Sisal Organosolv Pulp as Reinforcement for Cement Based Composites

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The present work describes non-conventional sisal (*Agave sisalana*) chemical (organosolv) pulp from residues of cordage as reinforcement to cement based materials. Sisal organosolv pulp was produced in a 1:1 ethanol/water mixture and post chemically and physically characterized in order to compare its properties with sisal kraft pulp. Cement based composites reinforced with organosolv or kraft pulps and combined with polypropylene (PP) fibres were produced by the slurry de-watering and pressing method as a crude simulation of the Hatschek process. Composites were evaluated at 28 days of age, after exposition to accelerated carbonation and after 100 soak/dry cycles. Composites containing organosolv pulp presented lower mechanical strength, water absorption and apparent porosity than composites reinforced with kraft pulp. The best mechanical performance after ageing was also achieved by samples reinforced with kraft pulp. The addition of PP fibres favoured the maintenance of toughness after ageing. Accelerated carbonation promoted the densification of the composites reinforced with sisal organosolv + PP fibres.

Keywords: *fibres, fibre/matrix bond, mechanical properties, physical properties*

1. Introduction

In several developed countries, cellulose fibres are used as reinforcement of cement-based materials and in order to provide an alternative for low cost buildings by adaptation of the former asbestos-cement production process[1].

Tropical countries present significant opportunities for the production of non-wood lignocellulosic fibres[2], especially if they are available from by-products of the main commercial agricultural activities (e.g., cordage). With the low cost of raw materials and simplified pulping methods, the resulting cellulose pulp has considerable potential for fibre-cement production at significantly lower costs than those associated with the use of conventional kraft wood pulps[3].

Alkaline kraft pulping is the dominant chemical pulping process today, but it presents some serious shortcomings, as air and water pollution and the high investment costs. These shortcomings have led to the development of several organosolv methods capable of producing pulp with properties near those of kraft pulp[4].

Diverse solvents, pure or in mixtures, can be used to promote delignification[5-7]. Amongst them, the process that involves ethanol is the most used, regarding the recovery facilities, the better impregnation of vegetal tissue by solvent, the easier recovery of lignin and polysaccharides from the pulping liqueur beyond the efficient delignification and favourable conditions of operation in alcohol producer's countries[8-10].

The lignin dissolution in the organosolv processes is a result of hydrolysis of ether bonds, as α-O-4 and β-O-4 bonds of lignin macromolecules[11]. Organosolv delignification also consists in the breaking of ether bonds between carbohydrates and carbon atoms from the lateral chains of lignin[12]. According to Aziz and Goyal[13] cleavage of alpha-ether linkages is the most important reaction in the lignin molecule breakdown during organosolv pulping. The bulk delignification in ethanol:water pulping is a phenomenon involving breakdown of the lignin with high molecular weight and solubilisation of its breakdown products[14]. Ethanol acts as a scavenger for the free radicals formed during pulping and reduces the extent of lignin condensation. Some side chain rearrangement and ethoxylation of benzyl alcohol groups occurs. This reaction prevents the lignin molecule from recondensing during the pulping process[15].

In the kraft process the lignin extraction from cell wall occurs at the initial stage of delignification, whereas the lignin from middle lamella is extracted at the final stage of delignification. In the organosolv processes, the lignin extraction occurs first at the middle lamella and lignin from cell wall is poster dissolved[16,17]. This characteristic of the organosolv pulp must be of great interest since it decreases the tendency of fibre interlayer debonding during the soak/dry cycling of the fibre-cement composites, and consequently prevents the reprecipitation of hydration products within the fibre cell wall, minimizing fibre mineralization[18].

This work reports on the investigation of an alternative chemical (organosolv) pulping process applied to residues of sisal (*Agave sisalana*) strand fibres from industry of cordage. The organosolv pulp is used as reinforcement of cement based composites in comparison to commercial sisal pulp obtained by the conventional kraft pulping process.

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2. Experimental

2.1. Materials

Sisal (*Agave sisalana*) field by-product was provided by Associação de Desenvolvimento Sustentável e Solidário da Região Sisaleira (Apaeb), Brazil. Sisal strand fibres originated from residues of the cordage industry, with the following physical and mechanical characteristics: around 5 mm long and approximately 0.2 mm average diameter, around 360 MPa tensile strength[19], 15.0 GPa elastic modulus[20] and 5% strain at failure[19]. The raw material was first chemically characterized and then pulped under organosolv process.
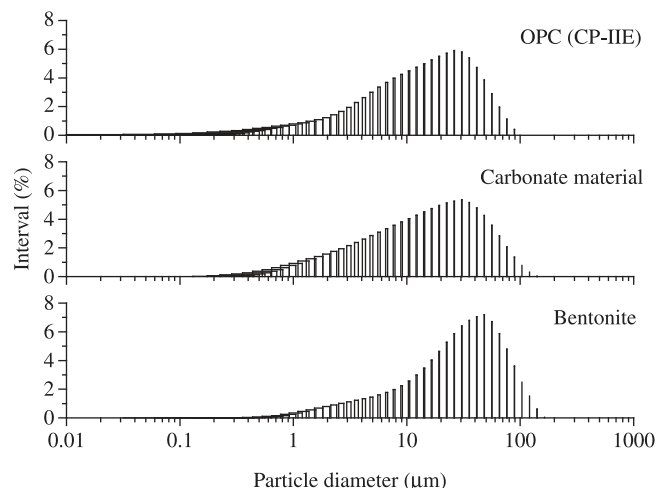

Figure 1. Particle size distribution of OPC (CP-IIE), carbonate material and bentonite.

Conventional sisal kraft pulp with up to 3% total Klason lignin was provided by Lwarcel Celulose e Papel, Brazil. The unrefined pulp with fibres concentration of 5.3 g/L in water was submitted to a stirring process in water and was post-refined by several passes through the 300 mm diameter disc refiner (3 mm width bar, 3 mm width groove and 7.5° angle bar configuration) until the achievement of CSF 220 mL refinement degree. It was used for the refinement a specific edge load (SEL) of approximately 0.3 W.s/m, operating at current intensity of 50 A. The Canadian Standard Freeness test (CSF) is a widely recognized standard measure of the drainage properties of pulp suspensions[21]. Low freeness values (less than 300 mL) are indicative of high degree of external fibrillation and/or shortage of the fibres, leading to long drainage periods during the test. The refinement greatly improves the manufacturing processes of fibre-cement based on slurry dewatering techniques followed by pressing[22].

