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Surface modification of banana-based lignocellulose fibres

NEREIDA CORDEIRO,^{1,*} LÚCIA OLIVEIRA,¹ HELENA FARIA,¹
MOHAMED NACEUR BELGACEM² and JOÃO C. V. P. MOURA³

¹*Centro de Estudos da Macaronésia, Universidade da Madeira, 9000-390 Funchal, Portugal*

²*LGP2, Ecole Française de Papeterie et des Industries Graphiques, BP65,
38402 St Martin D'Hères, France*

³*Departamento de Química, Universidade do Minho, 4700-320 Braga, Portugal*

Abstract—Lignocellulosic raw materials were isolated from rachis of *Musa acuminata* Colla var. *cavendish* and characterised before and after chemical modification. The rachis was submitted to different mechanical treatments, milling and defibration, resulting in rachis powder and rachis fibres, respectively. The chemical composition of these two samples was established and it was shown that rachis fibres exhibited higher polysaccharide and lignin contents and lower amounts of ash and extractives components, as compared with the rachis powder. The effects of solvent extraction, alkali treatment and chemical modification using phenyl isocyanate, maleic anhydride, alkenyl succinic anhydride and alkyl ketone dimer as grafting agents were studied. The materials were characterized in terms of chemical structure by ATR–FT-IR and ¹³C-CP-MAS-NMR spectroscopy, morphology by scanning electron microscopy and surface energies by inverse gas chromatography and contact angle measurements. The surface energy of these materials was found to be very close to other similar lignocellulosic materials. Finally, the water absorption of these materials before and after treatment was ascertained. The modified fibres showed considerable changes in ATR–FT-IR and ¹³C-CP-MAS-NMR spectra and surface properties, providing very convincing evidence that chemical grafting had occurred.

Keywords: “Dwarf Cavendish”; banana plant; rachis fibres; surface modification; morphology characterization; surface properties.

1. INTRODUCTION

The use of lignocellulosic fibres as a reinforcing agent in composite materials has spurred renewed interest recently, as evidenced by numerous publications from various laboratories and reviews [1–4]. The incorporation of these natural fibres into polymeric matrices has been shown to be interesting, because of the certain excellent characteristics of these fibrous materials, such as their good mechanical properties, wide availability directly from numerous vegetal species, renewable

*To whom correspondence should be addressed. Tel.: (351-29) 170-5107;
Fax: (351-29) 170-5149; e-mail: ncordeiro@uma.pt

character, low density compared with, for example, glass fibre, and their low cost in most instances [1–4].

The quality and the suitability of a composite material obviously depend on the appropriate choice of its two basic components (matrix and fibre), depending on specific applications envisaged for it. Thus, in order to prepare high-performance composite materials, one should ascertain the properties of each constituent.

Cellulose-based composites are gaining increasing interest because of the many advantages of this renewable natural polymer. Moreover, recycling of such composites is much easier to accomplish when compared to glass-fibre-based counterparts. Cellulose is a very highly polar macromolecule, which makes it poorly compatible with non-polar matrices commonly used for composite materials. Moreover, this hydrophilic character induces high affinity for water molecules in the surrounding atmosphere, which negatively affects the mechanical properties and the dimensional stability of the resulting materials. These are the main reasons for submitting cellulose to chemical modification before its incorporation into a given matrix. In the literature, many different approaches are documented for treating cellulosic material to make it compatible with common matrices. These approaches were recently reviewed [5].

The island of Madeira currently has a reduced forest area of pine and eucalyptus; nevertheless, it has an extensive area of banana plants. After harvesting the bunch of bananas from each plant, the pseudo-stems are cut giving rise to large amounts of agricultural waste. Before commercialisation, the rachis is cut from the bunch of banana, which is presently unused and is an undesirable waste. In this context, we recently started a research program to investigate banana plant as a source of lignocellulosic fibres, in view of its value as a renewable resource for papermaking [6, 7] and composites fabrication [8].

Here we present the main bulk and surface properties of the fibrous materials studied, in order to predict their suitability for composite preparation and to help in the choice of the appropriate matrix or in the selection of the most suitable chemical modification for a given combination. In this study we have carried out chemical modification of the surface of the banana plant derived fibrous material, using mono-functional molecules, with a view to use the modified banana rachis with polymeric matrices such as polypropylene, styrene–butadiene latex, or polyethylene. Thus, chemical modification of rachis and rachis fibres from banana plants was carried out and the resulting modified fibres fully characterised.

2. MATERIALS AND METHODS

2.1. Lignocellulosic material

Rachis was harvested from mature banana plants *Musa acuminata* Colla var. *cavendish* in Funchal, Portugal and kindly supplied by Cooperativa Agrícola dos Produtores de Fruta da Madeira. Two kinds of material were used: (i) the raw ma-

terial (labeled rachis) and (ii) mechanically isolated fibres of rachis obtained from a prototype defibration machine (labeled rachis fibres).

After air-drying for two weeks, the samples were milled and sieved to 40–60 mesh fractions, in order to determine their chemical composition.

2.2. Chemical composition

The ash content was determined by calcination at 600°C for 6 h. The different materials were extracted in a Soxhlet extractor for 8 h sequentially with n-hexane, dichloromethane, ethyl acetate, ethanol and water. The lignin content was determined by Klason's method according to Tappi standard T222 om-88. The holo-cellulose content was quantified by the peracetic acid method [9] whereas the cellulose content was determined by the Kurschner–Hoffner procedure [9]. In order to obtain the respective amounts of hemicelluloses A and B and cellulose, holo-celluloses were submitted to fractionation by extraction with KOH under a nitrogen atmosphere as described elsewhere [10]. All chemical analysis and fractionation experiments were carried out, at least, in duplicate.

In alkali treatment the material was dipped in 2% and 10% aqueous solutions of NaOH for 30 min and washed in a very dilute hydrochloric acid to remove the unreacted alkali. Washing continued until the fibres were alkali free. The washed fibres were then dried in an oven at 70°C for 3 h.

2.3. Chemical modification

For grafting reactions the samples were thoroughly dried in vacuum at 80°C for 3 days before carrying out surface modification. They were then placed in dry toluene under a nitrogen atmosphere at 80°C and the grafting agents (Fig. 1), phenyl isocyanate (PI) and maleic anhydride (MA) (commercial high purity products); alkenyl succinic anhydride (ASA) and alkyl ketone dimer (AKD) (industrial products), were added, in large excess, and stirred under reflux in an inert atmosphere. In the reaction with PI a small amount of triethylamine was used as a catalyst (1% of the added NCO). The suspensions were left under magnetic stirring to complete the reaction, i.e., at least for 10 days under reflux, taking particular care to prevent any spurious inlet of moisture [11].

The treated lignocellulosic materials were then recovered by filtration and washed with dichloromethane. In order to eliminate all the ungrafted species, the modified materials were submitted to exhaustive Soxhlet extraction for 48 h using methylene chloride. Then the materials were dried at 40°C. The modified products were characterized by spectroscopic, morphological and surface energy methods, in order to evaluate the efficiency of these modifications.

