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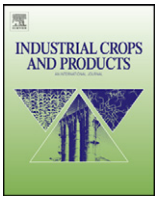

Investigation of surface properties of physico-chemically modified natural fibres using inverse gas chromatography

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ABSTRACT

Inverse gas chromatography (IGC) is a suitable method to determine surface energy of natural fibres when compared to wetting techniques. In the present study, the surface properties of raw and modified lignocellulosic fibres have been investigated by IGC. The fibres chosen for the study were flax, hemp, kenaf, agave, agave hybrid, sisal and pineapple. The treatments used were 4% NaOH and 2% zein. The uniqueness of zein treatment is that it is bio-based and therefore maintains the biodegradable character of the natural fibres. Fourier transform infrared spectroscopy (FTIR) and environmental scanning electron microscope (ESEM) were also performed to characterize the surface changes in fibres. The surface properties of fibres are influenced by the chemical composition, crystallinity and morphology of the fibres. Bast fibres exhibited higher surface dispersive energy than leaf fibres. The raw fibres have a predominant basic character, whereas the alkaline treatment makes the fibres more acidic. Both alkaline and zein treatments decrease the dispersive surface energy and the specific free energy of adsorption.

1. Introduction

The application of natural fibres is being targeted in various fields due to both environmental and economical benefits. Natural fibres are renewable, biodegradable, safe to use and the most important reason being its high specific strength to weight ratio. This is of special significance in transportation applications as it leads to weight reductions and thus savings in fuel consumption.

Natural fibres are hydrophilic in nature as they are lignocellulosic, which contain strongly polarized hydroxyl groups. These fibres, therefore, are inherently incompatible with hydrophobic thermoplastics, such as polyolefins. The major limitations of using these fibres as reinforcements in such matrices include poor interfacial adhesion between polar-hydrophilic fibres and non-polar-hydrophobic matrix, and difficulties in mixing due to poor wetting of the fibres with the matrix. Therefore, it is imperative that natural fibres should be subjected to physico-chemical modification to increase the compatibility and adhesion between fibres and matrix (Jacob et al., 2008; John and Anandjiwala, 2008).

The knowledge of the surface properties of cellulose materials is of great interest since, for instance, cellulose and its derivatives are increasingly used for the preparation of biocomposites (Papirer et al., 2000). Surface properties are widely described in terms of the surface free energy which is used for the description of interaction between solid surfaces and is therefore directly related to adhesion properties of materials.

The surface energy consists of a dispersive term, γ_S^D, and a specific term, γ_S^{sp}, caused by London forces and polar interactions, respectively. As the dispersive component of surface energy, γ_S^D, is highly sensitive to changes in the surface chemistry, γ_S^D is an appropriate parameter for the characterization of porous materials (Rückriem et al., 2010).

Inverse gas chromatography (IGC) is being widely used in studies of adsorption thermodynamics and the properties of organic and inorganic materials (Belgacem and Gandini, 1999; Cordeiro et al., 1995, 1997, 2010; Schultz et al., 1989). This technique provides information about the adsorption properties, acid–base characteristics and a better comprehension of surface chemistry.

In the present study, IGC was used to characterize the surface properties of physico-chemically modified lignocellulosic bast and leaf fibres. The surface dispersive energy and the acid–base characteristics were evaluated and co-related to the changes occurring during physico-chemical modifications.

1.1. IGC theory

The dispersive component of the surface energy (γ_S^D), as well as the specific free energy (ΔG^0_{ads}) of adsorption, was measured

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with dispersive (non-polar) and acid–base (polar) probe molecules through pulse technique. The relation between the retention volume and ΔG^0_{ads} is given by the following equation:

$$\Delta G^0_{ads} = RT \ln V_N + K \quad (1)$$

where R is the gas constant and K is the De Boer or Kemball/Rideal constant (De Boer, 1953; Kemball and Rideal, 1946).

ΔG^0_{ads} is also related to the energy of adhesion W_A (Belgacem and Gandini, 1999; Schultz et al., 1989) and the Eq. (2) can be obtained:

$$RT \ln V_N = 2N_A(\gamma_S^D)^{1/2} a(\gamma_L^D)^{1/2} + K \quad (2)$$

where γ_S^D and γ_L^D as the dispersive surface energy of the solid adsorbent and surface tension of the liquid adsorbate, respectively, a is the cross sectional area of the adsorbate and N_A the Avogadro constant.

Thus, the dispersive component of the surface tension (γ_S^D) can be calculated from the plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$.

A comprehensive insight in the Lewis acid–base surface interactions can provide better understanding of the influence of the chemical properties of the fibres, as well as their ability to change via physico-chemical modifications, which is of great importance in fibre–matrix interface studies (Dorris and Gray, 1980).

