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Effect of drying and rewetting cycles on the structure and physicochemical characteristics of softwood fibres for reinforcement of cementitious composites

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ABSTRACT

The changes produced in cellulosic fibres when they are subjected to successive drying and rewetting cycles could have an important impact on the resistance and durability of cement mortar composites based on these fibres. In this paper, unbleached, oxygen delignificated, semi-bleached, and fully bleached softwood pulps have been subjected to drying and rewetting cycles and the corresponding dried pulps characterized. The morphological structures and thermal stabilities were investigated with X-ray diffraction and thermogravimetric analysis. While the water retention values decrease significantly with drying and rewetting cycles, an overall increase in the crystallinity index and in the thermal stability was found in the hornificated pulps. Natural fibres from cotton linters were also studied and the results compared with the fibres from these softwood pulps.

1. Introduction

Early research which focused on replacing asbestos fibres with other fibres with low prices and good performance in cementitious composites were motivated by the lack of availability of these mineral fibres during the Second World War. In later years, as a result of the banning of the use of asbestos in most developed countries, many companies began to replace these mineral fibres with natural ones of vegetable origin. Despite the fact that these cellulosic fibres provide lower resistance than asbestos fibres do, they are sufficiently resistant for use in building materials.

Besides ecological and sustainability considerations, natural fibres are cheaper and bring to cement or mortar cement matrixes resistance, low thermal conductivity (Balaguru & Shah, 1992), and better resistance to fire (De la Fuente, 2007), among other benefits. In particular, softwood fibres from chemical pulps have great potential as cellulosic reinforcement because of their availability and low price. Nevertheless, the use of these cellulosic fibres in vegetable fibre reinforced cement composites (VFRC) is hampered by their low durability and poor adhesion (MacVicar, Matuama, & Balatinecz, 1999; Savastano, Warden, & Coutts, 2001; Tolêdo Filho, Scrivener, England, & Ghavami, 2000), which in recent years has led to the replacement of these fibres by synthetic ones such as polypropylene, polyethylene, and glass, among others. For this reason, in order to improve the durability of the VFRC, recent researches have focused on analysing fibre matrix interactions. The lack of durability of VFRC is mainly caused by the presence of calcium hydroxide on the matrix, which degrades the fibres, and by changes in the environmental moisture, which induce dimensional changes in the vegetable fibres (Tolêdo Filho et al., 2000).

It is well known that drying and rewetting cycles principally cause shrinkage of the natural fibres due to the formation of hydrogen bonds in cellulose. This irreversible effect (Jayme, 1944; Page & Tydeman, 1963; Weise & Paulapuro, 1999), known as "hornification" and quantified as the percentage reduction in water retention values (WRV), occurs in the cell wall matrix of the fibres, resulting in intensely bonded structures (Ackermann, Göttsching, & Pakarinen, 2000). The reduction in the WRV of the hornificated fibres could have beneficial effects on VFRC. On one hand, the hornificated fibres will have higher dimensional stability (Garcia-Hortal, 2007), and thus higher fibre–matrix adherence is expected. On the other hand, as a consequence of the lower WRV of these hornificated fibres, a reduction in the formation of incrustations of calcium hydroxide on the surface and lumen of the fibres and consequently a reduction in the degradation of the cellulose in the cementitious matrix are expected. Taking this into account, it is of practical significance to understand and predict the effects of drying and rewetting cycles on the structure and physicochemical characteristics of vegetable fibres in order to analyse the potential use of hornificated fibres in improving fibre–matrix adhesion and durability of VFRC.

In this study, we analyse the effects of the irreversible drying and rewetting cycles on the morphology, composition, and

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structure of four chemical pulps from softwood with differences in the percentage of lignin. The results are compared with those for natural fibres from cotton linters.

2. Experimental procedure

2.1. Pulp treatment

Unbleached softwood kraft pulp (*Pinus insignis*) was supplied by Smurfit Kappa Nervión, S.A. (Spain). In order to obtain pulps with different percentages of lignin, the unbleached pulp was subjected to an *Elemental Chlorine Free* (ECF) bleaching sequence.