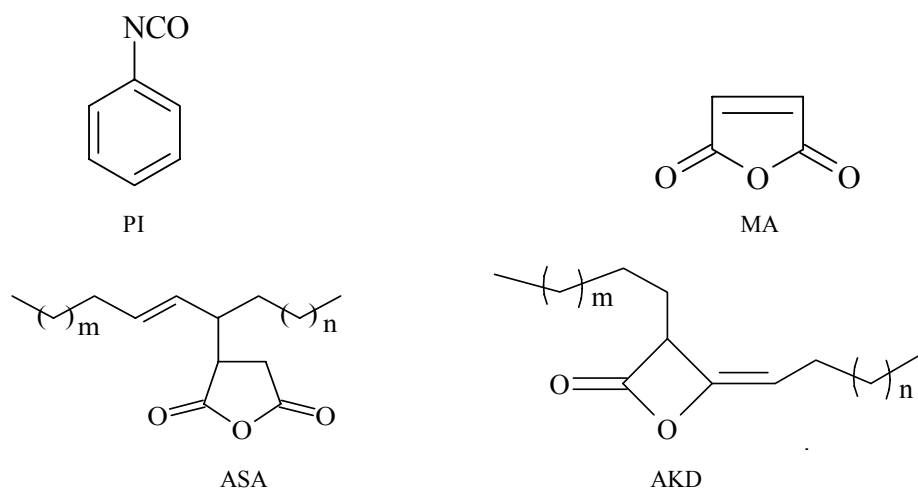


Figure 1. Structures of grafting agents: phenyl isocyanate (PI), maleic anhydride (MA), alkenyl succinic anhydride (ASA); alkyl ketone dimer (AKD).

2.4. Characterization of the modified samples

ATR spectra were obtained on a Bruker IFS 55 spectrophotometer equipped with a horizontal micro-ATR Golden Gate unit (SPECAC). Solid-state ^{13}C -NMR spectra were recorded at 100.6 MHz (9.4 T) on a Bruker MSL-400 spectrometer.

The surface morphology of the materials was analysed by scanning electron microscopy (SEM) using a Jeol JSM-6100 microscope.

Inverse gas chromatography was performed using an HP 5890 Series II chromatograph equipped with a flame ionisation detector and a 100 cm \times 4 mm stainless steel column. The practical details as well the calculation methods and the probes used were reviewed recently [12]. Contact angles were measured with a home-made apparatus designed to acquire up to 200 images per second as described in a previous publication [13].

The water absorption was determined for lignocellulosic materials. A minimum of three samples were tested for each material. After drying overnight at 70°C, the samples were cooled and weighed, and then stored at 25°C. The water absorption in the samples was determined by conditioning the sample in a high moisture atmosphere. The samples were stored at 25°C in desiccators containing sodium sulphate to ensure an atmosphere with RH of 98%. The samples were removed at specified intervals and weighed using a four-digit balance. The water absorption (WA) was determined using equation (1):

$$\text{WA (\%)} = \frac{(M_t - M_0)}{M_0} \times 100 \quad (1)$$

where: M_t and M_0 are the weights of the sample after exposure to 98% RH atmosphere for time t and before exposure, respectively.

3. RESULTS AND DISCUSSION

3.1. Chemical characterization

The quantitative results on the chemical composition of “Dwarf Cavendish” rachis samples are shown in Table 1, from which several remarks can be made when rachis and rachis fibres are compared. A high amount of ashes (*ca.* 48%) is extracted during rachis defibration, as confirmed by the decrease of the ash content in rachis fibres (Table 1). The ash content of rachis is quite high when compared to other fast growing plants [14–17]. However, the ash content of rachis fibres is similar to that obtained, for example, for the stalk fibre of rice straw (15–20%) [15]. The extractives content for rachis (18.1%) is similar to those obtained for other fast growing plants [14–17]. The defibration process reduced the extractives content. Lignin was found in a slightly higher amount in rachis fibres (11.8%) than in rachis (10.5%). The high lignin content indicates that the mechanical treatment did not extract any appreciable amount of lignin, as expected due to the high molecular weight and cross-linked character of this macromolecule. The low lignin content is a good feature, since it does not contribute as well as do cellulose macromolecules in the mechanical performance of these fibres.

Holocellulose and cellulose contents were found to be higher in rachis fibres than in rachis (Table 1). The cellulose content of the rachis fibres (56.1%) is in agreement with that reported for other stalk fibres (43–66%) [15]. These results can be explained in terms of significant removal of ashes and extractives in the juice plant during the defibration process. Hemicelluloses and cellulose contents differ significantly for these two materials. Cellulose was the major component of holocelluloses, representing *ca.* 77 and 75% for rachis fibres and rachis, respectively. The cellulose content of rachis fibres (51.5%) is quite high when compared with the values obtained for other stalk fibres (26–45%) [15]. The hemicelluloses

Table 1. Chemical composition (% in dry material) of rachis and rachis fibres of “Dwarf Cavendish”

Component	Rachis	Rachis fibres
Ash	26.8	14.0
Extractives ^a	18.1	10.2
Lignin ^a	10.5	11.8
insoluble	9.6	11.1
soluble	0.9	0.7
Holocellulose ^a	41.8	67.0
Cellulose	31.5	51.5
Hemicellulose A	4.3	8.5
Hemicellulose B	4.0	6.2
Cellulose ^a	34.9	56.1

^a Corrected for ash content.

content in rachis fibres was higher than that of the starting rachis, probably because of the extraction procedure. In order to confirm the above arguments, the analysis of the extracted juice during defibration is in progress.

3.2. Spectroscopic characterization

Figures 2 and 3 show the ATR-FT-IR spectra of the rachis and rachis fibres, before and after solvent extraction. All these spectra are characterised by common features, namely (i) a strong band around 3400 cm^{-1} , attributed to hydrogen-bonded -OH stretching vibration; (ii) a band at *ca.* 2900 cm^{-1} due to CH stretching vibration of aliphatic moieties; (iii) a peak near 1250 cm^{-1} associated with C-C, C-O and C=O stretchings in the lignin; and (iv) a prominent band in the range $1200\text{--}900\text{ cm}^{-1}$, attributed to the presence of polysaccharides. The high intensity of this band in all samples shows that polysaccharides are present in large amounts. The absorptions at 1157 and 1033 cm^{-1} are attributed to the C-O-C and C-O stretchings in polysaccharides, respectively, whereas the C-H deformation in cellulose can be seen at 898 cm^{-1} .