In order to measure how easily the surface can interact with polar molecules, the specific free energy of adsorption, ΔG^{sp}_{ads}, is determined by the equation:

$$\Delta G^0_{ads} = \Delta G^D_{ads} + \Delta G^{sp}_{ads} \quad (3)$$

were ΔG^{sp}_{ads} is given by the vertical distance between the total free energy of the polar probe and the total free energy of a hypothetical *n*-alkane reference line having the same value on the abscissa:

$$\Delta G^{sp}_{ads} = RT \ln V_{N,polares} - RT \ln V_{N,n\text{-}alkanes} \quad (4)$$

The acid–base parameters can be determined using the ΔG^{sp}_{ads} value (Voelkel, 1991):

$$-\frac{\Delta G^{sp}_{ads}}{AN^*} = \frac{DN}{AN^*} K_a + K_b \quad (5)$$

where DN and AN^* are the donor and acceptor values of the polar probes, respectively. The constants K_a and K_b characterize the ability of the solid sample to accept or to donate electrons.

2. Materials and methods

2.1. Fibres

In the present work, good quality lignocellulosic fibres were analyzed: flax (*Linum usitatissimum*), hemp (*Cannabis sativa*), kenaf (*Hibiscus cannabinus*), agave (*Agave americana*), agave hybrid (*Sharkskin agave*), pineapple (*Ananas comosus*) and sisal (*Agave sisalana*). These fibres were procured from local sources in Port Elizabeth (South Africa). Zein was obtained from Scientific Polymer Product Company, Ontario, NY. All other chemical reagents used in this study were of analytical grade.

2.2. Modification of fibres

2.2.1. Alkaline treatment

All the fibres were treated for 3 h under ambient conditions with 4% NaOH solution and washed with water containing acetic acid. Further the fibres were washed again with fresh water and dried in an oven at 70 °C until completely dry.

2.2.2. Zein modification

Zein belongs to the characteristic class of proteins known as prolamines which occur specifically in cereals. The protein products from corn wet milling are corn gluten meal (CGM) and corn gluten feed (CGF) and zein is obtained as a by-product from corn gluten meal (Momany et al., 2006; Shukla and Cheryan, 2001; Wang et al., 2004). 2% zein solution was prepared by mixing the required weight of zein with an ethanol/water mixture in the ratio of 80/20. The fibres were immersed in this solution and were allowed to stand for 2 h. The ethanol/water mixture was drained out and the nonwovens were dried in air and then in an oven at 110 °C until completely dry.

2.3. IGC analysis

IGC measurements were carried out on a commercial inverse gas chromatograph (*i*GC, Surface Measurements Systems, London, UK) equipped with a flame ionization (FID) and thermal conductivity (TCD) detectors. The *i*GC system is fully automatic with SMS *i*GC Controller v1.8 control software. Standard glass silanized (dymethyldichlorosilane; Repelcote BDH, UK) columns with 0.4 cm ID and 30 cm in length were used.

About 1.5 g of the fibres (raw and modified) was packed in the columns by vertical tapping. The columns with the samples were conditioned over night at 333 K with helium at 10 ml/min of flow rate, in order to remove the impurities adsorbed on the surface. After conditioning, pulse injections were carried out with a 250 μl gas loop. The retention volume and subsequent data were analyzed using *i*GC Standard v1.3 and Advanced Analysis Software v1.25 based on the equations explained in the previous section. The physical constants for probes used in IGC calculations were taken from the literature (Farinato et al., 1990; Gutmann, 1978; Schultz et al., 1989) and are reported in Table 1. Measurements of the dispersive interaction were made with non-polar probes (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane and *n*-decane) at 298 K and a flow rate of 10 ml/min of carrier gas (Helium). For the acid–base studies, polar probes (dichloromethane, ethyl acetate, acetone, acetonitrile and tetrahydrofuran) were used. All experiments were performed at 0% RH. Methane (>99.99% purity) was used as a non-interacting reference probe and the carrier gas utilized was helium (>99.99% purity), all supplied by Air Liquide Company.

2.4. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra of the untreated and treated fibres were recorded with an FT-IR spectrometer, Perkin Elmer Spectrum 100 FTIR Spectrometer with an ATR (Attenuated Total Reflectance) sampling accessory. The spectra were analyzed over the range of 4000–650 cm^{-1}, with a resolution of 8 cm^{-1} and with 256 scans.

2.5. X-ray diffraction

X-ray diffractograms (XRD) of the vegetable fibres were recorded in a PHILIPS X-ray diffractometer model XĭPert with a PW3050/60 goniometer using 50 kV, 30 mA and Cu Kα radiation. A step size of 0.02° and a step scan of 1.05 s were used for the entire reading range (4–60°).

2.6. Environmental scanning electron microscopic studies

Environmental Scanning Electron Microscopic (ESEM) analysis was carried out using a FEI ESEM-EDS Quanta 200 scanning electron microscope. Fibre samples were clamped and sectioned in such a way that a freshly cut surface was presented to the analysing electron beam.

Table 1
Physical constants for probes molecules used in IGC experiments.