Table 1 shows the conditions of the bleaching process. The samples characterized were the unbleached pulp (U), the oxygen delignificated pulp (O), the semi-bleached pulp (OD), and the fully bleached pulp (OD(EP)D).

Cotton linters were supplied by Celsur (Cotton South, S.L., Spain).

The softwood pulps and the cotton linters were subjected to four drying and rewetting cycles and the resulting pulps characterized. The sequence of the drying and rewetting cycles was as follows: (1) Drying in an oven with air recirculation at 60 °C for 7 h; (2) rewetting by soaking overnight; (3) disintegration of the wet pulp for 30,000 revolutions (ISO 5263-1:2004); and (4) Filtration of the pulp suspension through a Buchner funnel equipped with a wire screen (150 mesh). The first filtrate was recirculated during the pad formation with the objective of retaining pulp fines.

2.2. Characterization of the fibres

2.2.1. Chemical analysis

The Kappa number (*K*) was determined by the TAPPI test method (TAPPI 236 cm-85, 1994) three times. *K* is defined as the volume in mL of 0.02 M potassium permanganate that is consumed by one gram of moisture-free pulp under specific conditions.

The Lignin content was calculated as (Data Sheet D-6, Canadian Pulp and Paper Association):

$$\text{Lignin}(\%) = 0.147 \times K \quad (1)$$

2.2.2. Water retention value (WRV)

The WRV was determined by centrifugation according to ISO 23714:2007 (“Pulps. Determination of Water Retention Value”).

2.2.3. Morphology

The fibres’ morphology was characterized using a Jeol-820 scanning electron microscope (SEM).

Table 1
Conditions of the ECF bleaching sequence.

Conditions	O[a]	D[b]	EP[c]	D_2[d]
t (min)	60	60	90	120
T (°C)	110	70	70	70
Consistency (%)	10	7	10	7
O_2 (MPa)	0.6			
ClO_2 (% as active chlorine)		9		2.63
H_2O_2 (% o.d.p.[e])			1.5	
NaOH (% o.d.p.)	2		4	
DTPA (% o.d.p.)				
$MgSO_4$ (% o.d.p.)	0.5		0.2	

[a] Oxygen delignification.
[b] Chlorine dioxide delignification.
[c] Alkaline extraction with addition of hydrogen peroxide delignification.
[d] Second oxidation with chlorine dioxide delignification.
[e] Oven dry pulp.

2.2.4. Viscosity measurements

Viscosity was measured according to ISO 5351-1:2004 (TAPPI T 230, 1994) using cupriethylenediamine (CED) as a solvent and a Schott capillary viscometer.

2.2.5. Fibre dimensions

The length, width, lineal mass (coarseness), and curl index were measured on a Kajaani FS300 Analyzer according to ISO 16065-1 (“Pulps. Determination of Fibre Length by Automated Optical Analysis. Part 1. Polarized Light Method”). The measures were performed on more than 10,000 fibres.

2.2.6. X-ray diffractometry

X-ray diffraction (XRD) was performed using a Siemens D-500 diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm) operating at 40 kV and 30 mA. The crystalline-to-amorphous ratio of samples was determined using the empirical procedure first proposed by Segal, Creely, and Conrad (1959). This method consists of estimating the crystallinity index for the Cellulose I (Cr.I.) according to the following equation:

$$\text{Cr.I. } (\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \quad (2)$$

where I_{002} is the maximum intensity (in arbitrary units) of the diffraction from the (0 0 2) plane at $2\theta = 22.6°$ and I_{am} is the intensity of the background scatter measured at $2\theta = 16°$.

2.2.7. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851[e] using Mettler Toledo Star SW 7.01 software. Samples weighing about 5.5 mg were heated in the temperature range from 25 to 600 °C with a heating rate of 20 °C/min under a nitrogen atmosphere (60 mL/min).