Nevertheless, some peaks are present only in the rachis (Fig. 2a and 2b), namely those near 1731 and 1600 cm^{-1} . The signal of the non-cellulose components at 1731 cm^{-1} is characteristic of the carboxyl-containing substances present in extractives, such as fatty acids widely present in the rachis [10]. The peak at

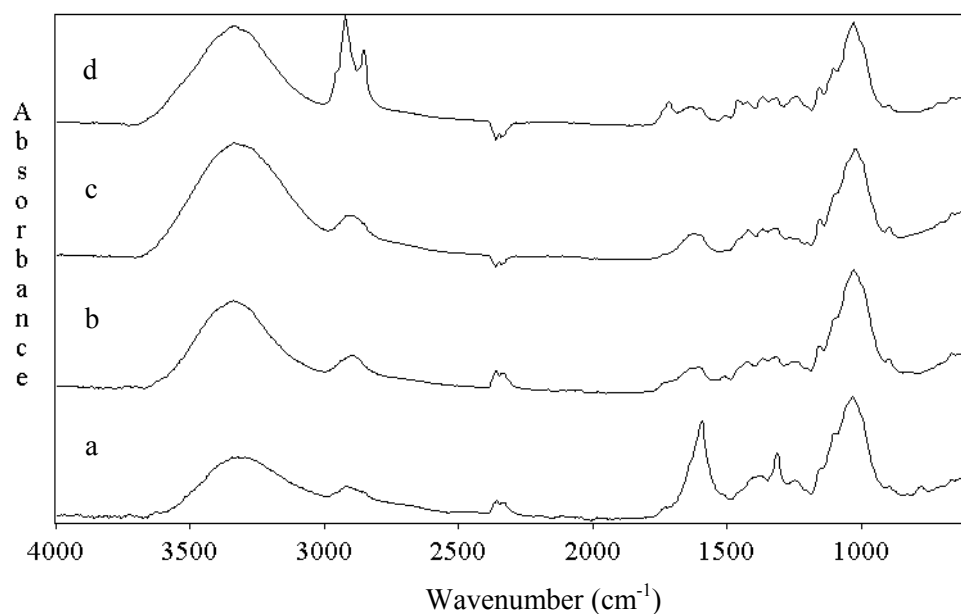


Figure 2. ATR-FT-IR spectra of (a) rachis, (b) extracted rachis, (c) rachis treated with 10% NaOH, and (d) rachis chemically modified with AKD.

1600 cm^{-1} can be assigned mainly to the C=C bond of extractives and appears with much more pronounced intensity in the rachis spectrum, before extraction (Fig. 2a). In the ATR-FT-IR spectra of rachis fibres the signals attributed to extractives decreased significantly after the defibration process (Fig. 3Ia). This is in agreement with the results obtained for the chemical composition (Table 1). The ATR-FT-IR spectrum of rachis before extraction presents also some differences in the region of 1500–1300 cm^{-1} due to extractives removal (Fig. 2b).

The ATR-FT-IR spectrum of the rachis submitted to alkali treatment with NaOH is shown in Fig. 2c. The spectrum of the treated rachis with 2% NaOH (not presented here) was very similar to that of the extracted material, which indicates that even a small alkali concentration is capable to extract high quantities of extractives and ashes. The increase of NaOH to a level of 10% (Fig. 2c) caused disappearance of the C=O band at *ca.* 1739 cm^{-1} . However, high amounts of polysaccharides were removed with 10% NaOH solution, as seen from the weakening of the band at 1200–900 cm^{-1} .

The occurrence of chemical modification of the samples, when submitted to reactions with grafting agents was verified by ATR-FT-IR spectroscopy, as illustrated in Figs 2 and 3. Despite the chemical modification taking place mainly on the material surface, some changes were detected in the ATR-FT-IR spectrum of the extracted fibres, namely, two peaks at 1720 cm^{-1} and 1540 cm^{-1} , characteristic of the carbonyl groups, with higher intensity in the case of MA-modified fibres, and NH moieties of the urethane group (R–O–(CO)–(NH)–) in the case of PI-modified materials. This observation is also verified by the ATR-FT-IR spectroscopy for PI-, MA- and ASA-modified unextracted as well as extracted material. In all these cases, the chemical modifications were more pronounced in the extracted material as compared with the non-extracted one. Figure 2d shows a significant alteration in the ATR-FT-IR spectrum of the AKD-modified original

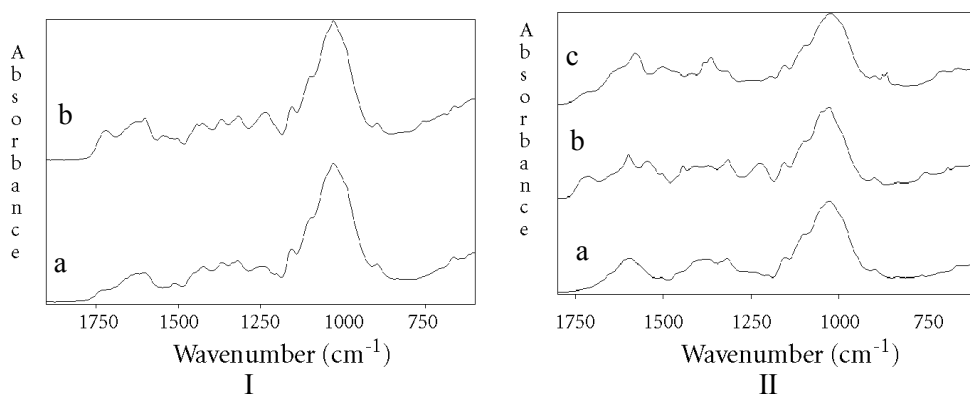


Figure 3. ATR-FT-IR spectra of **I:** (a) extracted rachis and (b) extracted rachis chemically modified with PI; **II:** (a) rachis fibres and rachis fibres modified with: (b) MA and (c) ASA.

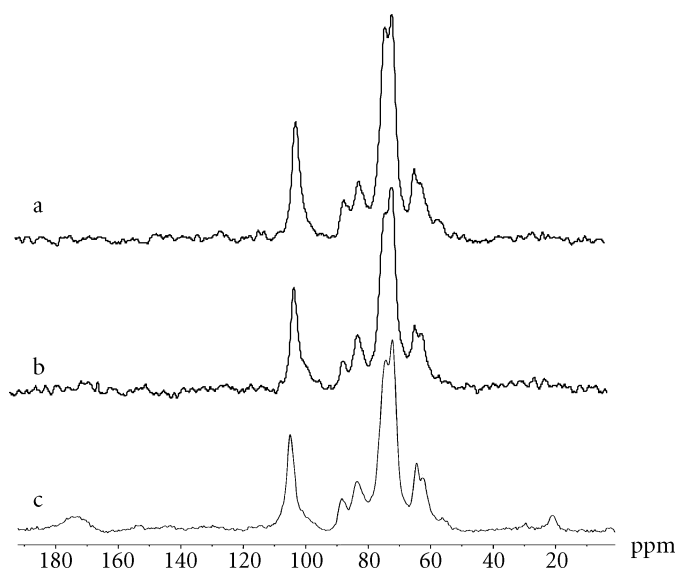


Figure 4. ^{13}C -CP-MAS-NMR spectra of (a) rachis fibres, (b) rachis and (c) rachis modified with ASA.

rachis, namely the intensity increase of the peaks at 2922 and 2851 cm^{-1} attributed to the aliphatic moiety of AKD and the appearance of three strong peaks at 1720 , 1460 and 1370 cm^{-1} characteristics of the carbonyl and CH groups.

^{13}C -CP-MAS-NMR spectra of rachis and rachis fibres are shown in Fig. 4. The main difference is with respect to the peak of methoxy at 56 ppm , attributed to the presence of both hemicellulose and lignin, which was stronger in the rachis fibres (Fig. 4a). This fact can be explained by the removal of high amount of components, principally extractives, during the defibration process (Table 1). The peaks between 61 and 105 ppm , which arose from the overlapping signals of carbohydrates and lignin aliphatic carbons, are very similar in both spectra. However, different relative intensities of the signals at 62 , 74 and 88 ppm in rachis fibres spectrum suggested that during the defibration process some sugars were extracted. The sugar analysis [10] showed that the predominantly removed sugars were glucose-containing.