Probe	Cross-sectional area (a) (10^{-19} m^2)	Surface tension (γ_L^D) (mJ/m^2)	DN (kcal/mol)	AN^* (kcal/mol)	Specific characteristic
n-Hexane	5.15	18.4	–	–	Neutral
n-Heptane	5.73	20.3	–	–	Neutral
n-Octane	6.30	21.3	–	–	Neutral
n-Nonane	6.90	22.7	–	–	Neutral
n-Decane	7.50	23.4	–	–	Neutral
Acetonitrile	2.14	27.5	14.1	4.7	Amphoteric
Ethyl acetate	3.30	19.6	17.1	1.5	Amphoteric
Acetone	3.40	16.5	17.0	2.5	Amphoteric
Dichloromethane	2.45	24.5	0	3.9	Acid
Tetrahydrofuran	2.90	22.5	20.0	0.5	Basic

AN^*: electron acceptor number [$AN^* = 0.288(AN - AN^d)$]; DN: electron donor number, defined by Gutmann (1978).

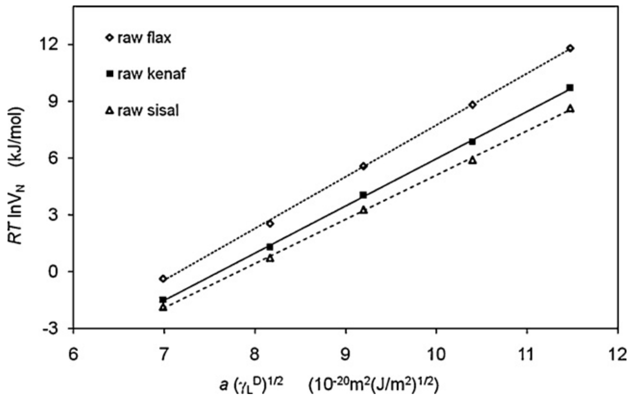

Fig. 1. Plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$ for the *n*-alkanes series onto flax, kenaf and sisal raw fibres.

3. Results and discussion

3.1. Dispersive surface energy

3.1.1. Untreated fibres

A series of *n*-alkanes was used to determine the dispersive surface energy, γ_S^D, of the different fibres, at 298 K. Gaussian peaks were obtained for all the fibres. Fig. 1 shows the plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$ (Eq. (4)) for the *n*-alkanes series onto flax, kenaf and sisal raw fibres. Excellent linear corrections (0.9991–0.9997) were obtained for the *n*-alkanes series for all samples analyzed. The calculated γ_S^D values of the different fibres are summarized in Table 2. It can be observed that raw flax fibres presents the highest γ_S^D (51.37 mJ/m^2) while sisal and agave hybrid exhibited the lowest (37 mJ/m^2). Similar values for γ_S^D in raw fibres were observed by Mills et al. (2008) who studied the γ_S^D of several lignocellulosic fibres at different temperatures by IGC.

It is well known that the chemical composition of the fibres is highly influenced by the plant species from which the fibres were extracted. However, the chemical composition may also differ dependent on the growing conditions and the fibre location in the plant (Satyanarayana et al., 2007). Based on the average of the chemical composition data and the experimentally obtained γ_S^D, Mills et al. (2008) observed that the leaf fibres show higher γ_S^D than bast fibres. The same correlation was observed in our study (Table 2): the bast fibres exhibit higher γ_S^D (47.0 mJ/m^2) than the leaf fibres (39.1 mJ/m^2). This can be attributed to differences in the percentage of cellulose, hemicellulose and lignin in the fibres (Bismarck et al., 2005). The γ_S^D is seen to decrease for fibres containing higher lignin and hemicellulose content but increases with the cellulose content. The fibres under study were analyzed by FTIR and the spectra showed the presence of low percentage of non-cellulosic and high cellulosic components. Fig. 2 exhibits the FTIR spectra of flax and pineapple raw fibres (bast and leaf fibre, respectively). The higher concentration of lignin and hemicellulose content in pineapple (leaf fibre), compared to raw flax (bast fibre), can be seen by the more intense peaks around 1590 cm^{-1} and 1510 cm^{-1}, assigned to aromatic C=C groups in lignin, and the peak at 1731 cm^{-1}, assigned to C=O groups in acids and esters of p-coumaric and uronic acids (main constituents of hemicelluloses) (Oudiani et al., 2009; Reddy et al., 2009). Meanwhile, the peak at 1020 cm^{-1} is assigned to bonds of hollocellulose. The presence of lignin was also revealed by the peak around 1246 cm^{-1} which is assigned to CO groups (Oliveira et al., 2007).

Table 2
Dispersive component of the surface tension (mJ/m^2) of the fibres surfaces before and after treatments.

