there is some moisture which is retained into the fibres.

Under air, the DTA curve of untreated natural fibres, presented in Fig. 2a, presents three exothermic reactions: a first peak located between 240 and 340 °C is attributed to the thermal depolymerisation of hemicelluloses and pectins. An exothermic signal between 390 and 420 °C is attributed to the cellulose decomposition. Finally, a last peak at higher temperatures corresponds to the decomposition of charred residues.[22] However, the interpretation of DTA measurements of composite cellulosic materials is complicated by the decomposition over the whole temperature range (280–500 °C) of lignin residues. In fact, the decomposition of cellulose is endothermic.[23] The decomposition of lignin is strongly exothermic and affect the signal attributed to cellulose decomposition.

Treatments with caustic soda and lime saturated solution shift the first peak to higher temperatures, 335 and 355 °C, respectively. This result implies that after treatments in a strongly basic medium, modified hemp fibres are thermally more stable than untreated ones.

The peak characteristics of cellulose decomposition is shifted at higher temperatures with caustic soda (≈410 °C) and PEI (≈450 °C) treatments, whereas EDTA and a saturated lime solution treatments decrease the initial temperature of decomposition of cellulose by 10 and 20 °C, respectively. However, under argon, where the oxidation of the charred residues is suppressed, this phenomenon is not observed (Fig. 2b). Thus, the effect observed under air is a result of the combination of lignin degradation and oxidation of some residues. Based on the data obtained under inert atmosphere, we can conclude that the position of the cellulose decomposition peak is barely affected by the treatments. This means that all treatments applied do not modify the structure of natural cellulose and probably only affect the outside of the fibres, as show on the different micrographs (Fig. 1). Nonetheless, NaOH treatment preferentially degrades amorphous polysaccharides, leaving crystalline and heat-resistant cellulose molecules behind.[9,11–13]