Polypropylene (PP) fibres measuring 6 mm long and around 0.3 mm width, with 300 MPa tensile strength, 3.3 GPa elastic modulus and 25% strain at failure (data furnished by Fitesa® S.A., Brazil), was used for the mix-design with hybrid reinforcement.

Physical and chemical properties of ordinary Portland cement (OPC) and carbonate filler are summarized in Tables 1 and 2 respectively. Carbonate filler was used for partial substitution of OPC in order to reduce costs concerning the production of fibre-cement. Bentonite (specific surface area = 0.2152 m²/g) was used to improve the water retention. Particle size distribution was evaluated by Mastersizer S long bed 2.19 version in a Malvern equipment and was depicted in Figure 1.

According to Figure 1, 50% of the particles are smaller than 13.59, 14.49 and 28.23 µm for OPC, carbonate filler and bentonite respectively. Most of particles (90%) are smaller than 41.75, 50.08 and 71.92 µm for OPC, carbonate filler and bentonite respectively.

Table 1. Physical, chemical and mechanical characterization of ordinary Portland cement (CP-IIE[a]).

Physical properties		Chemical properties											Mechanical properties	
Specific surface area (m²/g)	Specific mass (g/cm³)	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	P_2O_5	K_2O	SrO	MnO	ZrO_2	Loss of ignition	$\sigma_{c,7d}$ (MPa)	$\sigma_{c,28d}$ (MPa)
		(% by mass)												
0.5211	3.010	25.3	58.6	5.83	2.88	3.02	0.19	0.84	0.19	0.08	0.03	3.0	30.4	41.0
Retention # 200[b] (%): 1.57														
Retention # 325[c] (%): 9.90														

[a]Data provided by the supplier. Brazilian Standards NBR 11578[23] (1991): blast furnace slag = 6-34%; carbonate filler = 0-10%; [b]200 mesh sieve (# 0.074 mm); and [c]325 mesh sieve (# 0.045 mm).

Table 2. Physical and chemical characteristics of the carbonate filler.

Physical properties		Chemical properties										
Specific surface area (m²/g)	Specific mass (g/cm³)	SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	P_2O_5	K_2O	SrO	MnO	TiO_2	Loss of ignition
		(% by mass)										
0.4298	2.650	2.47	44.6	0.45	0.37	8.56	0.08	0.17	0.05	0.06	0.04	43.3
Present phases (DRX): $CaCO_3$, $CaMg(CO_3)_2$, Fe_2O_3, SiO_2, $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$												

Source: Laboratory of Technological Characterization, Escola Politécnica, Universidade de São Paulo, Brazil.

2.2. Fibre characterization

2.2.1. Determination of insoluble and soluble Klason lignin

- Insoluble lignin - The content of insoluble Klason lignin was determined according to Tappi Test Method[24]. Dry fibres (1 g) were solubilised with 15 mL of H_2SO_4 72% under magnetic agitation during 2 hours. After this, the mixture was placed in a 1 L glass balloon added to 560 mL of distilled water under reflux. The mass of fibres left after filtration was dried at 100 °C until the constant mass was attained.

Reflux was performed during 2, 3, 4 and 5 hours for the sisal strand fibres in order to determine the maximum hydrolyses. The optimal time of reflux with sulphuric acid for sisal strand fibres was 4 hours and it was used also for organolsolv pulp. The content of Klason lignin was defined by Equation 1:

$$\%R_1 = \frac{m_1}{m_m} \times 100 \tag{1}$$

where m_m is the dry mass of fibres (g), m_l is the mass of dry Klason lignin (g) and $\%R_l$ is the content of insoluble Klason lignin (%).

- Soluble lignin - The filtered solution after insoluble determination was diluted to 1 L with distilled water for Ultra Violet (UV) spectroscopy analyses in order to determine the soluble lignin, following the procedures described by Goldschimid[25]. It was prepared a reference solution from 1.5 mL 72% sulphuric acid in 100 mL of water. An aliquot was collected for the absorbance analyses at 280 and 215 nm. The amount of lignin (g/L) in the diluted samples was calculated using Equation 2:

$$C(g/L) = \frac{4.53 \times A_{215}\quad A_{280}}{300} \tag{2}$$

where C (g/L) is the content of soluble Klason lignin (g/L), A_{215} is the absorbance at 215 nm and A_{280} is the absorbance at 280 nm.

2.2.2. Determination of holocellulose content

Holocellulose content was determined by the use of sodium chlorite in acid solution, and it is designated chlorite holocellulose. The procedure is described in the literature[26]. The amount of 1 g of fibres was diluted in 60 mL of distilled water under magnetic agitation at 70 ± 2 °C during 0.5 hours. After thermal equilibrium 1.5 g of sodium chlorite and 2 mL of acetic acid were added. This procedure was repeated after 1 and 2 hours, resulting in a 3 hours reaction. Finally, the resultant mass was filtered and dried at 100 °C until constant mass. The content of holocellulose was calculated according to Equation 3:

$$\%R_{holo} = \frac{m_{holo}}{m_m} \times 100 \tag{3}$$

where m_m is the dry mass of fibres (g), m_{holo} is the dry mass of holocellulose (g) and $\%R_{holo}$ is the content of holocellulose (%).

2.2.3. Determination of cellulose and polyose

The filtered solution after the determination of insoluble Klason lignin was used for the determination of carbohydrates by high performance liquid chromatography (HPLC). The sample to be analyzed was prepared as cited by Pasquini et al.[27]. The amounts of cellobiose, glucose, arabinose, formic acid, acetic acid, hydroxymethylfurfural and furfural were determined. Determinations of cellobiose, glucose, xylose, arabinose and acetic acid, were performed in a Shimadzu®, model CR 7A chromatograph equipped with Infrared Shimadzu R10-6A detector, column Aminex HPX 87H

(300 mm × 7.8 mm, Biorad), using H_2SO_4, 0.005 mol.L^{-1} as eluent and a flow rate of 0.6 mL/min. For the determinations of furfural and hydromethylfurfural, the same chromatograph was employed with a Shimadzu Ultraviolet detector (254 nm), model SPD-10A, column RP 18 (C18) Hewlett-Packard, using acetonitrile/water 1:8 (v/v) with 1% acetic acid (v/v) as eluent and flow rate equals to 0.8 mL/min.