Fibre	Untreated fibres	Alkaline treatment	Zein treatment
Flax	51.37	43.23	43.38
Hemp	46.68	41.92	40.54
Kenaf	42.83	35.50	38.01
Agave	42.01	34.69	39.67
Agave hybrid	37.17	29.72	35.17
Pineapple	39.58	41.74	42.19
Sisal	37.49	35.09	36.78

3.1.2. Alkali treatment

Alkaline treatment is one of the most commonly used chemical treatments for natural fibres. Treatment of the cellulose fibres with alkali results in swelling, during which the natural crystalline structure of the cellulose–cellulose I changes to cellulose II (Fig. 3). The basic differences in both are that the chains in cellulose I run in a parallel direction while cellulose II has an antiparallel packing. Also, the inter-chain hydrogen bonding in cellulose I is O6–H···O3 while in cellulose II it is O6–H···O2 (O'Sullivan, 1997). During mercerization, cellulose I is converted to cellulose II which is thermodynamically the more stable configuration and hence will

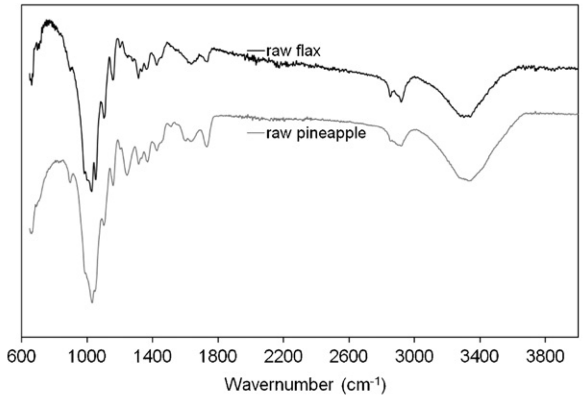

Fig. 2. FTIR spectra of flax and pineapple raw fibres.

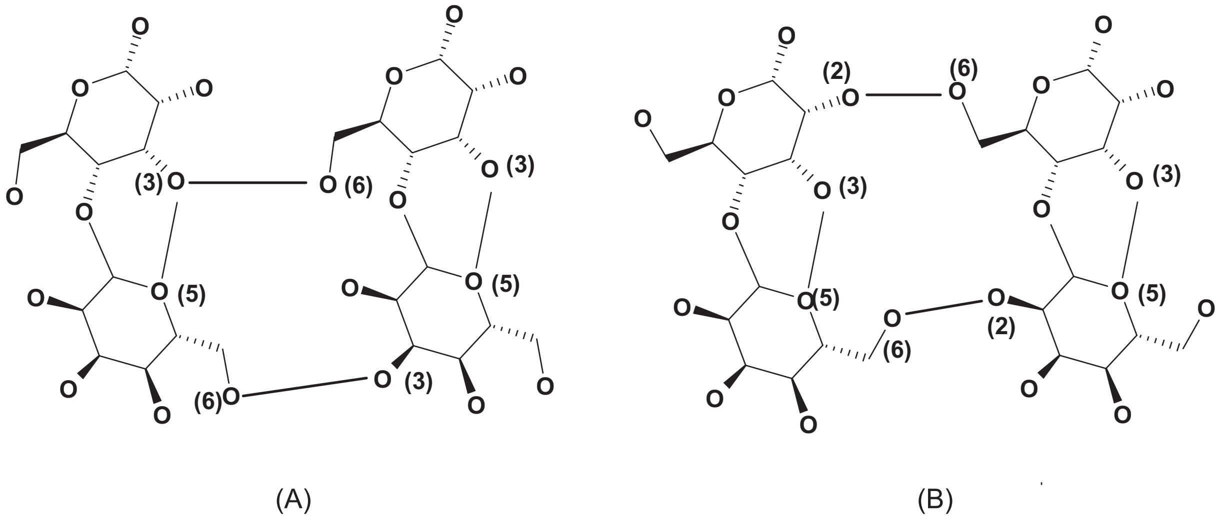

Fig. 3. Hydrogen bonding pattern for cellulose I (A) and cellulose II (B).

exhibit lower surface dispersive energy. The extent of transformation from cellulose I to cellulose II can be influenced by the nature of fibres, concentration and alkali type, temperature and the time of treatment (John and Anandjiwala, 2008). The decrease in surface dispersive energy can also be attributed to the decrease in free OH– groups in from surface of fibres and intermolecular hydrogen bonding.

Alkalization of lignocellulosic plant fibres changes the surface topography and their crystallographic structure. Apart from truly crystalline and truly amorphous, there are some regions of intermediate order where the molecular configuration is liable to change by the chemical treatment. This is because treatment with alkali leads to the removal of cementing materials like lignin, hemicellulose and pectin which results in the increase of crystallinity of the fibres. Abraham and Pothen (2010) investigated the effect of alkali treatment on different natural fibres by XRD and observed an increase in the crystallinity index of the natural fibres upon mercerization. Similar results have been reported by other authors as well (Cherian et al., 2008). In our study an increase in the crystallinity was observed and can be seen by the example give in Fig. 4 for sisal fibres. This crystallinity increase can be attributed to the removal of amorphous components, like lignin and hemicelluloses, as observed in FTIR spectrum of sisal fibres after alkaline treatment (Fig. 5). In the untreated fibres (Figs. 2 and 5) the peaks around 3329 cm^{-1} and 1050.98 cm^{-1} are assigned to –OH stretching and –C–O/C–C stretching vibrations, respectively. The peaks ranging from 1200 to 1400 cm^{-1} are assigned to C–H and CH_2 stretching vibrations. The peak at 1731 cm^{-1} present in raw fibres corresponds to C=O in acids and esters of p-coumaric and uronic acids which are the main constituents of hemicellulose (Oudiani et al., 2009; Reddy et al., 2009). This peak is absent in alkaline treated fibres (Fig. 5) due to the removal of non-cellulosic components by alkali treatment.