The occurrence of chemical modifications in rachis can also be observed by ^{13}C -CP-MAS-NMR. As an example, in Fig. 4c is presented the spectrum of the modified rachis with ASA. As expected, two signals appear in the rachis spectrum after reaction with ASA: one signal at 21 ppm characteristic of the aliphatic moiety of the grafting agent and a large signal at 175 ppm , indicative of the presence of the carbonyl groups.

3.3. Morphological characterization

The cross-sectional and longitudinal views of rachis, before and after extractives removal, are shown in Figs 5 and 6. The original rachis showed some irregularities and defects (Fig. 5a–c) at the surface of the fibres, which does not allow observation of fibrillar structure of the material in longitudinal view. However, in cross section we see that original rachis has a circular and fibrillar structure

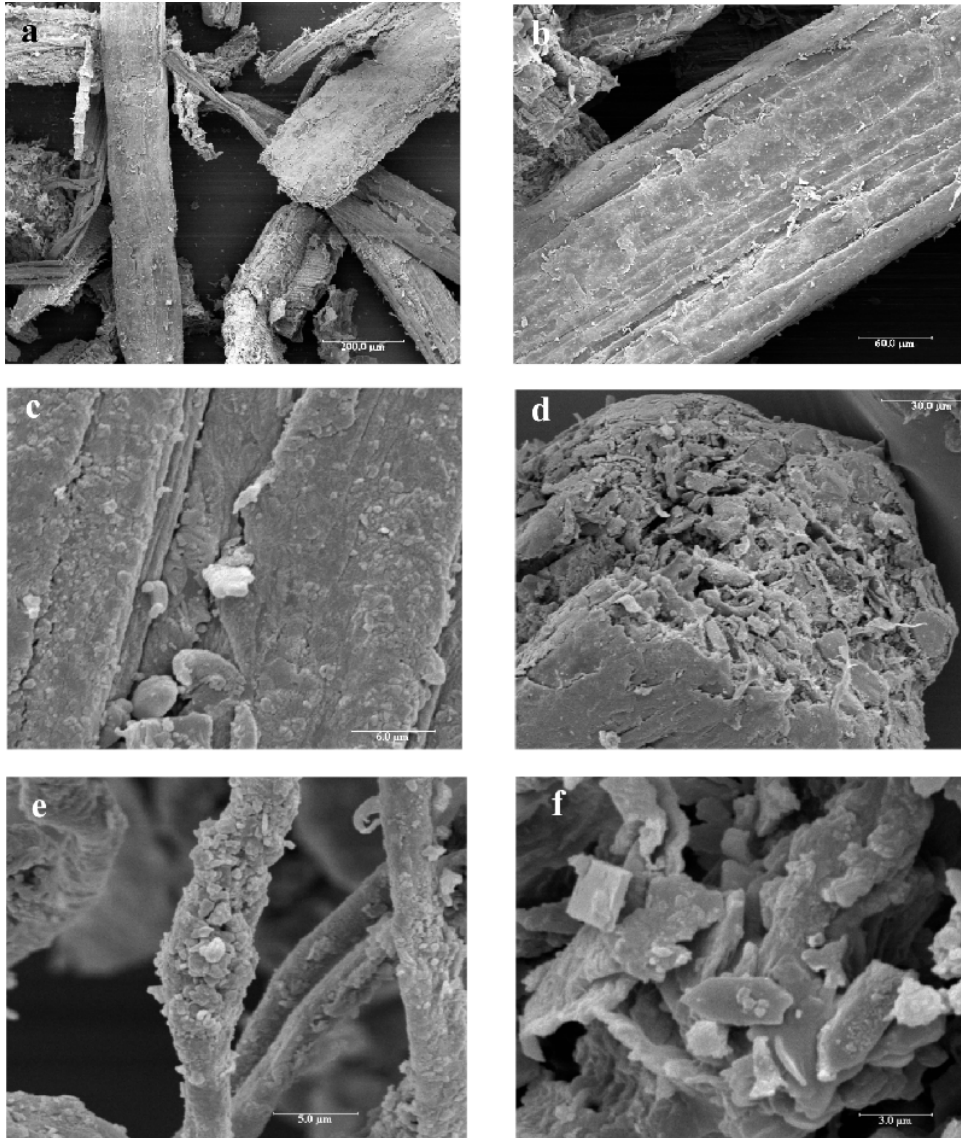


Figure 5. SEM micrographs of rachis: (a) 80×; (b) 300×; (c) 3500×; (d) 600×; (e) 3000×; (f) 6000×.

(Fig. 5d). Particular attention should be paid to Fig. 5e and 5f, which show very well organised mineral crystals in rachis. Mineral elemental analysis revealed the presence of different constituents, mainly potassium, calcium and silicon [10].

The location of these minerals was studied and it was found that they were grown not only at the surface of the fibres, but also inside the channels, which