3. Results and discussion

3.1. Physicochemical characterization

Due to its complex chemical structure, the direct measurement of the residual lignin in chemical pulps in the processes of pulping and bleaching is difficult. Usually it is estimated from the Kappa number, measured with a titration with potassium permanganate in acidic medium. Nevertheless, depending on the vegetal species and the processes of pulping and bleaching, there are different factor values to relate the Kappa number and the percentage of lignin. In our case, the factor used was 0.147, which is commonly used in unbleached chemical pulps as well as in pulps after oxygen delignification and other types of pre-bleaching stages.

The values obtained for the pulps under study are presented in Table 2. As expected the percentage of lignin decreases with the sequence of the bleaching process.

The phenomenon hornification was quantified as a percentage reduction in the WRV measured in the pulps and in the cotton linters after they were subjected to the drying and rewetting cycles. As shown in Table 3, overall, WRV decreases with the number of cycles, with this decrease being more significant in the bleached

Table 2
Lignin percentages of the softwood pulps.

	Kappa number	Lignin (%)
Unbleached (U)	53	7.8
Oxygen delignificated (O)	31	4.6
Semi-bleached (OD)	14	~2
Fully bleached OD(EP)D		~0

Table 3
Values of WRV (%) after the drying and rewetting cycles and percentages of hornification.

	Wet/dry cycles					Hornification (%)
	Initial	I	II	III	IV	
Unbleached (U)	126	112	102	97	90	28.6
Oxygen delignificated (O)	122	107	95	91	86	29.5
Semi-bleached (OD)	121	94	89	82	79	34.7
Fully bleached OD(EP)D	126	95	84	78	75	40.5
Cotton linters	–	58	54	52	50	13.8

Table 4
Variation in the viscosity with the drying and rewetting cycles.

	Viscosity (cm^3/g)				
Wet/dry cycles	Initial	I	II	III	IV
Unbleached (U)	968	945	916	902	888
Oxygen delignificated (O)	873	832	860	862	858
Semi-bleached (OD)	822	817	776	763	764
Fully bleached OD(EP)D	714	711	710	687	670
Cotton linters	–	755	741	770	779

pulps. The explanation for this phenomenon is related to the elimination of the interface lignin–hemicelluloses by the bleaching process. This interface prevents the formation of hydrogen bonds between the microfibrils during the drying process and maintains the accessibility of water. With the loss of hemicelluloses through the bleaching process, the flexible bonds between cellulose and hemicellulose are replaced by stiffer cellulose–cellulose bonds, making the accessibility of water difficult. On the other hand, because of the higher percentage of hemicelluloses in softwood fibres than in the cotton linters, the percentage of hornification was significantly lower in the linters.

Table 5
Variation in the crystallinity index with the drying and rewetting cycles.

	Crystallinity index (%)				
Wet/dry cycles	Initial	I	II	III	IV
Unbleached (U)	56.8	57.1	57.8	60.4	58.0
Oxygen delignificated (O)	67.4	68.8	68.1	68.2	67.1
Semi-bleached (OD)	66.7	67.1	68.4	69.2	72.7
Fully bleached OD(EP)D	68.2	67.5	69.3	67.9	67.2
Cotton linters	78.5	78.7	82.0	81.0	80.9

The viscosity of chemical pulps dissolved in CED solution is considered to be a measure of degradation of cellulosic material and an indication of its general strength potential. As could be seen in Table 4, the changes in the CED viscosity with the drying and rewetting cycles were insignificant. Only a slight decrease was observed in the softwood pulps.

X-ray diffractograms of the softwood pulps and cotton linters are shown in Fig. 2. Two peaks were observed for softwood pulps at around $2\theta = 16°$ and at $2\theta = 22.6°$. The approximately 16° reflection corresponds to the overlapping of the $(1\ \bar{1}\ 0)$ and $(1\ 1\ 0)$ crystallographic planes, and the peak at 22.6° corresponds to the $(0\ 0\ 2)$ plane. In cotton linters, which have a higher content of cellulose, the two peaks corresponding to the $(1\ \bar{1}\ 0)$ and $(1\ 1\ 0)$ planes could be observed around 16° (Tserki, Zafeiropoulos, Simon, & Panayiotou, 2005).