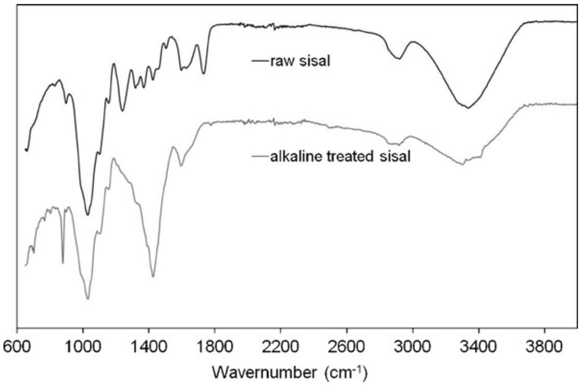

Fig. 5. FTIR spectra of sisal and alkaline treated sisal fibres.

Fig. 6 presents the ESEM of untreated and alkaline treated sisal fibres. The raw fibres show the unidirectional structure of the fibre while alkaline treated fibre presents a rough surface due to removal of non-cellulosic constituents. Fibre fibrillation is also evident.

The interpretation of the IGC results obtained on lignocellulosic materials is difficult, due principally to the complex nature of natural fibres. From a chemical point of view, different functional groups

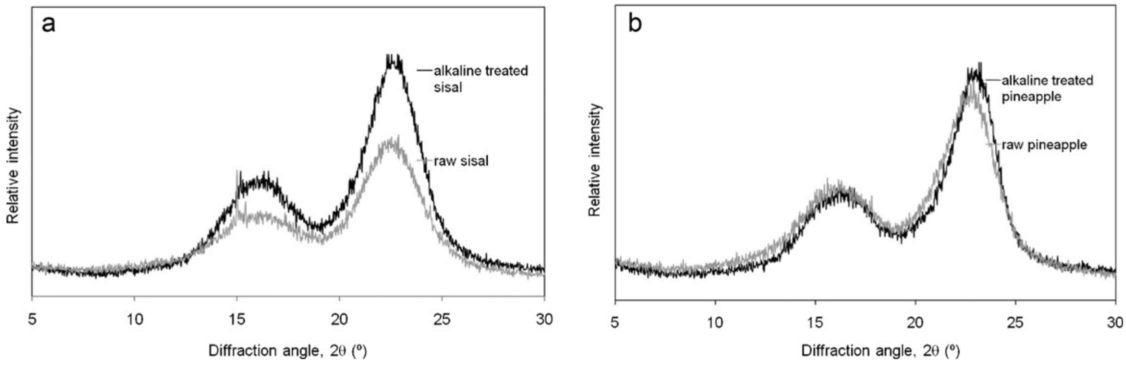

Fig. 4. X-ray diffractogram of sisal (a) and pineapple (b) fibres, before and after alkaline treatments.

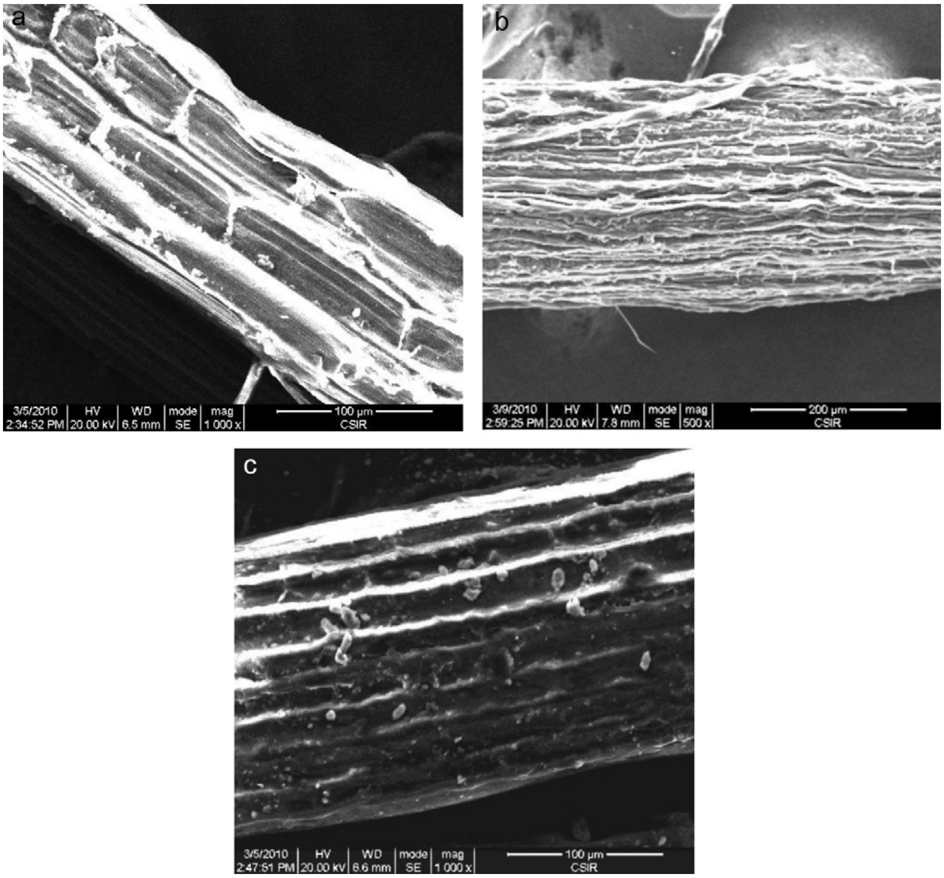

Fig. 6. ESEM of untreated (a), alkaline treated (b) and zein treated (c) sisal fibres.