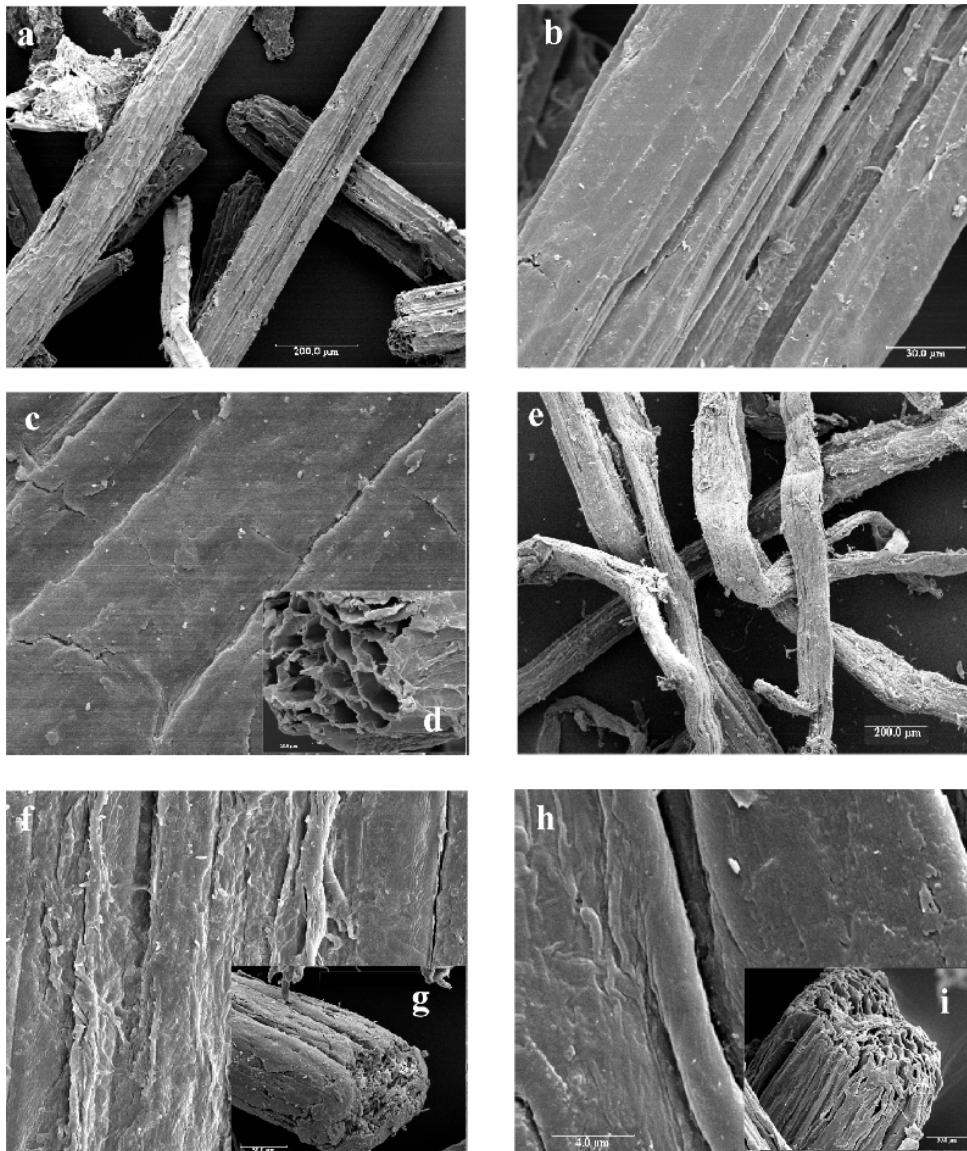


Figure 6. SEM micrographs of extracted rachis (a) 80 \times , (b) 600 \times , (c) 1500 \times , (d) 1500 \times ; rachis fibres (e) 80 \times , (f) 1500 \times , (g) 600 \times ; extracted rachis fibres (h) 4000 \times , (i) 600 \times .

explains that even after exhaustive water extraction, a significant amount of ashes remained in the material [10]. After extraction (Fig. 6), the rachis surface became smoother, displaying a multi-layer organisation (Fig. 6b, c). A large number of surface cracks, or pit formations, were observed when compared to virgin samples. These cracks might occur because of the partial removal of wax or fatty substances. The cross-section of the extracted rachis shows that the extraction removed a high amount of wax or fatty substances leaving a tubular structure (Fig. 6d).

The rachis fibres were also investigated by SEM (Figs 6e to 6i) and showed similar features as those found for rachis, except for two main differences: (i) fibres seem to be thinner than in the rachis (Fig. 6a and 6e), due to compression during the defibration process and (ii) the surface of fibres shows a fibrillar structure of this material, which indicates that defibration removed a significant amount of components, principally ash, as observed previously from the chemical composition data (Table 1).

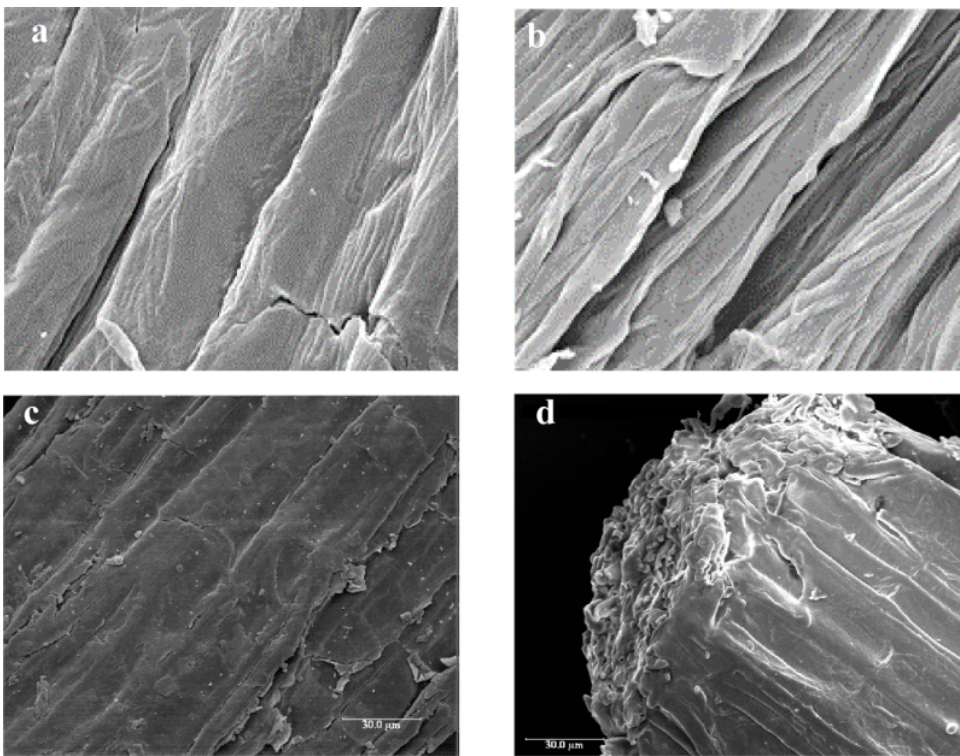


Figure 7. SEM micrographs of rachis treated with: (a) 2% NaOH, 4000 \times ; (b) 10% NaOH, 4000 \times ; (c) ASA, 600 \times ; (d) AKD, 600 \times .

The rachis extracted with different alkaline solutions was also analysed by SEM (Fig. 7a and 7b). Micrographs of the two samples confirmed the ATR-FTIR observations, i.e., the use of a higher concentration of NaOH was more efficient in the components removal, where the border between individual fibres can be easily observed in the extracted rachis with 10% NaOH (Fig. 7b). Similar observation was also made in rachis extracted with 2% NaOH, but to a smaller extent.

Alkali treatment induced extraction of the carbohydrate–lignin complex and led to breaking down of the composite fibre bundle into smaller fibres by breaking linkages between the constituents in the cell wall. This increase of the surface area available for contact with the polymeric matrix will play a beneficial role. In other words, alkali treatment reduces the fibre diameter, enhances the development of surface roughness, which, in principle, will offer better fibre–matrix interface adhesion and, consequently, higher mechanical properties.

Finally, the SEM micrographs of the materials showed the presence of longitudinally-oriented unit cells with more or less parallel orientations. The intercellular spaces are probably filled up by cellulose macromolecules, hemicellulose as a compatibiliser, and lignin as a binder.

The SEM micrographs of the grafted materials did not show significant differences, principally in cases of PI and MA agents (small molecules). In the ASA and AKD cases the surface of the material showed a slight coverage (Fig. 7c and 7d, respectively).

3.4. Surface characterization

The surface characterization of the samples was carried out by using the IGC technique. The excellent linearity relative to n-alkane probes provides a reliable method for the calculation of the dispersion component of the surface energy of the samples. With this method, the dispersion component of the surface energy, γ_s^D as a function of temperature was obtained, as summarised in Table 2. The relative retention of the characteristic acidic (chloroform) and basic (tetrahydrofuran) probes provided an estimate of the Lewis acid–base properties of the surfaces and is reflected by the ratio K_a/K_b (acidic and basic parameters, respectively [18]).