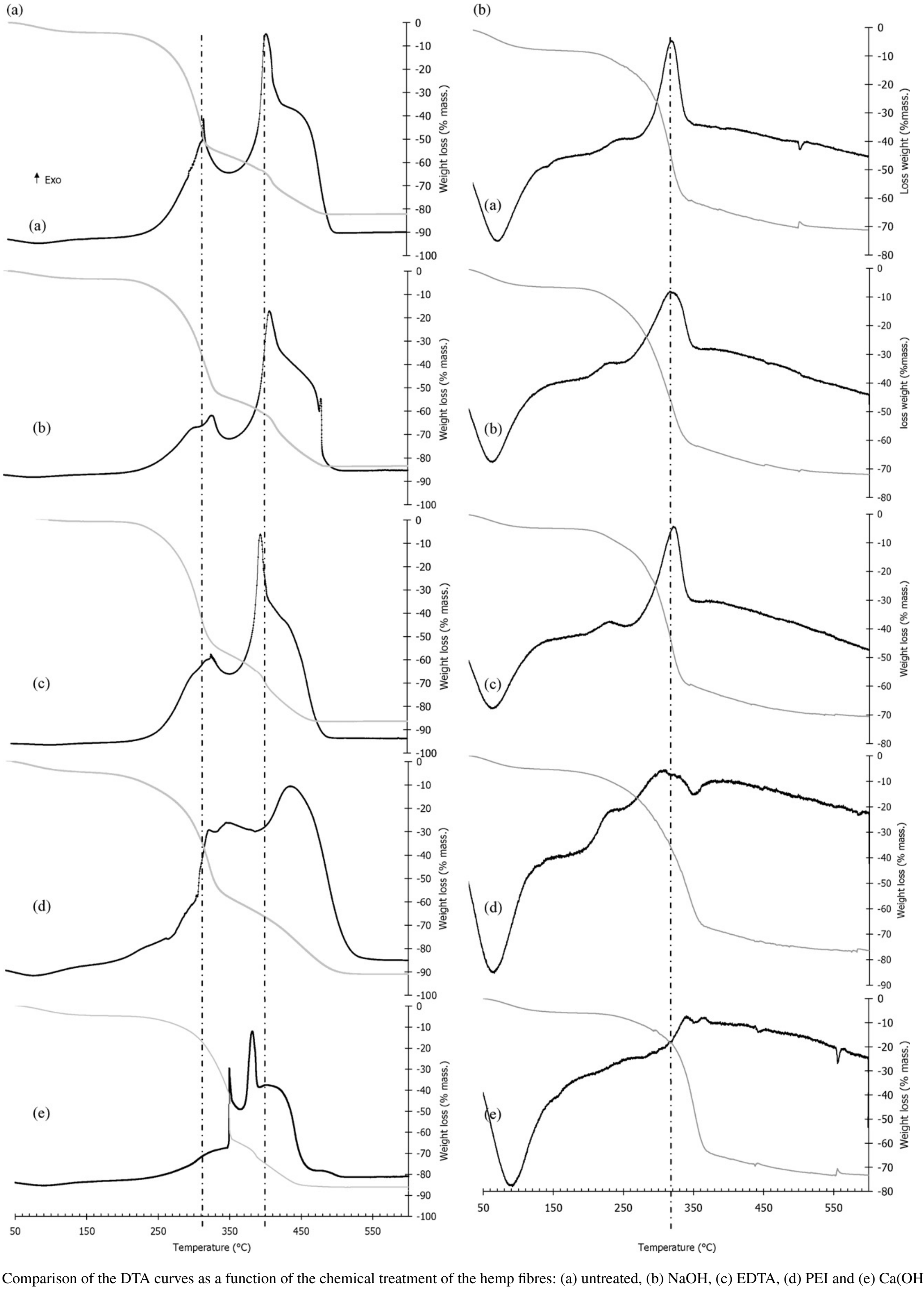

Fig. 2. Comparison of the DTA curves as a function of the chemical treatment of the hemp fibres: (a) untreated, (b) NaOH, (c) EDTA, (d) PEI and (e) $Ca(OH)_2$.

Table 1
Principal infrared transitions for hemp fibre.

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	Xylans (hemicelluloses)
1650–1630	OH (water)	Water
1505	C=C aromatic symmetrical stretching	Lignin
1425	CH_2 symmetrical 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	Polysaccharides
670	C–OH out-of-plane bending	Cellulose

3.1.3. Fourier transform infrared spectroscopy

FTIR allows the measurement of variations of hemp fibre composition after chemical treatments. Table 1 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. 3. Modifications in the FTIR spectra are principally observed in the 500–4000 cm^{-1} range. One of the most noticeable modification generated by NaOH, $Ca(OH)_2$ and PEI treatments is the disappearance of the peak centered at 1732 cm^{-1}, characteristic of hemicelluloses. Indeed, treatments with lime water, PEI and NaOH, are known to remove hemicelluloses.[24] EDTA treatment does not affect hemicelluloses. 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 fibres. With caustic soda treatment, the intensity of the peak characteristic of waxes and oils present at 2850 cm^{-1} decreases whereas the