2.3. Organosolv pulping

In order to observe the higher yield of the process, organosolv pulping was conducted by three periods of reactions,. In theses different experiments, pulping times were respectively 1, 2 and 3 hours of reaction from the moment in which the reactor temperature reached 190 °C.

The quantity of 25 g of by-product sisal (around 5 mm long) was added in a blend of ethanol and water in the range of 1:1 v/v in a locked 1 L reactor. Temperature was then raised up to 190 °C. After each cooking time (1, 2 and 3 hours), the reactor was cooled during 20 minutes and the pulp was filtered in a Buchner funnel. Pulp was triple washed with ethanol and dried at 100 °C. The yielding was calculated according to Equation. 4:

$$\%R_0 = \frac{m_0}{m_m} \times 100 \tag{4}$$

where m_m is the dry mass of the by-product sisal (g), m_o is the dry mass of the pulp (g) and $\%R_o$ is the pulp yield (%).

2.3.1. Physical characterization of fibres and pulps

The main physical attributes of the organosolv and kraft pulps were characterized by the particle size analyser Galai CIS-100. The analysis with Galai CIS-100 consists in the evaluation of the physical attributes of the whole fibrous material present in the pulp. Average length and width, coarseness, number of fibres per gram and fines content were analysed and stored with the aid of the Wshape v.1.0 software.

2.4. Composite preparation

Cement based composites were reinforced with sisal unrefined organosolv or refined kraft pulp and polypropylene fibres. The cement based composites were moulded in plates measuring 200 × 200 mm. They were prepared in laboratory scale using a slurry vacuum dewatering followed by pressing technique described in details by Savastano Jr. et al.[22].

Formulations in Table 3 were established based on prior studies published elsewhere[28,29]. They refer to the dry mass of the solid raw materials before mixing with water.

Bentonite was previously dispersed separately in water during 10 min and post added jointly with the pulp, which was dispersed in water by mechanical stirring at 1,700 rpm during 1 hour. The mixture formed with approximately 20% of solids was stirred at 1,700 rpm for 20 minutes. The slurry was transferred to the evacuable casting box and the vacuum was applied (~80 kPa gauge) until a solid surface formed. Three pads of each formulation were pressed simultaneously at 3.2 MPa for 5 minutes. The final water/cement ratio reached after this operation was around 0.3. Pads were then sealed wet in a plastic bag to cure at room temperature for two days and immersed in water during 26 days. Pads were cut wet into four 165 mm × 40 mm flexural test specimens using a diamond saw cooled with water. Specimen thickness was approximately 6 mm. On completion of the cure, specimens were tested under saturated condition at 28 days after production.

Table 3. Mix-design of the fibre-cement composites.

Raw material	SO	SO-PP	SK	SK-PP
	w/w (%)			
Sisal pulp (SO = unrefined organosolv, SK = refined kraft)	4.7[a]	3.0[b]	4.7	3.0
Polypropylene fibres (PP)	-	1.7[c]	-	1.7
Ordinary Portland cement (CP-IIE)	77.8	77.8	77.8	77.8
Carbonate filler	16.5	16.5	16.5	16.5
Bentonite	1.0	1.0	1.0	1.0

[a]Equivalent volume fraction = ~5.0%; [b]Equivalent volume fraction = ~3.1%; and [c]Equivalent volume fraction = ~2.6%.

Table 4. Sisal pulp and fibre physical properties[a].

Pulp (Sisal)	Average length (mm)	Average width (μm)	Aspect ratio	Coarseness (mg/100 m)	Fibrous material (10^6 fibres/g)	Fines content (%)
Organosolv (unrefined)	1.10 ± 0.04	26.4 ± 0.2	42	11.5 ± 1.7	8.1 ± 1.6	25.8 ± 2.2
Kraft (unrefined)[b]	1.66 ± 0.02	22.2 ± 0.5	75	12.8 ± 0.1	4.7 ± 0.1	27.2 ± 1.2
Kraft (CFS 220 mL)	1.13 ± 0.05	18.7 ± 0.2	60	10.0 ± 0.6	8.9 ± 0.9	40.6 ± 1.3

[a]Pulp and Paper Laboratory, Department of Forestry Engineering of the Federal University of Viçosa, Brazil; and [b]Tonoli et al.[29].

2.5. Accelerated carbonation

Accelerated carbonation of the composites was carried out in a climatic chamber with carbon dioxide (CO_2) saturated environment and with controlled temperature and humidity (30 °C and 80% RH respectively). The composites were submitted to the climatic chamber environment during two weeks until the complete carbonation of the samples. The carbonation degree was evaluated by the exposure to a solution with 2% of phenolphthalein diluted in anhydrous ethanol as described by Agopyan et al.[30].

2.6. Soak/dry accelerated ageing cycles

The soak/dry accelerated ageing cycles involved comparative analysis of the physical and mechanical performance of the composites before and after this test. Specimens were successively immersed in water at 20 ± 5 °C during 170 minutes, followed by the interval of 10 minutes, and then exposed to the temperature of 70 ± 5 °C for 170 minutes in a ventilated oven and with the final interval of 10 minutes. This procedure was based on recommendations of the EN 494[31] Standards. Each soak/dry set represents one cycle and was performed for 100 times (i.e., 100 cycles).

2.7. Physical and mechanical characterization

Water absorption (WA), bulk density (BD) and apparent void volume (AVV) values were obtained from the average of ten specimens for each design, following procedures specified by the ASTM C 948-81[32] Standards.

Mechanical tests were performed in a universal testing machine Emic DL-30,000 equipped with 1 kN load cell. A four-point bending configuration was employed for the determination of the values of modulus of rupture (MOR), limit of proportionality (LOP), and toughness. A span of 135 mm and a deflection rate of 1.5 mm/min were adopted in the bending test. Equation 5 defines MOR:

$$MOR = \frac{P.L_v}{b.h^2} \tag{5}$$

where P is the maximum load, L_v is the major span between the supports, b and h are the specimen width and depth respectively.