Table 2 shows that both the dispersion component and acidic character (K_a/K_b ratio) of surface energy in extracted materials were higher than for original material. These could be attributed to the high amount of extractives removal (with high percentage of ashes), which increases the dispersion component of surface energy and makes the lignocellulosic –OH groups more accessible, increasing the acidic character. Similar results were previously reported for other lignocellulosic materials [19–21]. The mechanical defibration increased the dispersion component of surface energy and the K_a/K_b ratio.

The chemically-modified materials showed that grafting increased the dispersion component of surface energy in particular in the case of AKD. The observed increase of K_a/K_b ratio can be attributed to the introduction of nucleophilic sites

Table 2.

Values of the dispersion component of surface energy, γ_S^D , at different temperatures, K_a/K_b ratio, obtained by IGC, and water contact angles ($^\circ$) at 25 $^\circ$ C

Sample	Grafting agent	γ_S^D (mJ/m ²)			K_a/K_b	Contact angle ($^\circ$)
		60 $^\circ$ C	70 $^\circ$ C	80 $^\circ$ C		
Rachis						
original	None	34	31	29	0.7	71
	Phenyl isocyanate	38	36	34	1.7	67
	Maleic anhydride	38	35	33	2.4	56
	ASA	42	38	32	1.9	72
	AKD	40	39	37	0.5	85
extracted	None	40	34	29	3.7	69
	Phenyl isocyanate	44	40	35	1.8	63
Rachis fibres						
original	None	35	31	27	0.9	71
	Phenyl isocyanate	40	36	32	2.1	73
	Maleic anhydride	38	35	32	3.1	63
extracted	None	41	38	31	2.2	46
	Phenyl isocyanate	54	49	40	2.2	72
Rachis treated with 10% NaOH				n.d.		50
Cellulose from rachis fibres				n.d.		37

n.d., not determined.

by the urethane, ester and acid moieties resulting from the grafting reaction. Thus, a higher K_a/K_b ratio for MA and a smaller value for AKD (due to the long aliphatic chain) are observed.

The γ_S^D values for the materials under study were found to be close to those reported in the literature for similar materials. For example, the Avicell cellulose before and after purification had values of 38 and 42 mJ/m², respectively, and after modification with ASA the values did not change significantly (41–43 mJ/m²). In the case of Whatman paper before and after treatment with AKD, the K_a/K_b ratios were 1.6 and 0.7, respectively [20, 21].

The contact angles on the rachis fibres were measured with five different liquids, in order to determine both the dispersion and polar components of surface energy of these materials according to the Owens–Wendt method [22]. The evolution of contact angles for different liquids used with time for rachis fibres is shown in Fig. 8. The calculated total surface energy of rachis fibres gives a value of 41 mJ/m², with 33 and 8 mJ/m² for γ_S^D and γ_S^P , respectively. The dispersion

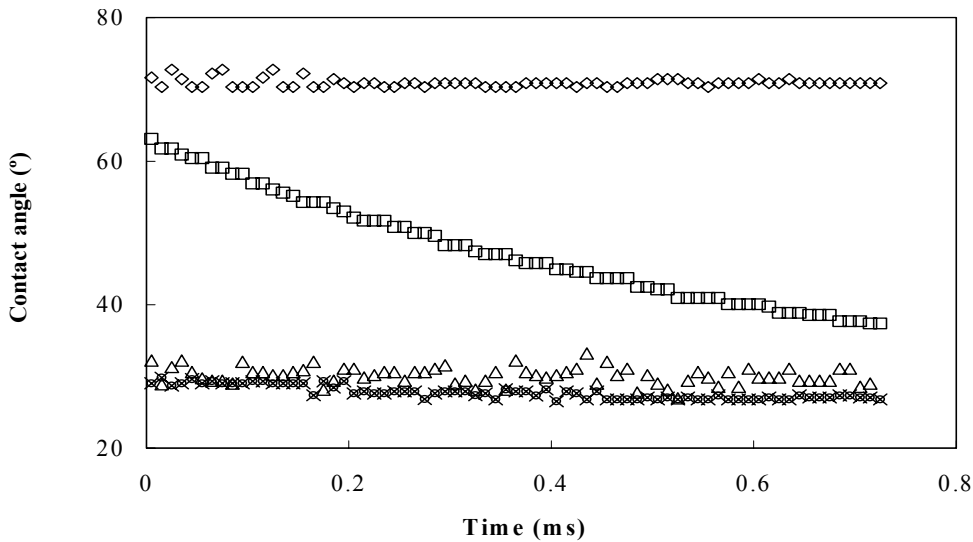


Figure 8. Variation of contact angle as a function of time for various liquids on rachis fibres: (\diamond) water; (\square) formamide; (Δ) diiodomethane; (\circ) bromonaphthalene; ($+$) hexadecane.

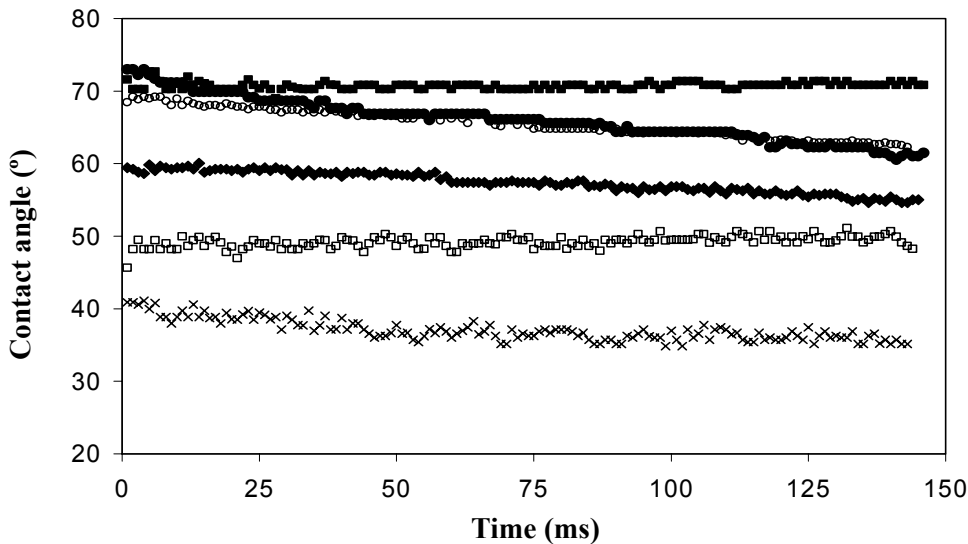


Figure 9. Short-time evolution of water contact angles on the surfaces of: (\bullet) rachis; (\circ) extracted rachis; (\blacklozenge) rachis treated with 10% NaOH; (\blacksquare) rachis fibres; (\square) extracted rachis fibres; (\times) cellulose from rachis fibres.

component of the rachis fibres was lower than that obtained by IGC (44 mJ/m^2 at 25°C), as already observed by different authors [18, 20, 21, 23].

The contact angles of water drops deposited on the surface of the investigated materials are presented in Table 2 and Fig. 9. We can remark that the extracted materials seem to be most capable of establishing hydrogen bonds (high hydrophilicity) since they have the lowest initial contact angle. This could be attributed, as referred above, to the removal of the compounds from the surface of the material, which makes the fibre more exposed (as observed by SEM micrographs) and, consequently, the $-OH$ groups of cellulose fibres are more accessible.