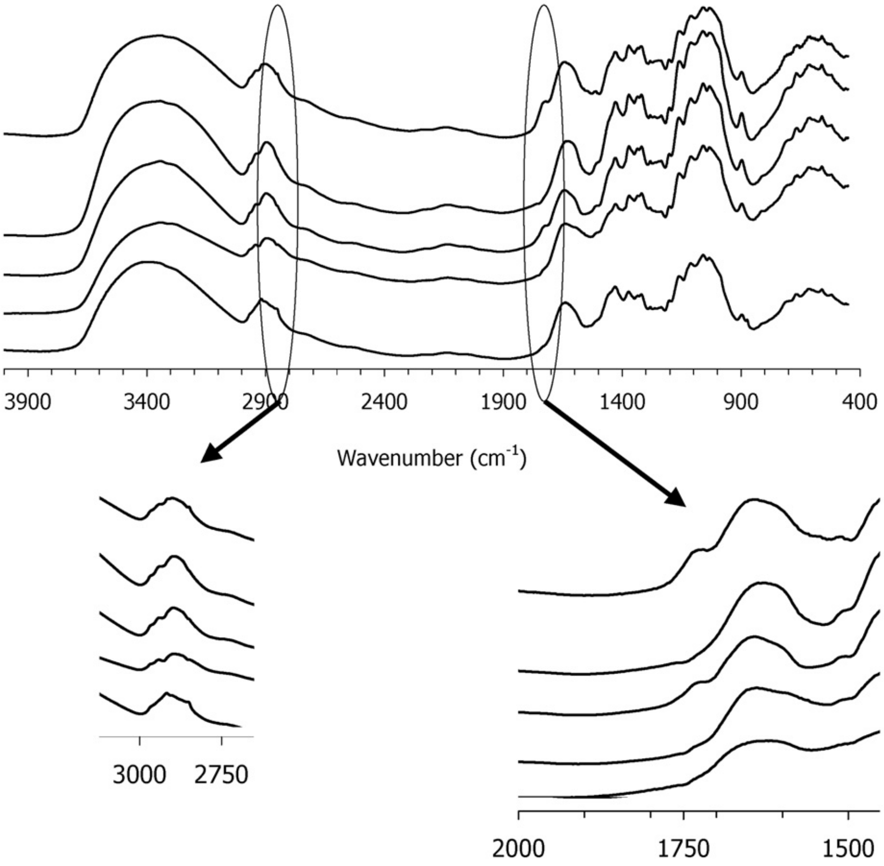

Fig. 3. FTIR spectra (4000–2000 cm^{-1}) of (a) untreated, (b) NaOH, (c) EDTA, (d) PEI and (e) $Ca(OH)_2$ treated hemp fibres.

intensity of the peak characteristic of polysaccharides hydroxyl bonds and located near 3300 cm^{-1} increases (Fig. 3).

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

Some authors differentiate the peaks associated to pectins[24]:

- 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 analyze the percentage of calcium pectates, it would be necessary to first completely remove the water molecules from hemp fibres.

3.2. Influence of the chemical treatments of fibres on mechanical properties of composites

3.2.1. Behaviour analysis

Fig. 4a represents the typical evolution of the force applied versus displacement for a pure lime sample and for 10 vol.% fibres content one.

The addition of hemp fibres into the lime matrix, modifies significantly the mechanical behaviour of the sample. In contrast to the linear brittle behaviour observed for the pure lime sample, a more non-linear and pseudo-ductile behaviour is noticed for the composite sample after the first drop of load. We can also observe a controlled load decrease after that the maximum were reached. In this figure, we can distinct three main domains and two characteristic points.

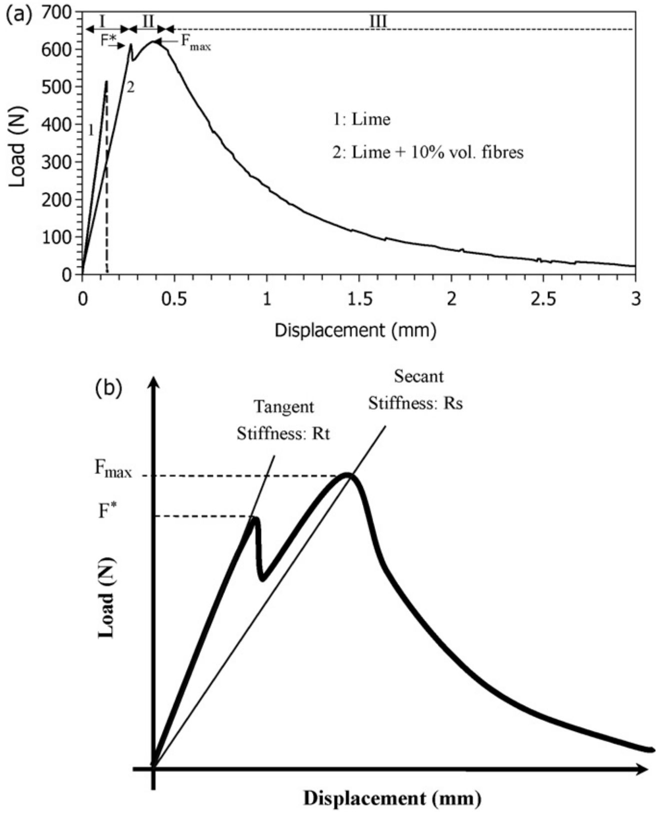

Fig. 4. (a) Load versus displacement curves (three point bending test) and (b) experimental stiffness.