The limit of proportionality (LOP) was described as the stress corresponding to the upper point of the linear portion of the stress-strain curve.

Toughness (Equation 6) was defined as the energy absorbed during the flexural test and divided by the specimen cross-sectional area. The absorbed energy was calculated by integration of the area below the load-deflection curve.

$$Toughness = \frac{absorbed\,energy}{b \times h} \tag{6}$$

where b and h are the specimen width and depth respectively.

Scanning electron microscopy (SEM) was applied for the characterization of fibre-matrix interface on a fractured surface of specimens undergone to mechanical tests, similar to the procedures used in Savastano Jr. et al.[33]. Samples were gold coated in a Bal-Tec MED 020 coating system before being analysed in a Zeiss® LEO 440 microscope.

3. Results and Discussion

3.1. Characterization of the sisal strand fibres

Sisal strand fibers were characterized. Lignin content was determined after reflux with sulphuric acid as described above. Cellulose and polyose contents were determined by HPLC. The content of lignin, polyose and cellulose was 16 ± 1, 20 ± 1 and 65 ± 2, respectively. The values obtained for cellulose and polyoses are in accordance with the literature[34].

3.2. Characterization of the organosolv pulps

It can be observed in Figure 2 that the yield for 1 hour pulping was the higher. It is attributed to the low removal of lignin, resulting in a higher mass of dry pulp. This fact indicates that 1 hour was not enough to get a satisfactory removal of lignin. Results obtained for the yield, holocellulose and lignin contents after 2 and 3 hous (Figure 2) indicated no significant variations in these properties. The period of 2 hours of pulping was sufficient to extract the maximum lignin possible of the by-product sisal. This fact would represent an economy of energy by the adoption of 2 hours of reaction instead of 3 hours.

The physical characterization of the fibrous material, i.e., entire plus damaged fibres performed in Galai equipment gives a precise idea of the actual morphology of the pulp. Results follow in Table 4.

In a previous study, Tonoli et al.[29] evaluated commercial sisal kraft pulp at different intensities of refinement (CSF 680, 220 and 20 mL). The physical properties of the unrefined kraft pulp (CSF 680 mL) are
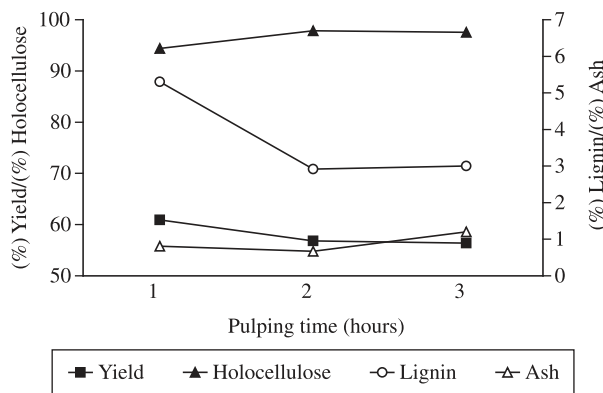
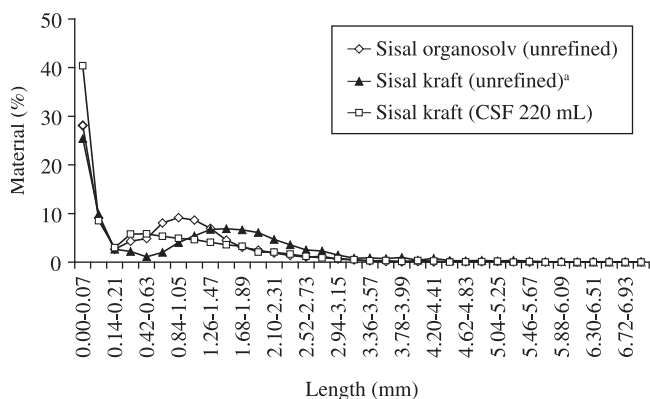**Figure 2.** Results of chemical characterization of organosolv pulps at different pulping times.

Figure 3. Length distribution of the fibrous material. ([a]) Tonoli et al.[29].

Figure 4. Width distribution of the fibrous material. ([a]) Tonoli et al.[29].

3.3 Physical results of the composites

According to the results shown in Figure 5, at 28 days and after 100 cycles (not submitted to fast carbonation), composites with only organosolv pulp presented lower water absorption and apparent void volume than composites only reinforced with sisal kraft. Bulk density of the composites was weakly influenced (no statistical significance) by the pulping and/or refining processes of vegetable fibre.

Water absorption and apparent void volume have decreased significantly for composites fast carbonated and aged. Water absorption of the unaged composites with sisal organosolv + PP fibres was less influenced by 100 ageing cycles.

Bulk density increased significantly with the accelerated carbonation for both composites reinforced with only organosolv or kraft sisal and with sisal + PP fibres. Results for bulk density were not significantly different for composites at 28 days when compared to those after 100 ageing cycles.

Composites with sisal organosolv pulp and PP fibres as reinforcement presented higher water absorption after 100 ageing cycles over composites only reinforced with sisal organosolv pulp. This behaviour can be attributed to deficient distribution of long and hydrophobic synthetic fibres in the matrix, which can contribute to higher void content after ageing, as a probable consequence of capillaries associated to the poorer packing. In the case of the composites with refined sisal kraft the homogeneity in distribution of PP fibres was improved with the consequent low variation of the WA and AVV before and after the exposition to ageing cycles. Another fact that could contribute to lower values of water absorption in the sisal aged composites is the probable formation of hydration products around and into the cores of the cellulose fibres after the ageing cycles. Composites with only sisal kraft presented higher water absorption than those with only sisal organosolv at 28 days and after the 100 ageing cycles. A possible explanation is that aqueous ethanol penetrates easily into the structure of the fibre resulting in uniform delignification[36] and besides decrease the recondensation of lignin on surface of the fibres[15] by the rearrangement and ethoxylation of benzyl alcohol groups. Lower content of lignin on the fibre surface permits improved fibre-matrix bonding, decreasing porosity and water absorption of the composite.