exist on the surface. Morphologically, the surface texture and surface morphology at the molecular scale are complex and difficult to evaluate. Depending on the composition of the lignocellulosic fibres, the alkaline treatment may decrease or increase the surface energy. Belgacem et al. (1996) observed that microcrystalline cellulose showed a significantly higher γ_S^D value (41.0 mJ/m^2) than amorphous cellulose (27.4 mJ/m^2). Papirer et al. (2000) found that increase in γ_S^D is not dependent only on the surface chemistry of a cellulosic material, but also on the surface morphology. On the other hand, Newell et al. (2001) showed that crystalline lactose exhibited a lower γ_S^D than amorphous lactose (31.2 and 37.1 mJ/m^2, respectively). In a recent work, Buschle-Diller et al. (2005) observed a decrease of around 6 mJ/m^2 for mercerized cotton.

In our study it can be observed in Table 2 and in Fig. 7 that there has been a significant change in γ_S^D when the fibres were subjected to 4% NaOH treatment. While γ_S^D of all the fibres decreased upon alkaline treatment, mercerized pineapple fibres registered an increase. This can be attributed to the higher amount of cellulose (70–82%) present in pineapple fibres (Bismarck et al., 2005). As the amount of cellulose is significantly higher in pineapple fibres, some of the swollen cellulose may not recrystallize into cellulose II. Interestingly alkali treated pineapple fibres only exhibit a small increase in the crystallinity as seen in the XRD presented in Fig. 4b, compared to the large increase seen in the case of sisal fibres (Fig. 4a).

3.1.3. *Zein treatment*

For the zein treated fibres, it can be observed that γ_S^D values have decreased for all the fibres, except pineapple fibre.

The amino acid composition in zein (Di Gioia et al., 2000) indicates the presence of both polar and non-polar constituents, the major proportion being glutamine. The dispersive surface energy is caused by London dispersion forces which are directly propor-

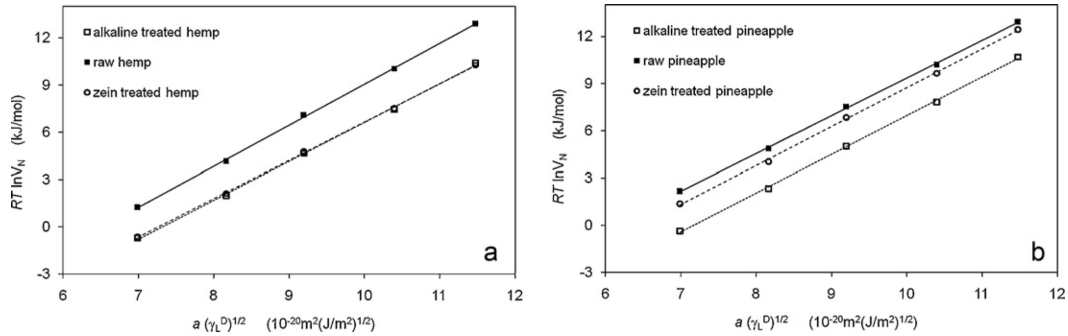

Fig. 7. Plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$ for the *n*-alkanes series onto hemp (a) and pineapple (b) fibres, before and after alkaline and zein treatments.

Table 3
Specific free energy of adsorption (kJ/mol) of untreated and treated fibres.

Fibre	Acetonitrile			Ethyl acetate			Acetone			Tetrahydrofuran			Dichloromethane		
	Raw	NaOH	Zein	Raw	NaOH	Zein	Raw	NaOH	Zein	Raw	NaOH	Zein	Raw	NaOH	Zein
Flax	17.67	13.35	8.23	9.47	7.19	8.24	7.62	5.58	6.83	10.50	7.99	9.18	10.84	8.34	9.56
Hemp	18.63	11.83	19.28	8.90	7.09	7.17	7.44	5.50	5.87	9.81	8.86	8.33	9.10	8.63	7.33
Kenaf	11.67	5.75	18.63	7.52	5.88	7.13	6.28	5.83	6.15	8.16	3.43	4.83	7.38	5.52	9.48
Agave	16.55	7.06	9.55	7.81	6.29	6.34	6.62	4.69	4.80	9.68	7.06	7.12	8.13	6.20	6.52
Agave hybrid	18.79	9.71	8.58	7.46	5.15	6.34	6.40	3.42	4.80	8.02	6.41	7.12	7.59	4.26	10.68
Pineapple	16.30	11.88	8.58	8.07	7.41	9.03	7.65	5.95	9.59	8.75	8.25	9.01	8.53	7.76	10.68
Sisal	18.60	9.14	15.64	6.61	6.24	6.77	5.29	4.50	5.46	7.75	6.83	8.09	6.71	6.00	14.95