The crystallinity index (Cr.I) obtained from X-ray diffractograms for the softwood pulps and the cotton linters and its variation with the drying and rewetting cycles are shown in Table 5. As shown, the bleached softwood pulps have higher values of Cr.I. than the unbleached one (around 10% higher). Similar results were found

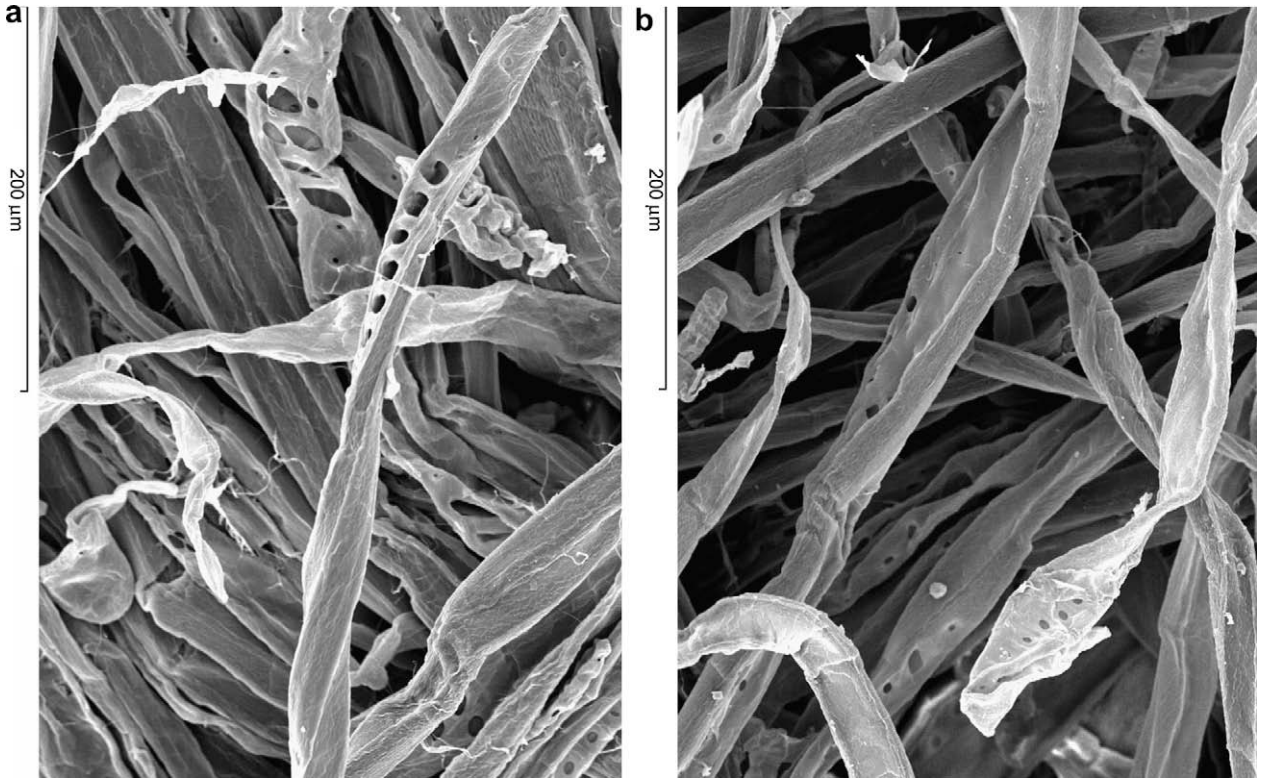

Fig. 1. Scanning electron micrographs of (a) the initial unbleached pulp (b) the hornificated unbleached pulp.