The critical load F^*, which can be considered probably as the initial pull-out debonding force, and the peak load $F_{\max}$, which can be interpreted as the highest failure force (closely related to the pull-out failure force).

In domain I [from 0 to F^*], the material exhibits a linear evolution of the load versus displacement curve. In this step, it seems that the lime matrix is supporting the main part of the applied load due to an efficient load transfer process (from fibres to matrix).

Domain II [from F^* to $F_{\max}$], corresponds to a significant change in the mechanical behaviour of the composite. Indeed, after a noticeable drop of the load at F^*, most probably associated to the beginning of the macroscopic damage related itself with the onset of an internal fibre pull-out process, the behaviour evolves to a more non linear behaviour up to $F_{\max}$. In a fibre pull-out process, the applied load is transferred and distributed along the fibre/matrix interface and causes interfacial failure which can induce this increase of the non-linear character of the evolution due to a controlled phase of the crack propagation. In this domain, the efficiency of the load transfer process is significantly reduced.

After the peak load $F_{\max}$ (Domain III), the mechanical behaviour is totally different than the one observed for the lime sample. This part is very interesting because it reveals the change in behaviour mostly due to the presence of fibres in the composite. Indeed, no sudden failure is observed but a continuous fall of the load is recorded. This behaviour underlines the major role of the debonding process on the ruin of the material.

3.2.2. Quantitative analysis

Several characteristics have been extracted from the experimental stress displacement curves and experimental stiffness has been calculated as depicted in Fig. 4b. The tangent stiffness (Rt) is obtained by calculating the slope from the origin up to F^*, and the secant stiffness (Rs) corresponds to the slope between the origin and $F_{\max}$. All these parameters have been summarised in Table 2

Firstly, and regardless of treatment, the adding of hemp fibres increases by about 23% the stress average compared to lime samples prepared without fibres. Concerning the stiffness, we observe that the incorporation of hemp fibres affects the stiffness of mortars compared to a lime matrix sample. Interestingly, fibre treatment enhances the stiffness of the composites compared to the composite with untreated fibres. Introduction of hemp fibres into a lime matrix:

- modifies the behaviour of materials, which evolves from a fragile to a non linear one representing associated to the occurrence and the propagation of damage within the material,

Table 2
Influence of chemical treatments on the results obtained in three-point bending test.

Type of fibres contained in the lime mortar	Maximum stress (MPa) ± scattering	Displacement at maximum stress (mm) ± scattering	Experimental stiffness (kN/mm)		(Rt − Rs)/Rt (%)
			Tangent stiffness, Rt	Secant stiffness, Rs	
No fibres	1.54 ± 0.14	0.16 ± 0.01	3.86	3.86	0.0
Untreated fibres	1.89 ± 0.23	0.65 ± 0.15	1.09	0.92	15.6
NaOH treated fibres	1.92 ± 0.16	0.29 ± 0.02	2.59	2.05	20.8
EDTA treated fibres	2.01 ± 0.05	0.40 ± 0.08	1.67	1.61	3.6
PEI treated fibres	1.95 ± 0.22	0.48 ± 0.11	1.51	1.30	13.9
$Ca(OH)_2$ treated fibres	1.43 ± 0.21	0.42 ± 0.15	1.32	1.25	5.3

- increases the maximum stress average by 23% but globally decreases the stiffness values compared with a lime matrix sample.

Concerning chemical treatments of fibres, it seems that these treatments do not modify the global mechanical behaviour of the composite.

If we focus now on the values extracted from Table 2 and compared with the ones taken from a untreated fibres composite (Maximum stress, displacement at maximum stress, Rt, Rs and the loss of stiffness expressed by (Rt − Rs/Rt)), some interesting remarks can be done:

Chemical treatments result globally in an increase of the experimental stiffness values, associated with a decrease of the displacement at maximum stress. For example, NaOH treated fibres composite exhibit the highest tangent stiffness (Rt = 2.59 kN/mm) associated with the lowest value of the displacement at maximum stress (0.29 mm). In the same way, and excepted for the $Ca(OH)_2$ fibre treatment, all the value of the maximum stress for all sample (included untreated fibres sample) are relatively close. As already noticed, one treatment has a completely different effect on the maximum stress value, the $Ca(OH)_2$ pre-treatment diminishes the maximum stress values comparable to what is obtained in a pure lime matrix, even if the behaviour is composite like one.