The surface of rachis treated with NaOH has a lower value of θ . This is due to the higher extraction of the components from the surface of fibres (as shown in Fig. 7a and 7b), which is also found for other alkali-treated cellulose fibres [24].

As expected, the rachis fibres (high content of cellulose) have a smaller water contact angle. The water contact angle decreases by 35% for rachis fibres after a simple extraction. This could indicate that defibration process made the hydrophilic component present in the surface of the material more accessible for extraction.

The values of water contact angle for chemically modified materials are also given in Table 2 and Fig. 10. We can remark that, in general, the contact angles of water decrease in the case of reaction with MA, due to the presence of new acid groups on surface of the material. In the case of the surface modified with ASA and AKD the contact angles have higher values due to the presence of non-polar long aliphatic hydrophobic chains (lower density of polar groups). This effect is more pronounced in the case of AKD, because its aliphatic chains are saturated and longer.

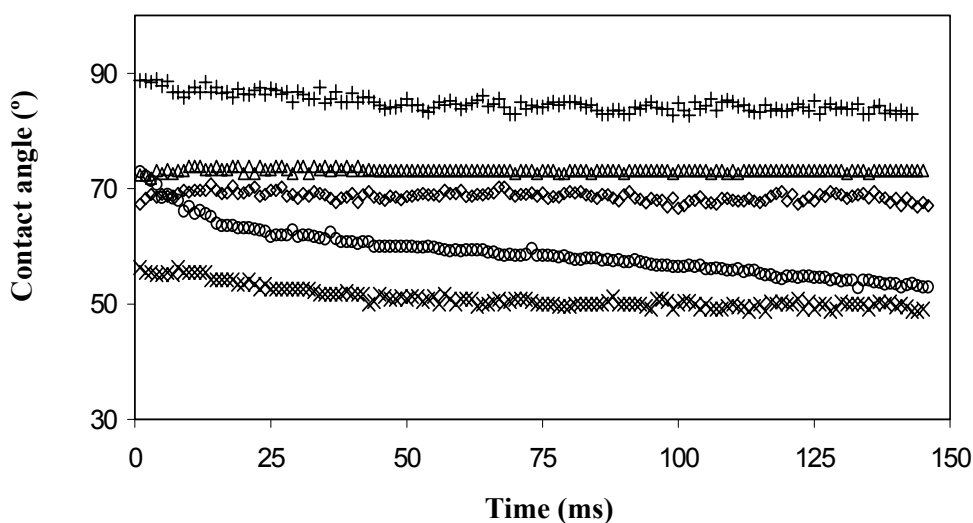


Figure 10. Short-time evolution of water contact angles on the surfaces of (○) rachis and rachis modified with: (◇) PI; (×) MA; (Δ) ASA; (+) AKD.

3.5. Water absorption

The samples were conditioned in a high moisture atmosphere (98% RH). The water absorption of rachis and rachis fibres, before and after extraction, as a function of time, was evaluated as presented in Fig. 11 and Table 3. These absorption data are means of several trials, and reliability of measurements was very good.

The first remark is that all samples absorbed water during the experiment. The second remark is the existence of two well-separated regions: region I at shorter times, where the kinetics of absorption was fast, whereas at extended times the kinetics of absorption slowed down and reached a plateau, i.e., region II. Region II corresponds to equilibrium water absorption. The initial absorption of water results in hydrogen bonds with the remaining $-OH$ groups on the material surface and increases until it reaches a point of saturation. In general, in the materials studied the rate of water absorption was high during the first 16 h, and after that it decreased. An exception was observed for the unextracted materials, where the equilibrium was reached at longer times (*ca.* 75 h), probably because of the presence of extractives (wax or fatty substances), which made water penetration difficult into the material. The water absorption at equilibrium is presented in Table 3.

The extracted materials show two times less absorption of water than the respective original materials. These observations are in apparent discord with the water contact angles, which decrease with the extraction. The same contradiction is observed for alkali-treated material. However, if on the one hand the water absorption is dependent on the polar component in the material; on the other hand, the compressed or more crystalline material makes water diffusion difficult, consequently the water absorption decreases. The effect of compression or

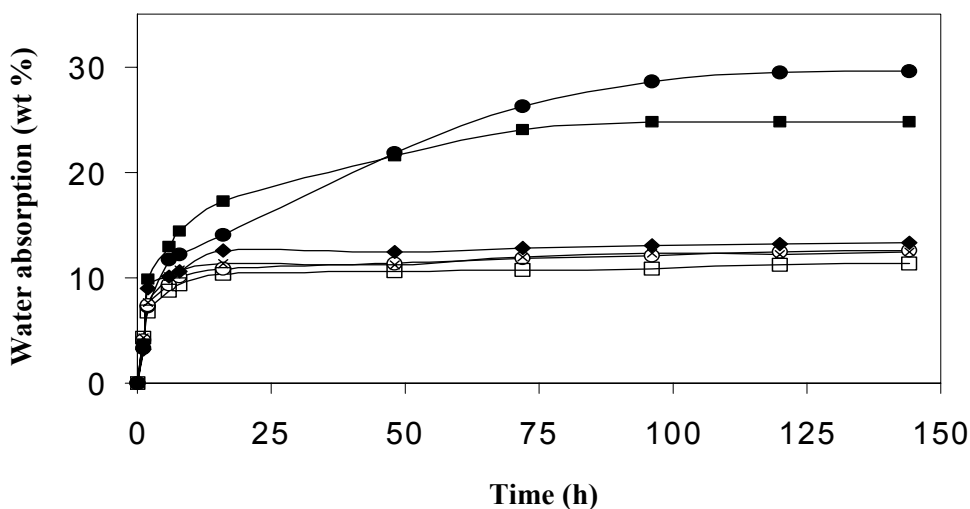


Figure 11. Water absorption *versus* time for rachis: (●) original; (○) extracted; (◆) treated with 10% NaOH; and from rachis fibres: (■) original; (□) extracted; (×) cellulose from rachis fibres.

Table 3.
Water absorption (wt%) for the samples conditioned at 98% RH

Material	Grafting agent	Water absorption
Rachis original	None	30
	Phenyl isocyanate	28
	Maleic anhydride	28
	ASA	23
	AKD	10
extracted	None	13
	Phenyl isocyanate	13
Rachis fibres original	None	25
	Phenyl isocyanate	23
	Maleic anhydride	25
	ASA	17
	extracted	None
extracted	Phenyl isocyanate	10
	Maleic anhydride	11
	Rachis treated with 10% NaOH	13
Cellulose from rachis fibres		12

crystallinity is more pronounced for water absorption measurements than for water contact angles measured in very short times.

It is observed that the original rachis absorbs 30 wt% of water (Table 3). The water content at equilibrium decreased with the solvent extraction to only 13 wt% (57% with respect to extracted material). For the rachis fibres the water absorption decreased by 54% for the extracted fibres. The smaller value in the rachis fibres is probably overcome by the high crystallinity which reduces water absorption capacity. Extracted materials have very similar values of water absorption when compared to cellulose. This could be attributed to fibre compression, making water absorption more difficult for the fibre.