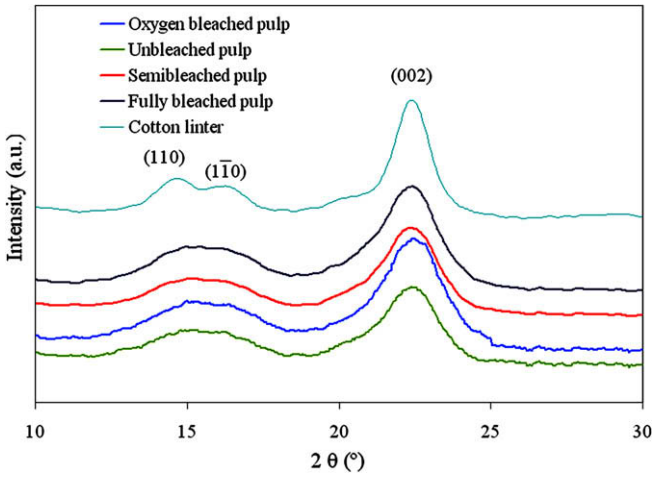

Fig. 2. XRD patterns of the softwood pulps and cotton linters.

by Roncero et al. in softwood pulps bleached with xylanase (Roncero, Torres, Colom, & Vidal, 2005). Nevertheless, no significant differences in crystallinity were found between the bleached pulps independently of the sequence used. Cotton linters showed the highest Cr.I. values.

On the other hand, overall, values of Cr.I. did not change significantly with the drying and rewetting cycles for the softwood pulps. Only a slight increase was found for the cotton linters and the OD pulp. Nevertheless it must be taken in account that the experimental error in the calculation of Cr.I. with XRD technique is in the order of 5%.

3.2. Morphological characterization

SEM pictures of the initial and hornificated pulps were taken to investigate the morphological changes. As could be seen (Fig. 1) no significant changes were observed in the unbleached pulp. Similar results were found in the pulps and cotton linters under study.

Although we did not observe significant changes in the length and width of the fibres after the drying and rewetting cycles (see Table 6), we expected to find a decrease in the thickness and, consequently, a decrease in the aspect ratio (length versus thickness) values of the hornificated fibres (Khantayanuwong, 2003). Fibre shrinkage occurs in two different phases. In the first phase, an orthogonal shrinkage in the lamellar plane is caused by the dewatering of large intrafibre cell wall pores. The second phase starts in the final phase of drying, when tightly bound water leaves the microstructure of the fibre, causing reversible shrinkage in the direction of the fibre width (Ackermann et al., 2000; Weise & Paulapuro, 1999).

The fibre curl index, defined as a gradual and continuous curvature of the fibres, was found to decrease with the drying and rewetting cycles of the softwood pulps. This decrease could be related to an increase in the stiffness of the fibres as a consequence of the hornification process. Nonetheless, the curl index values of cotton

Table 6
Morphological characteristics of the pulps and cotton linters.

		Length (mm)	Width (μm)	Lineal mass (mg/m)	Curl index (%)
Unbleached (U)	Initial	1.37	28.28	0.256	15.96
	I	1.49	28.32	0.252	15.79
	II	1.37	26.65	0.231	13.51
	III	1.32	26.72	0.261	12.15
	IV	1.36	25.91	0.252	12.94
Oxygen delignificated (O)	Initial	1.41	25.87	0.229	19.72
	I	1.37	25.85	0.238	17.9
	II	1.47	26.06	0.227	15.5
	III	1.48	25.64	0.219	15.14
	IV	1.36	25.28	0.219	15.49
Semi-bleached (OD)	Initial	1.33	25.4	0.224	21.28
	I	1.35	28.26	0.228	21.48
	II	1.38	25.21	0.205	20.9
	III	1.39	24.88	0.213	19.33
	IV	1.38	24.39	0.209	18.91
Fully bleached OD(EP)D	Initial	1.39	25.03	0.207	21.65
	I	1.38	25.07	0.211	22.21
	II	1.36	24.77	0.211	20.96
	III	1.39	24.55	0.209	19.6
	IV	1.41	24.35	0.192	19.35
Cotton linters	Initial	0.79	20.14	0.244	25.66
	I	0.81	19.95	0.24	26.98
	II	0.86	19.61	0.261	26.78
	III	0.84	19.63	0.237	27.16