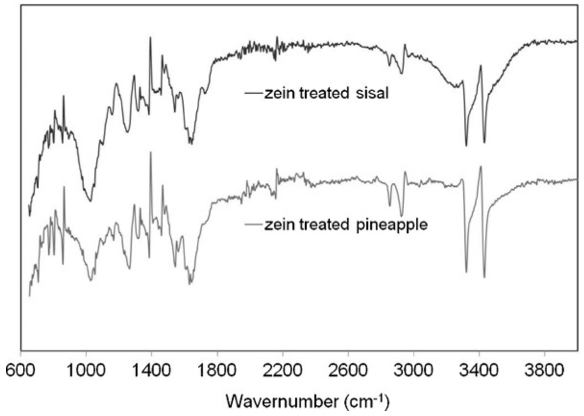

Fig. 8. FTIR spectra of sisal and pineapple zein treated fibres.

tional to the polarizability and surface area of the fibres. Due to interactions between amino groups in zein and hydroxyl groups in natural fibres, there are less free functional groups available hence the polarizability of the fibres decreases which creates a lowering of London dispersion forces. This leads to a decrease in the dispersive specific energy of the fibres. Similar results have been reported by other researchers where γ_S^D has been co-related to the polarizability of the system (Rückriem et al., 2010). Another possible explanation for the decrease in the γ_S^D values can be the extraction effect of the ethanol/water mixture used in the zein treatment. The removal of extractives components, aromatic groups or monosaccharide molecules, can expose the cellulose polymers and contribute to the decrease of the γ_S^D of the fibre surface.

In the FTIR spectra of untreated and zein treated pineapple and sisal fibres (Fig. 8), the peak at 1071 cm^{-1} assigned to C–O stretching is less intense than in the raw fibres indicating interactions between functional groups. The emergence of new bands on the zein coated fibres around 1530 cm^{-1} are assigned to C–N stretching and is indicative of the fact that zein coating has modified the fibre surface. Another interesting observation is the presence of two peaks around 3300 cm^{-1} which is attributed to the presence of amide group in zein treated fibres.

Fig. 6c presents the ESEM of untreated and 2% zein treated sisal fibres (Fig. 6a and c, respectively). The presence of zein coating on fibres is clearly seen by the presence of macrospheres on the fibre surface.

3.2. Acid–base characteristics

On the surface of the fibres there is the presence of hydroxyl and carboxylate groups that are able to establish both dispersive and specific interactions with a polar probe. A series of polar probes were used to determine the specific free energy of adsorption (ΔG_{ads}^{sp}) of all the fibres. Fig. 9 presents the plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$ for polar probes onto kenaf fibres before and after alkaline treatment, respectively. All the polar probes points are located above the *n*-alkanes line indicating, as expected, that the fibres are capable of exchanging additional interactions with polar probes comparatively to similar molecular size *n*-alkanes probes.

The ΔG_{ads}^{sp} was calculated using the difference between the adsorption energy of the polar probe and its dispersive increment (Eq. (4)), as shown in Fig. 9b and the results are presented in Table 3. All the raw fibres exhibited maximum interaction with acetonitrile which is an amphoteric compound that can interact with both acidic and basic groups. However, the nitrile group possess strong electron donating properties and, in IGC, they may be used to test the acidic properties of solid surfaces.

As observed by Papirer et al. (2000), in the case of celluloses with different crystallinity and cotton fibres, acetonitrile present the biggest values (around 15 kJ/mol) compared to the other probes like acetone or ethyl acetate. Similar results were also observed by Heng et al. (2007).

ΔG_{ads}^{sp} values were converted into acid–base constants using the Gutmann concept (Eq. (5)). The K_a and K_b values for the respective fibres were estimated, respectively, from the slope and intercept of the respective linear regression line of $\Delta G_{ads}^{sp}/AN^*$ as a function of DN/AN^*. These values are summarized in Table 4. The linearity

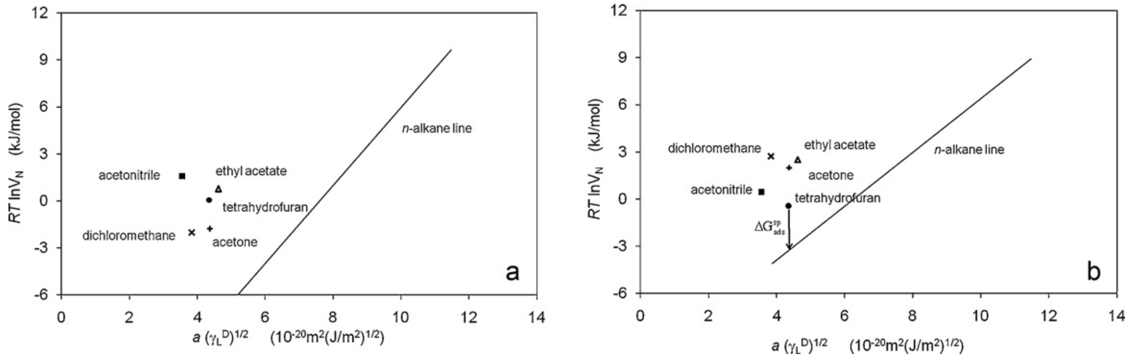

Fig. 9. Plot of $RT \ln V_N$ *versus* $a(\gamma_L^D)^{1/2}$ for *n*-alkanes and polar probes onto kenaf fibres before (a) and after (b) alkaline treatment.