If now, we look at the evolution of the loss of stiffness calculated with (Rt − Rs)/Rt, expressed as a percentage, it appears that the lowest value of this parameter (logically associated with a quiet good interface resistance quality) is observed for the EDTA treatment (3.6) and the highest one (associated to a poor quality of the interfacial resistance) is obtained for the alkali treatment (20.8). If we compare simultaneously the values of the displacement at maximum stress and the loss of stiffness for these two last chemical treatments (EDTA and NaOH), one can easily see that, for a same value of maximum stress (2.01 MPa for EDTA treatment and 1.92 for NaOH treatment) the EDTA treated fibre composite sample exhibits a higher level of displacement and a lower level of loss reduction. This observation is relatively important because it tends to demonstrate that the EDTA treatment has a more efficient contribution on the fibre-matrix interfacial resistance tha the NaOH one.

4. Conclusion

The objective of this work was to explore the potentialities of reinforcement of a lime mineral matrix with hemp fibres by improving the interface adhesion using various chemical treatments. Chemical exchanges between lime and fibres, in term of degradation of fibres structure with alkaline medium and effects of compounds present in fibres are modified by the chemical treatments carried out. Indeed, each treatment has a direct action on fibres surface:

- Treatment with caustic soda cleans fibres, removing the amorphous compounds, which improve the stress average and the rupture as well as the stiffness of mortars compared with mortar containing untreated fibres, and has a slight effect on the interface between fibres and matrix.
- EDTA treatment increases stress rupture of mortars, however this chemical treatment involves a diminution of the amount of calcium adsorbed on the fibres surface. Calcium present on the surface has an impact on the stress rupture of the composites. Perhaps this phenomenon is due to the fact that EDTA, a strong calcium complexant, destroys the pectin/calcium complex present on the surface of fibres to form a gel, which can improve the interface between fibres and matrix.
- PEI treatment involves an intermediate behaviour of all the studied properties, but its effect on mechanical properties is not as significant as EDTA.
- Lime water treatment modifies only the stiffness of mortars and has a limited impact on the stress average values.

Acknowledgements

The authors are grateful to the Region Limousin for financial support of Marianne Le Troëdec Ph'D. The authors want also to specially thank the referee for his remarks, which help them to improve the quality of this paper.

References

1. Sédaïbi, Y., Dheilly, R. M. and Quéneudec, M., A study of the viscosity of lime-cement paste: influence of the physico-chemical characteristics of lime. *Construction and Building Materials*, 2004, **18**, 653–660.