The absorption of water by different lignocellulosic materials is largely dependent on the availability of free $-OH$ groups on the surface. The difference in absorption of water between modified and original materials is due principally to blocking of $-OH$ groups by urethane formation and/or esterification. The water absorption on exposure to 98% RH of different lignocellulosic materials before chemical modification as a function of time was evaluated and is presented in Fig. 12.

Water absorption by original material is reduced by chemical modification with PI, MA and ASA but the maximum reduction was 22% when compared to

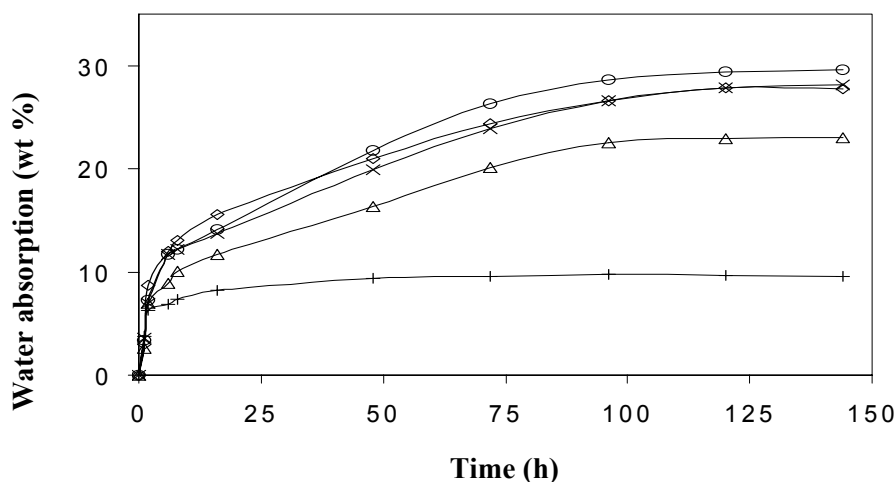


Figure 12. Water absorption *versus* time for (○) rachis and rachis modified with: (◇) PI; (×) MA; (△) ASA; (+) AKD.

original material (Table 3). Therefore, in the case of modification with AKD the reduction is around 30%. This phenomenon was ascribed to the long aliphatic chain in AKD, which prevented water absorption by the material. In conclusion, the minimum absorption is observed for the AKD agent, followed by extracted rachis. The order of absorption in rachis is: original rachis > modification with MA > PI > ASA > AKD. The order of absorption in rachis fibres is the same as for rachis. These results are in agreement with the chemical structures of the grafting agents used and provide evidence for the occurrence of modification.

4. CONCLUSIONS

In this paper data concerning the chemical composition, morphology and surface energy of “Dwarf Cavendish” are presented. The influence of both mechanical treatments and solvent extraction of these materials was also established. These structural changes induced a decrease of water absorption. These findings will be useful in the application of “Dwarf Cavendish” in different areas, such as paper-making and cellulose-based composite materials.

The chemical modification of rachis surface with grafts resulted in loss of hydrophilic character, leaving essentially the modified surface with a dispersion character. Thus, these results promise a better surface compatibility between the fibrous materials and polymer matrices possessing a predominantly dispersion character, such as polypropylene, natural rubber or latices. This work is in progress.

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REFERENCES

1. S. J. Eichhorn, C. A. Baillie, N. Zafeiropoulos, L. Y. Mwaikambo, M. P. Ansell, A. Dufresne, K. M. Entwistle, P. J. Herrero-Franco, G. C. Escamilla, L. Groom, M. Hughes, C. Hill, T. G. Rials and P. M. Wild, *J. Mater. Sci.* **36**, 2107 (2001).
2. T. Peys and G. Baillie (Eds.), *Composites Science and Technology*, Volume 63, issue 9. Elsevier, Amsterdam (2003).
3. A. K. Mohanty, M. Misra and G. Hinrichsen, *Macromol. Mater. Eng.* **1**, 276 (2000).
4. J. Gassan and A. K. Bledzki, *Prog. Polym. Sci.* **24**, 221 (1999).
5. M. N. Belgacem and A. Gandini, *Composite Interfaces*, in press.
6. N. Cordeiro, M. N. Belgacem, I. C. Torres and J. V. C. P. Moura, *Industrial Crop Prod.*, **19**, 147 (2004).
7. N. Cordeiro, M. N. Belgacem, I. C. Torres and J. V. C. P. Moura, *Cellulose Chem. Technol.* submitted.
8. H. Faria, L. Oliveira, N. Cordeiro, M. N. Belgacem and A. Dufresne, *Polym. Composites*, submitted.
9. B. L. Browning (Ed), in: *Methods of Wood Chemistry*, Vol. II, p. 406. Wiley, New York, NY (1967).
10. L. Oliveira, N. Cordeiro, A. J. D. Silvestre, I. C. Torres and D. Evtuguin, *Industrial Crop Prod.*, in press.
11. H. Faria, L. Oliveira, N. Cordeiro and M. N. Belgacem, *Proc. International Congress on Production, Processing and Use of Natural Fibres*, p. 94, Potsdam, Berlin (2002).
12. M. N. Belgacem and A. Gandini, in: *Interfacial Phenomena in Chromatography*, E. Pefferkorn (Ed.), p. 41. Marcel Dekker, New York, NY (1999).
13. P. Aurenty, V. Lanet, A. Tessadro and A. Gandini, *Rev. Sci. Instrum.* **68**, 1801 (1997).
14. C. Pascoal Neto, A. Seca, A. M. Nunes, M. A. Coimbra, F. Domingues, D. Evtuguin, A. Silvestre and J. A. S. Cavaleiro, *Industrial Crop Prod.* **6**, 51 (1997).
15. J. E. Atchison, in: *Pulp and Paper Manufacture*, F. Hamilton and B. Leopold (Eds.), Vol. III, p. 157. TAPPI Press, Atlanta, GA (1993).
16. C. Pascoal Neto, A. Seca, D. Fradinho, M. A. Coimbra, F. Domingues, D. Evtuguin, A. Silvestre and J. A. S. Cavaleiro, *Industrial Crop Prod.* **5**, 189 (1996).
17. A. Antunes, E. Amaral and N. M. Belgacem, *Industrial Crop Prod.* **12**, 85 (2000).
18. N. Cordeiro, C. Pascoal Neto, A. Gandini and M. N. Belgacem, *J. Colloid Interface Sci.* **174**, 246 (1995).
19. S. Katz and D. G. Gray, *Svensk Papperstidning* **8**, 226 (1980).
20. M. N. Belgacem, G. Czeremuszkina, S. Sapiha and A. Gandini, *Cellulose* **2**, 145 (1995).
21. M. N. Belgacem, A. Blayo and A. Gandini, *J. Colloid Interface Sci.* **182**, 431 (1996).
22. J. Schultz and L. Lavielle, in: *Inverse Gas Chromatography*, D. R. Lloyd, T. C. Ward and H. P. Schreiber (Eds.), ACS Symposium Series, No. 391. Am. Chem. Soc., Washington, DC (1989).
23. J. Felix and P. Gatenholm, *Nordic Pulp Paper Res. J.* **2**, 200 (1993).
24. A. Bismarck, J. Springer, A. K. Mohanty, G. Hinrichsen and M. A. Khan, *Colloid Polym Sci.* **229**, 278 (2000).