The higher bulk density of the formulations containing only sisal pulps in comparison with composites with polypropylene fibres is partially related with the substitution of the fraction of the matrix (density ~2.6 g/cm³) and cellulose fibres (density ~1.5 g/cm³) by polypropylene fibres (density ~0.9 g/cm³). Additionally, another reason to the lower bulk density of the composites with PP fibres is the difficulty of packing the particles into the composite when using PP fibres, since these fibres are longer, less flexible/malleable, hydrophobic, and reasonably with

presented in Table 4. Comparison with the properties of the unrefined organosolv pulp shows similar amount of fines. The definition of fines is related to the fibres with less than 75 μm of length[35]. The average length of organosolv pulp was lower and average width was higher in the present work, which gives a considerably lower aspect ratio. Besides, the coarseness of the organosolv pulp was lower and the amount of fibrous material per gram was higher than unrefined kraft pulp. The sisal source from residues of the cordage production should be taken in consideration in the evaluation of these data.

The refinement of the kraft pulp (CSF 220 mL), as well as the organosolv pulping, has promoted an increase of the values of fibrous material per gram and diminished the length, aspect ratio, and coarseness of the pulp. Kraft pulp CSF 220 was chosen as reinforcement by the similar behaviour to the organosolv pulp, regarding the properties cited above. In this way, comparisons could be made.

The distributions of length and width for the fibrous material (obtained with the particle size analyser) can be visualized in Figures 3 and 4 respectively. According to Figure 3, most of the filaments are lower than 1 mm (around 65% to sisal organosolv and sisal kraf refined, and around 47% to sisal kraft unrefined). Organosolv pulping generates shorter fibrous material than unrefined kraft pulp[29]. The length distribution of the organosolv pulp was similar to the refined kraft pulp (CSF 220 mL). For the width distribution (Figure 4) most of the fibres (around 90%) lie in the 5-40 μm region for the three samples. However, about 50% of the number of filaments of the sisal kraft fibres (CSF 220 mL) presents width lower than 15 μm. In the case of sisal organosolv fibres, this amount is around 25%, what indicates the more intensive external fibrillation and the ribbon like format for the refined kraft fibres.
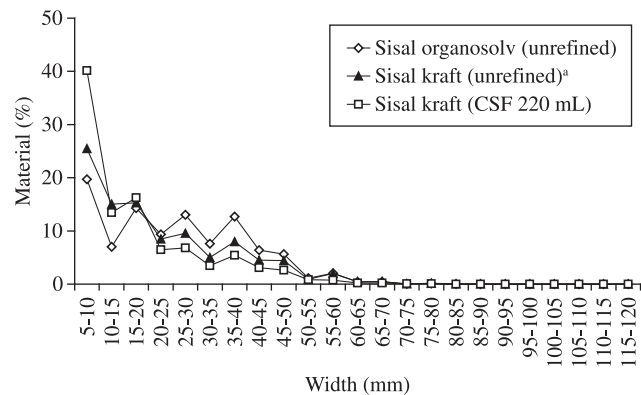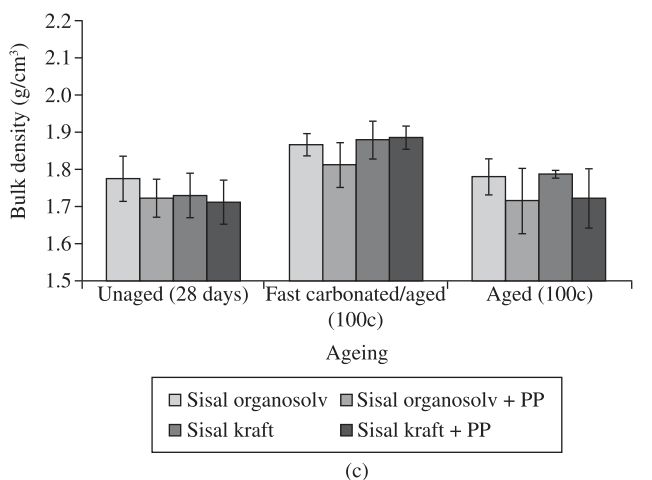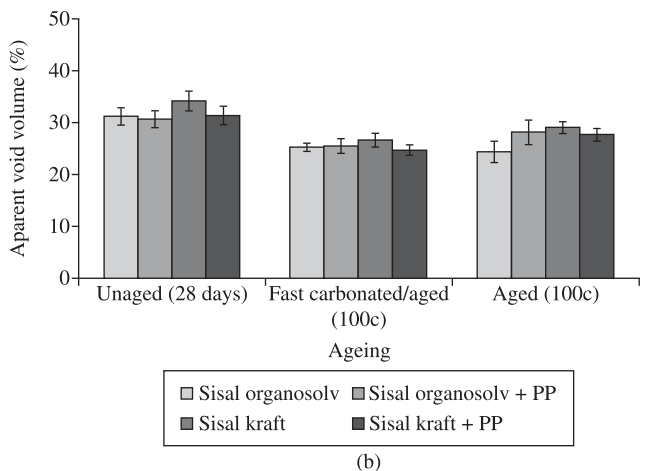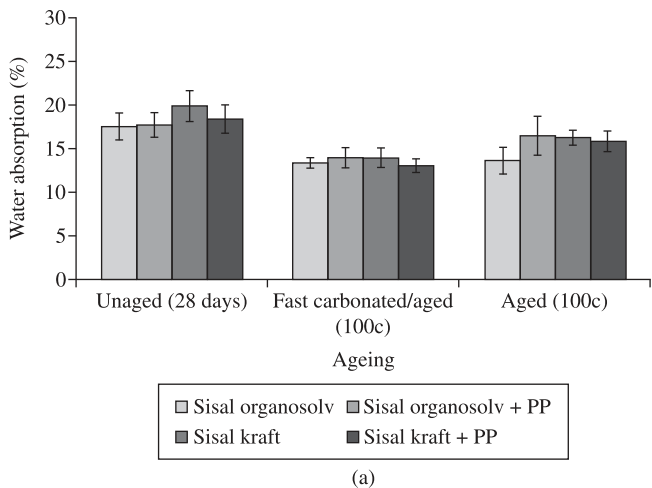
Figure 5. Physical properties of the composites reinforced with sisal organosolv and PP fibres at 28 days, fast carbonated/aged and aged. a) Water absorption, b) apparent void volume and c) bulk density.
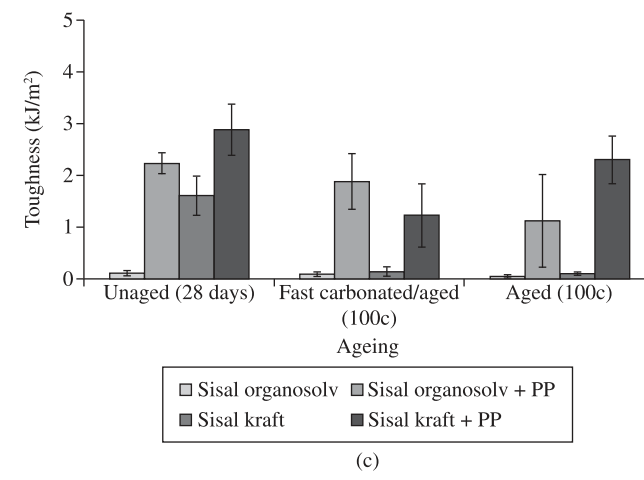
Figure 6. Mechanical properties of the composites reinforced with sisal organosolv and PP fibres at 28 days, fast carbonated/aged and aged. a) MOR, b) LOP and c) toughness.