2. Arandigoyen, M., Perez Bernal, J. L., Bello Lopez, M. A. and Alvarez, J. I., Lime-pastes with different kneading water: pore structure and capillary porosity. *Applied Surface Science*, 2005, **252**, 1449–1459.
3. Sédaïbi, Y., Dheilly, R. M. and Quéneudec, M., Study of the water-retention capacity of a lime-sand mortar: influence of the physicochemical characteristics of the lime. *Cement and Concrete Research*, 2003, **33**, 689–696.
4. Stefanidou, M. and Papayianni, I., The role of aggregates on the structure and properties of lime mortars. *Cement and Concrete Composites*, 2005, **27**, 914–919.
5. Lanas, J., Pérez Bernal, J. L., Bello, M. A. and Alvarez Galindo, J. I., Mechanical properties of natural hydraulic lime-based mortars. *Cement and Concrete Research*, 2004, **34**, 2191–2201.
6. Li, Z., Wang, X. and Wang, L., Properties of hemp reinforced concrete composites. *Composites: Part A*, 2006, **37**, 497–505.
7. Mac Vicar, R., Matuana, L. M. and Balatinecz, J. J., Aging mechanisms in cellulose fiber reinforced cement composites. *Cement and Concrete Composites*, 1999, **21**, 189–196.
8. Toledo Filho, R. D., Joseph, K., Ghavami, K. and England, G. L., The use of sisal fibre as reinforcement in cement based composites. *Revista Brasileira de Engenharia Agricola e Ambiental*, 1999, **3**, 245–256.
9. Mwaikambo, L. Y. and Ansell, M. P., Hemp fibres reinforced cashew nut shell liquid composites. *Composites science and technology*, 2003, **63**, 1297–1305.
10. Joshi, S. V., Drzal, L. T., Mohanty, A. K. and Arora, S., Are natural fibres composites environmentally superior to glass fibres reinforced composites? *Composites: Part A*, 2004, **35**, 371–376.
11. Bledzki, A. K. and Gassan, J., Composites reinforced with cellulose based fibres. *Progress in Polymer Science*, 1999, **24**, 221–274.
12. Valadez-Gonzalez, A., Cervantes-Uc, J. M., Olayo, R. and Herrera Franco, P. J., Effect of fibres surface treatment on the fibres-matrix bond strength of natural fibres reinforced composites. *Composites: Part B*, 1999, **30**, 309–320.
13. Knill, C. J. and Kennedy, J. F., Degradation of cellulose under alkaline conditions. *Carbohydrate Polymers*, 2003, **51**, 281–300.
14. Zhang, W., Okubayashi, S. and Bechtold, T., Fibrillation of cellulosic fibres-Part 4. Effects of alkali pre-treatment of various cellulosic fibres. *Carbohydrate Polymers*, 2005, **61**, 427–433.
15. Mwaikambo, L. and Ansell, M., Chemical modification of hemp, sisal, jute and kapok fibres by alkalisation. *Applied Polymer Science*, 2002, **84**, 2222–2234.
16. Sedan, D., Pagnoux, C., Chotard, T., Smith, A., Lajolly, D., Gloaguen, V. and Krausz, P., Reactivity of hemp fibres in calcium rich and alkaline solutions. *Journal of Material Science*, 2008, **42**, 9336–9342.
17. Stuart, T., Liu, Q., Hugues, M., McCall, R. D., Sharma, H. S. S. and Norton, A., Structural biocomposites from flax – Part 1: Effect of bio-technical fibre modification on composite properties. *Composites: Part A: Applied science and manufacturing*, 2005, 1–12.
18. Ramos-Tejeda, M. M., Ontiveros-Ortega, A., Giménez-Martin, E., Espinosa-Jimenez, M. and Molina Diaz, A., Effect of polyethyleneimine ion on the sorption of a reactive dye Leacril fabric: electrokinetic properties and surface free energy of the system. *Journal of Colloid and Interface Science*, 2006, **297**, 317–321.
19. Sedan, D., Pagnoux, C., Smith, A. and Chotard, T., Mechanical properties of hemp fibre reinforced cement: influence of the fibre/matrix interaction. *Journal of European Ceramic*, 2008, **28**, 182–183.
20. Adams, G. A., Arabinoglucuronoxylan, arabinoxylan, and xylan; purification using a copper complex and purification by fractional precipitation of acetates. *Carbohydrate Chemistry, New York*, 1965, **5**, 170–175.
21. Bailey, R. W., Quantitative studies of ruminant digestion, II, Loss of ingested plant carbohydrates from the reticulo-rumen. *New Zealand Journal of Agricultural Research*, 1967, **10**(1), 15–32.
22. Ouajai, S. and Shanks, R. A., Composition, structure and thermal degradation of hemp cellulose after chemical treatments. *Polymer Degradation and Stability*, 2005, **89**, 327–335.
23. Yang, H., Yan, R., Chen, H., Lee, D. H. and Zheng, C., Characteristics of hemicellulose, cellulose and lignin pyrolysis. *Fuel*, 2007, **86**, 1781–1788.
24. Himmelsbach, D. S., Khalili, S. and Akin, D. E., The use of FT-IR microspectroscopic mapping to study the effects of enzymatic retting of flax stems. *Journal of the science of food and agriculture*, 2002, **82**, 685–696.