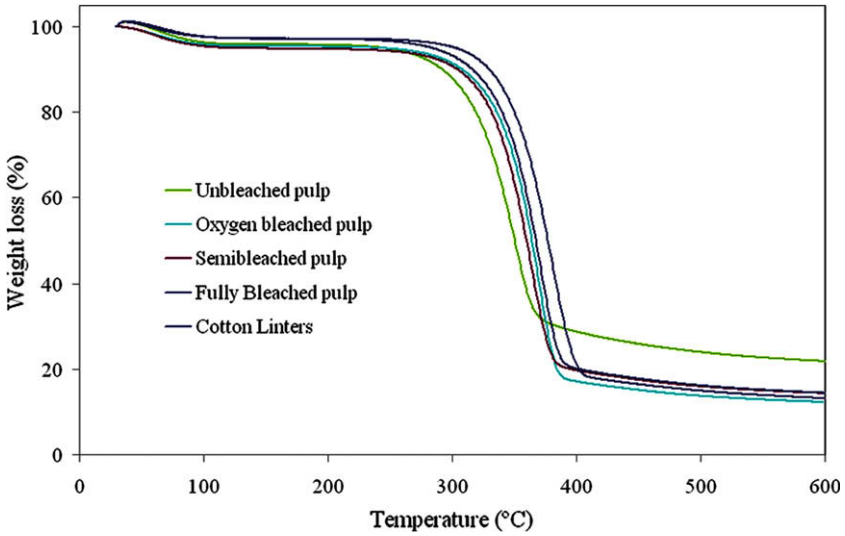

Fig. 3. TGA thermograms of the softwood pulps and cotton linters.

Table 7
Variation in the decomposition temperature obtained from TGA thermograms with the drying and rewetting cycles.

Wet/dry cycles	Decomposition temperature (T_p)[1] (°C)				
	Initial	I	II	III	IV
Unbleached (U)	350.4	357.9	371.2	371.6	379.2
Oxygen delignificated (O)	363.8	370.2	369.7	368.5	367.5
Semi-bleached (OD)	370.4	370.6	373.6	373.1	373.2
Fully bleached OD(EP)D	371.9	374.1	378.1	375.4	378.2
Cotton linters	380.9	383.7	381.8	383.3	383.3

linters showed a slight increase with the drying and rewetting cycles. In these fibres, probably as a consequence of the lower percentage of hornification than in the fibres from softwood pulps, the effects are less noticeable.

3.3. Thermal decomposition

Fig. 3 presents the overall thermogravimetric decomposition process of the softwood pulps and cotton linters. As shown, the thermal decomposition occurs in three main steps. The first, recorded below 110 °C, corresponds to the moisture evolution of the water absorbed. The second, which occurs above 200 °C until approximately 400 °C, resulted mainly from the thermal decomposition of hemicelluloses and cellulose, and supposes the most significant weight loss percentage (Spinacé, Lambert, Fermoselli, & De Paoli, 2009; Yao, Wu, Lei, Guo, & Xu, 2008). The high temperature tail shown mainly in the unbleached softwood pulp would be related to the degradation of lignin. As expected, the profiles of the fibres analysed are similar as a result of the material being cellulosic. The differences in the relative loss weight percentage and in the decomposition temperatures are related to the differences in the chemical composition of the samples and to the values of the crystallinity index. The degradation temperatures were found to be 350.4, 364.8, 370.4, and 371.9 °C for the unbleached, oxygen delignificated, semi-bleached, and fully bleached softwood pulps, respectively (see Table 7). These results clearly illustrate that the thermal stability of the softwood fibres increases after bleaching. This increase in the temperature of thermal decomposition after the bleaching sequence is related to the partial removal of hemicelluloses and lignin from the fibres and to the higher crystallinity of the cellulose. The highest degradation temperature found for the cotton linters (380 °C) supports this explanation (Alemdar & Sain, 2008; Nguyen, Zavarin, & Barrall, 1981).