the same size, while the sisal fibres are smaller and with a great variety of length and width (Figures 3 and 4), that can also give contribution for the improvement of composite packing.

3.4. Mechanical results of the composites

Figure 6 presents the results of mechanical properties of the composites before and after the ageing for both series subjected or not to fast
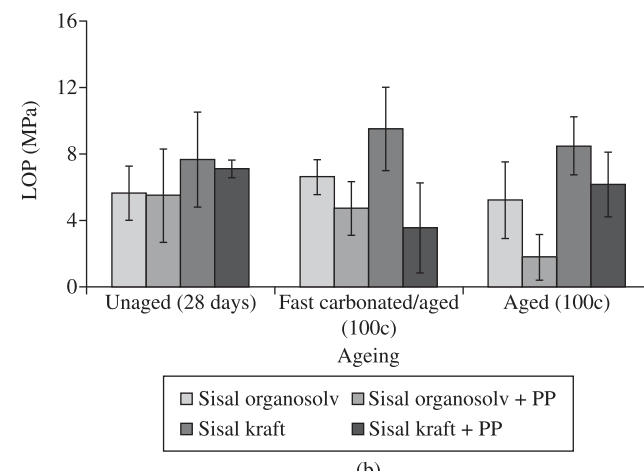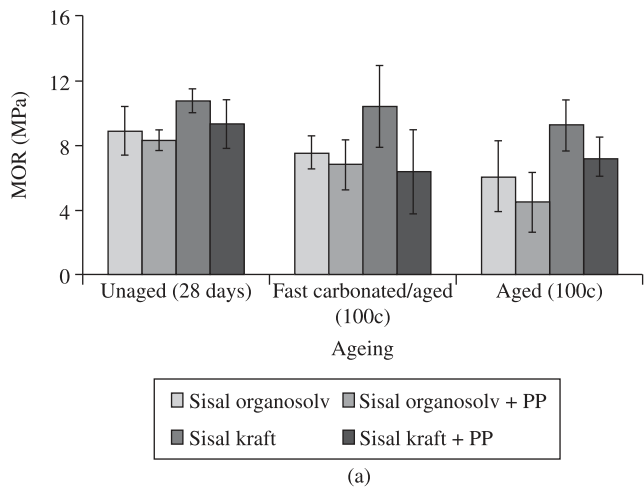
carbonation. Composites reinforced with kraft pulp present higher MOR and LOP than the corresponding ones with organosolv pulp. Accelerated carbonation was more effective to the maintenance of MOR for the composites only reinforced with sisal kraft than composites reinforced with only organosolv pulp. Fast carbonated/aged composites presented higher MOR, LOP and toughness than those only aged (without fast carbonation) reinforced with organosolv pulp + PP fibres.
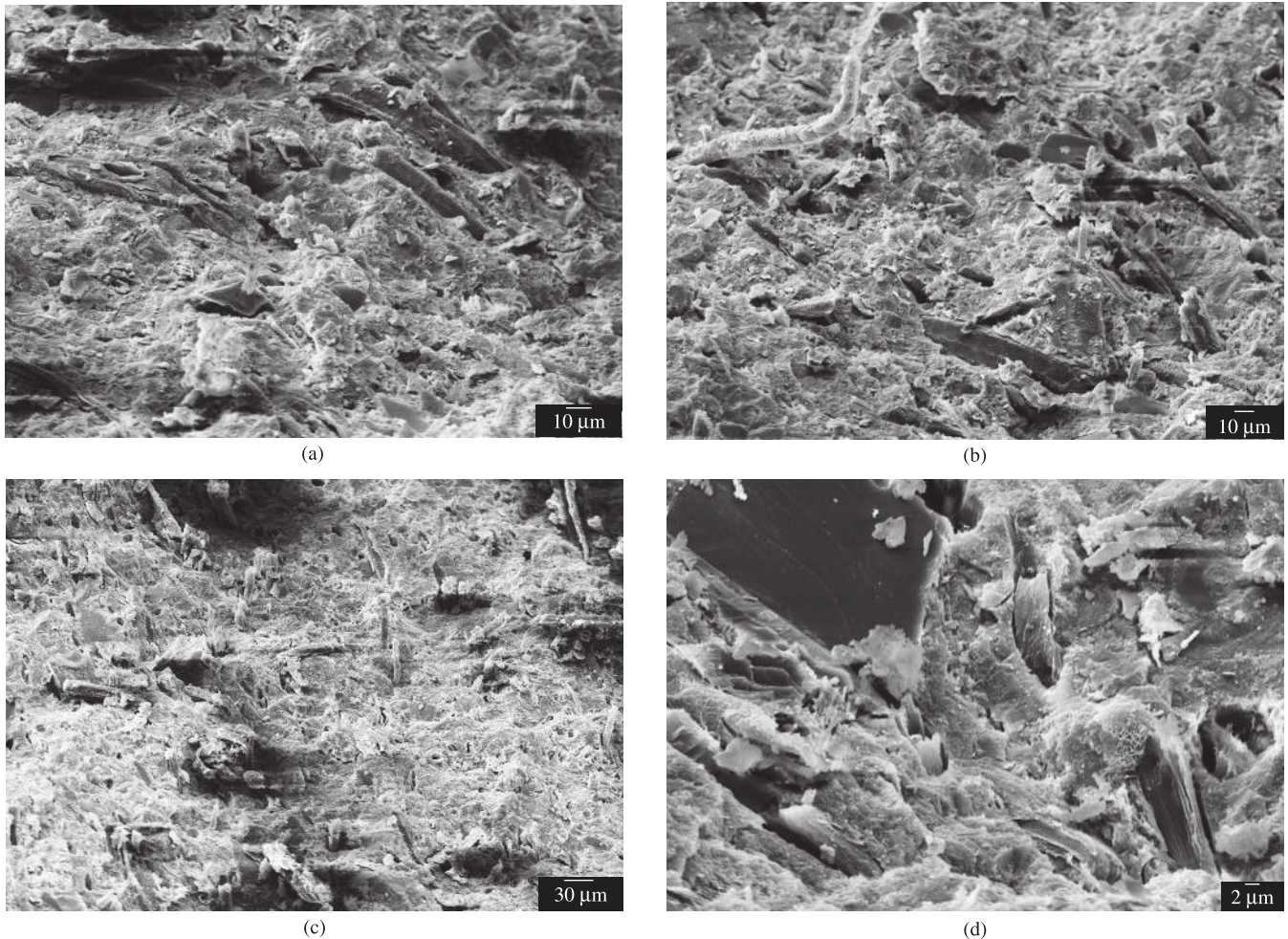
(a)