Table 4
Acid–base constants (K_a and K_b) of the fibres surfaces before and after treatments.

Fibre	Untreated fibres			Alkaline treatment			Zein treatment		
	K_a	K_b	K_b/K_a	K_a	K_b	K_b/K_a	K_a	K_b	K_b/K_a
Flax	0.12	0.22	1.83	0.09	0.16	1.78	0.11	0.02	0.18
Hemp	0.11	0.27	2.45	0.10	0.03	0.30	0.09	0.28	3.11
Kenaf	0.09	0.14	1.56	0.03	0.25	8.33	0.05	0.41	8.20
Agave	0.11	0.15	1.36	0.08	0.07	0.88	0.09	0.14	1.56
Agave Hybrid	0.09	0.33	3.67	0.07	0.03	0.43	0.08	0.07	0.88
Pineapple	0.10	0.28	2.80	0.09	0.12	1.33	0.10	0.20	2.00
Sisal	0.08	0.26	3.25	0.08	0.07	0.88	0.09	0.18	2.00

of the plots gives values in the range of 0.92–0.98, which suggests that the Gutmann's acid–base concept is valid for the studied system and the specific interactions may be considered due to electron donor–acceptor interactions. The surface of all raw fibres in the study presented a Lewis base character. Similar results were observed by other researchers for hemp fibres (Gulati and Sain, 2006) and it was attributed to the presence of extractives like triglycerides, which exhibit basic behaviour. Natural fibres also contain lignin which exhibits a dominant Lewis base character and hence that could influence the K_b and K_a results. This can explain why agave hybrid, sisal and pineapple fibres present the lowest γ_S^D and the higher K_b/K_a ratio (3.67, 3.25 and 2.80, respectively). However, agave hybrid exhibited the highest ratio K_b/K_a (1.83) that can be due to surface morphology that influences strongly its interaction capacity with polar probes.

After alkaline treatment, basic character was found to decrease for all fibres, except for kenaf fibres. Alkalization cleans the fibre surface by dissolving non-cellulosic components (as can be seen in Fig. 6c). This would increase the acidic character of the fibres due to exposure of cellulose, which is predominantly acidic. Other lignocellulosic fibres (Buschle-Diller et al., 2005) showed higher donor than acceptor constants, due to the influence of lignin and other non-cellulosic material.

Kenaf fibres showed a surprising increase of K_b/K_a ratio (Table 4). Previous work show that the retention of the probes could not be simply accounted for by pure enthalpic effects, but other parameters such as: crystallinity, degree of the probes diffusion in the bulk of the material, the surface arrangement and/or chemical groups orientation in the surface (Belgacem et al., 1996; Papirer et al., 2000). These factors can affect more largely the polar interaction in kenaf fibres case.

However, in this study the alkali treated fibres can be classified in two categories: a one with basic surface character (hemp, agave hybrid, agave and sisal) and another group with acidic surface character (kenaf, flax and pineapple); this knowledge could be important in viewing their applications for interactions with polar and non polar polymers.

Zein treatment of the fibres results in an increase of basic character for kenaf, agave and hemp fibres, and in a decrease for agave hybrid, flax, pineapple and sisal, when compared to raw fibres. The increase in basicity can be due to reduction of the accessible hydroxyl groups in the natural fibres and presence of amino groups.

The alkali treated fibres were found to be more acidic than the zein coated fibres. However, the lower ΔG_{ads}^{sp} for all polar probes in the treated fibres (alkaline and zein treatment), when compared to raw material, indicates a decrease in the active sites in the surface of treated fibres for specific interaction and was in good agreement with the lower acid and basic surface parameters (K_a and K_b).

4. Conclusions

The surface properties of untreated and physico-chemically modified lignocellulosic fibres were analyzed by inverse gas chromatography measurements. The dispersive surface energy of natural fibres was found to be dependent on chemical composition, crystallinity and morphology of natural fibres. Bast fibres exhibited higher surface energy than leaf fibres. All the natural fibres were found to have a predominant basic character, whereas the alkaline treated fibres exhibited a Lewis acid surface. The decrease in ΔG_{ads}^{sp} and γ_S^D with alkaline and zein treatment suggest that treatment decrease the active sites for specific and dispersive interaction at the fibre surface. The interpretation of surface properties in natural fibres by IGC is complex however, it is quite apparent that IGC is a successful technique for characterizing surface properties of natural fires.

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