The TGA curves of the unbleached pulp subjected to the drying and rewetting cycles and the initial sample are presented in Fig. 4. As shown, as a consequence of the hornification process, the thermal decomposition is shifted to higher temperatures. Similar results were found in the bleached softwood pulps and in the cotton linters. This behaviour could be attributed to the formation of a more closely-packed crystalline structure.

The increase in the thermal stability of these natural fibres with drying and rewetting cycles could be a very interesting result in composite applications, not only in cementitious matrix but also for use in thermoplastic ones. Moreover, it is expected that the hornificated fibres will have higher values of stiffness and tensile strength as a consequence of the formation of a more close-packed crystalline.

4. Conclusions

Experimental results show that the drying and rewetting cycles (hornification process) had the following effects on the softwood pulps and cotton linters analysed:

- WRV and curl index values decreased with the drying and rewetting cycles, with this effect being more significant in the softwood bleached pulps. Cotton linters showed the lowest value for the percentage of hornification. This decrease in the WRV and the shrinkage of the fibres will improve their dimensional stability against environmental changes in cement mortar composites, reduce the water gradient in the fibre–matrix interface, and will probably decrease the crystallization of calcium hydroxide particles on the surface of the fibres.
- Overall the values of Cr.I. did not change with the drying and rewetting cycles.
- The hornificated fibres exhibited enhanced thermal properties, increasing the thermal degradation temperature with the number of drying and rewetting cycles. This effect was more significant in the pulps with higher percentages of lignin.

From these results it can be concluded that the hornification process could have promising benefits in improving the fibre–ma-

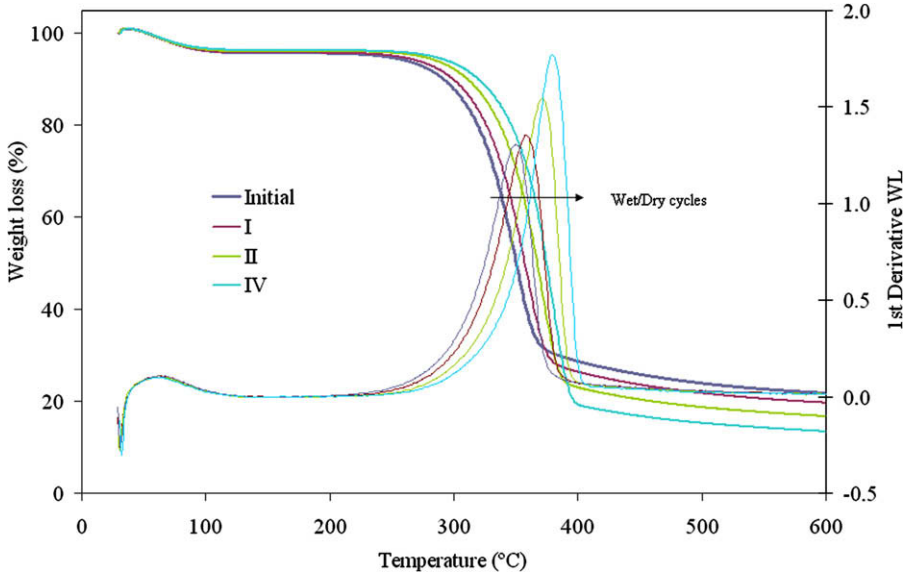

Fig. 4. Variation in the TGA thermograms of the unbleached softwood with the drying and rewetting cycles.

trix adherence, resistance, and durability of the vegetable fibres in cement mortar composites.

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