(b)

(c)

(d)

Figure 7. SEM of fracture surface of composites reinforced with: a) and b) sisal organosolv pulp after 100 soak/dry cycles; c) and d) sisal kraft after fast carbonation followed by 100 soak/dry cycles.

Composites reinforced with only sisal kraft pulp accomplished greater MOR and LOP than composites with hybrid reinforcement (kraft pulp + PP). This behaviour can be attributed to the better adhesion and packing between the cement matrix and cellulose fibres. Unaged composites with organosolv pulp did not present significant differences of MOR and LOP to those ones reinforced with organosolv + PP fibres.

Toughness is often correlated to the length of reinforcing fibre especially in the case of short fibre with length below the critical length. As the stress is transferred from the matrix to the fibre, debonding can take place at the interface and the fibre may be pulled out through the matrix, generating considerable frictional energy losses, which contribute to toughness[3]. At 28 days of cure, the refined kraft pulp provided higher values of toughness and also higher values of MOR than organosolv pulp. Organosolv fibres seem to be weaker than kraft fibres as the pull-out of the organosolv fibres was decreased. Composites reinforced with only organosolv pulped sisal also provided lower toughness than composites reinforced with unrefined kraft pulp according to previous work[29]. Young[37] suggested that, in general, the strength properties of organosolv pulps are inferior to those of corresponding kraft pulps, what may be related with the great amount of polyoses solubilized[38]. There may be significant contribution to the decay of

the reinforcement capacity with the consequent fragile behaviour of the composite.

After ageing, since the cellulose fibres are more adhered to the matrix, the fracture prevails (Figure 7) over the pull out inasmuch as the toughness decreases for samples with only sisal pulps.

Figure 8 presents the stress-strain curves of the composites according to the use of sisal organosolv and kraft pulp for samples without and with polypropylene respectively. The area below the stress-strain curves is related to the absorbed energy by the composites.

Toughness was greatly improved with the addition of PP fibres. The length of the PP fibres (6 mm), higher than sisal pulp fibres, and its intrinsic properties (tensile strength = 300 MPa and modulus of elasticity = 3.3 GPa), which do not adhere very well to the matrix in the initial ages, contribute to the enhancement of the composite toughness. The improvement of toughness with the addition of PP fibres is also related with the absence of fibrillation, favouring poor anchoring to the matrix and considerable incidence of pulled out fibres (Figures 9a and 9b).

The 100 ageing cycles decreased the toughness of both noncarbonated and fast carbonated composites with kraft pulp + PP fibres. Accelerated carbonation seems to be effective in the maintenance of the toughness of the composites with sisal organosolv pulp combined with PP fibres after ageing.
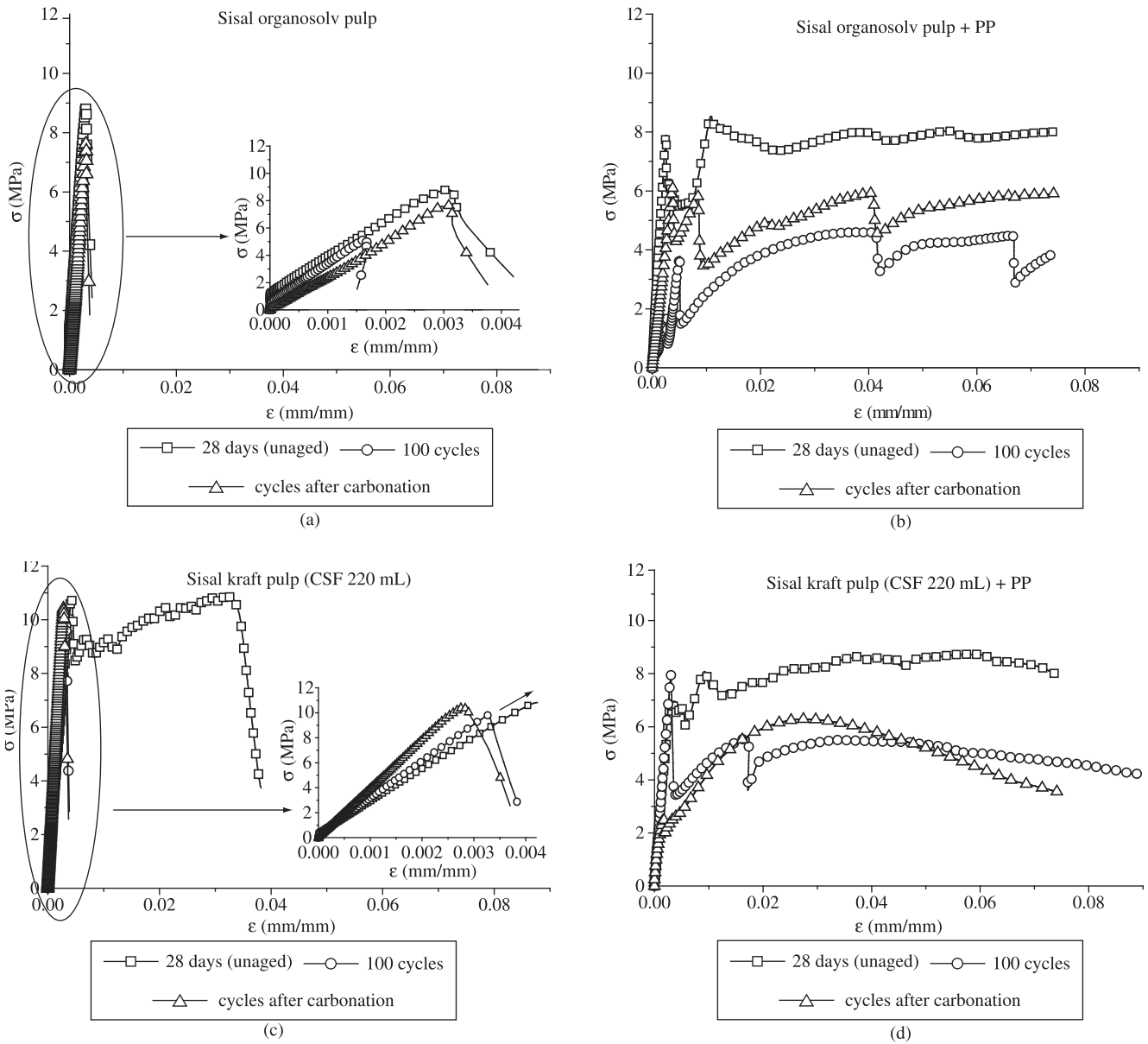
Figure 8. Stress-strain curves for composites with different reinforcing fibres at 28 days and after 100 cycles with/without fast carbonation: a) sisal organosolv pulp; b) sisal organosolv pulp with polypropylene fibres; c) sisal kraft pulp and d) sisal kraft pulp with polypropylene fibres.
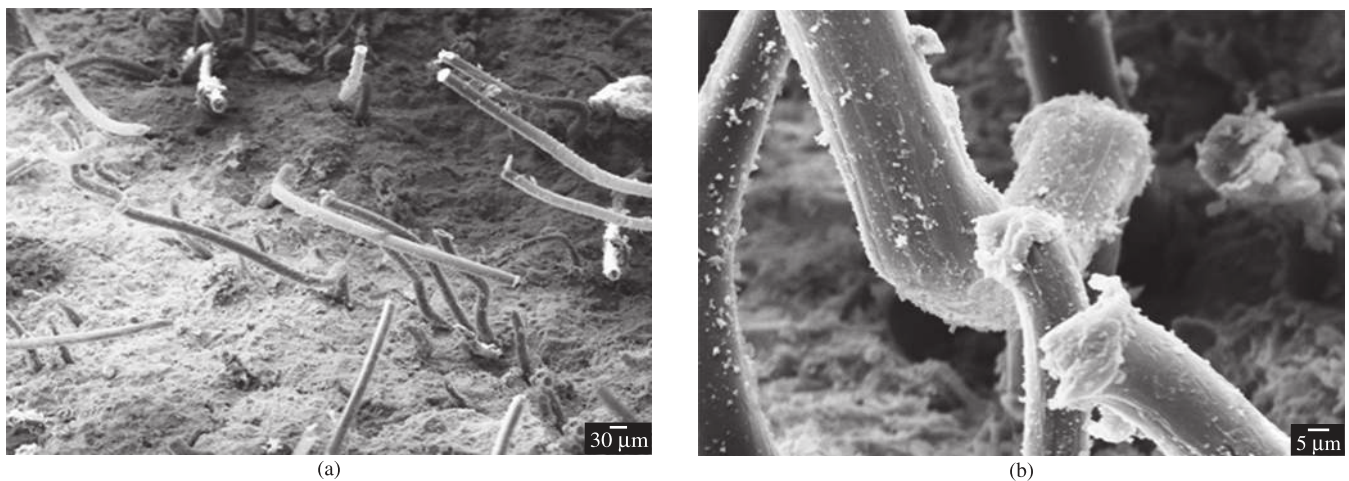

Figure 9. SEM of fracture surface of composites after 100 soak/dry cycles: a) and b) sisal organosolv pulp + PP fibres.

4. Conclusions

Studies concerning pulping time showed that 2 hours reaction has furnished a good result for delignification and 3 hours reaction was considered more than necessary. Sisal organosolv pulp (unre-fined) produced from residues of cordage industry presented smaller and thicker individual fibres than unrefined sisal kraft pulp. These properties had a good influence in physical properties of the compos-ites, since sisal organosolv pulp composites presented lower water absorption and apparent voids volume than composites reinforced with sisal kraft pulp.

In general the composites reinforced with refined kraft pulp have presented higher values of MOR, LOP and toughness. However, the performance of the sisal organosolv reinforced composites can be improved, once the pulping process is not well adapted for the production of this kind of material, differently of the fibre-cement with kraft pulp, which has been extensively studied and developed as reinforcement in cement based matrix.

Sisal organosolv pulp composites after 100 ageing cycles (with-out fast carbonation) presented lower water absorption and apparent voids volume than composites reinforced with sisal organosolv + PP fibres. Also, the density of the polypropylene (PP) fibres and the poor packing of the particles with this long fibres provided lower density to the respective composites. Accelerated carbonation promotes densification of the composites and has maintained the resistance of the composites reinforced with refined sisal kraft pulp and of the composites reinforced with sisal organosolv + PP fibres.

The highest toughness was found with the addition of polypropyl-ene fibres in the mixture. Polypropylene fibres are poorly adhered to the cement matrix, favouring insufficient anchorage and considerable incidence of pull out.

This work is part of a more comprehensive project dedicated to the development of asbestos free formulations applied to fibre-cement products to meet the needs of emerging countries. The tailoring of these non-conventional composites includes not only the optimization of the cellulose pulp from available raw materials but also the selection of adequate formulations and processes in the fibre-cement production. The obtained results bring encouragement to the continuation of the ongoing research with the compromise between physical and mechanical performance of the composite and its cost of production.

Acknowledgments

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