

Investigation on the surface properties of chemically modified natural fibers using inverse gas chromatography

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ABSTRACT

This paper presents the application of inverse gas chromatography (IGC) technique for characterization and comparison of the surface properties of the natural fibers as reinforcement fillers in wood plastic composites. The effects of chemical modification using 1% NaOH were also studied. The fibers used for this work were Iranian cultivated eucalyptus, spruce, bagasse, and wheat straw. Chemical composition of fibers was found to be modified after treatment as characterized by Fourier transform infrared spectroscopy (FTIR). The crystallinity of fibers and the specific interaction was improved by the alkaline treatment, with more relevance to the agro-fibers. The IGC shows also a general increase in the wettability of the modified fiber when compared with the raw (unmodified) samples. Alkaline treatment achieves the best overall improvement in the properties evaluated of the agro-fibers when compared to the wood fibers.

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1. Introduction

Composite materials based on natural fibers, namely wood plastic composites (WPCs), demonstrate remarkable environmental and economical advantages (Ziaei Tabari, Nourbakhsh, & Ashori 2011). Although the use of wood flour in plastic composites has several advantages over inorganic fillers, several drawbacks (limitations) of natural fibers such as low compatibility and low thermal stability, greatly reduce the overall performance of WPCs (Hamzeh, Ashori, & Mirzaei, 2011).

Wood, the most durable organic material, is a three dimensional polymeric composite, made up mainly of cellulose, hemicellulose and lignin. All species of wood and other plant tissues contain small to moderate quantities of chemical substances in addition to the macromolecules, namely extractives. Extractives content in most temperate and tropical wood species are 4–10% and 20% of the dry weight, respectively (Sjöström, 1993). Although extractives contribute merely a few percent to the entire wood composition, they have significant influence on its properties (Sheshmani, Ashori, & Farhani, 2012).

It is well known that the performance, for example the mechanical properties, of WPCs depend on the properties of the individual components and their interfacial compatibility. The interface between hydrophobic plastic and hydrophilic wood is typically

weak and fails to transfer stress. The effective use of wood particles in WPCs requires a fundamental understanding of the structural and chemical characteristics of wood. For example, a few reports have been published about the effects of wood extractives on the strength properties of the resulting WPCs (Kim, Harper, & Taylor, 2009; Shebani, van Reenena, & Meincken, 2009; Sheshmani et al., 2012). Wood extractives are hydrophobic substances with low molecular weights. In the preparation of WPCs, wood flour is thoroughly mixed with a thermoplastic at high temperatures, e.g. 170 °C. At such high temperature, wood extractives may tend to migrate to the wood flour surface, thus accumulating in the wood-plastic interphase (Nourbakhsh, Ashori, Ziaei Tabari, & Rezaei, 2010).

In recent years, inverse gas chromatography (IGC) has been used to characterize and optimize the interaction of natural fibers and polymer composites (Cordeiro, Gouveia, & Jacob John, 2011; Cordeiro, Gouveia, Moraes, & Amico, 2011; Tze, Wälinder, & Gardner, 2006). The technique uses a solid phase packed into a column, and the column is placed in an oven. The temperature is controlled, as a gas mobile phase flows through the column where an inert carrier gas contains “infinitely dilute” samples of probe gases. A detector measures the time required for the probe gases to go through the packed column. The retention time is then related to thermodynamic quantities to characterize the solid phase sample. The fiber/matrix acid base interaction can be quantified using IGC by matching the acidic parameter (K_a) of one component with the basic component (K_b) of the other component, and then, measuring the enthalpy of adsorption of the resin onto the fibers

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Table 1
Chemical compositions of used raw fibers (w/w, % of dry material).

Components	Eucalyptus	Spruce	Bagasse	Wheat straw
Holocellulose	74.0 ± 1.9	72.0 ± 2.3	73.7 ± 4.3	63.3 ± 4.1
Hemicellulose ^a	18.5 ± 0.9	27.0 ± 1.2	33.2 ± 1.8	25.8 ± 2.2
Alpha-cellulose	55.5 ± 2.2	45.0 ± 1.7	40.5 ± 3.2	37.5 ± 1.0
Lignin	26.4 ± 2.0	19.0 ± 0.8	20.7 ± 1.5	28.6 ± 1.8
NaOH solubles	14.7 ± 0.8	8.6 ± 0.6	31.8 ± 4.3	12.2 ± 1.1

^a Determined by the difference between holocellulose and α -cellulose contents.

(Belgacem and Gandini, 1999). This will allow for the prediction of the acid–base interactions of the natural fibers with the polyester matrix. Based on this, the selection of an appropriate coupling agent for the natural fibers may be made.

In the present study, IGC was used to characterize exhaustively the surface properties of several natural fibers (spruce, eucalyptus, bagasse, and wheat straw). The surface characteristics were evaluated and co-related to the changes occurring during the chemical modification.

2. Experimental procedures

2.1. Materials

The lignocellulosic materials used in this study were eucalyptus, a hardwood sample, spruce, a softwood sample, and two agro-waste samples: bagasse and wheat straw. All samples were taken from the southern and northern parts of Iran. The samples were separately ground into a fine “meal” using a Wiley mill. The ground meals were screened and the particles that passed through BS 40 mesh (425 μ m) and retained at BS 60 mesh (250 μ m) sieve screens were used for chemical treatment. The samples were dried and stored in sealed plastic bags prior to testing.

The chemicals used, namely NaOH, acetic acid and sodium hypochlorite, were all of analytical grade.

IGC measurements were carried out on the samples using several non-polar and polar molecules, all GC grade (>99% purity) supplied by Sigma–Aldrich. The methane, used as a non-interacting reference probe, and the carrier gas, helium, had the high purity (>99.99%) and were supplied by Air Liquide Company.

2.2. Chemical characterization

The chemical characterization of the above-mentioned samples was carried out following the appropriate TAPPI Test Methods (2002) and the other published procedures as indicated. The samples were subjected to the following determinations: holocellulose (Wise & Karl, 1962), α -cellulose (T 203 cm-99), Klason lignin (T 222 om-02), (T 212 om-98). Table 1 shows the mean and standard deviations of three replicate determinations of each sample.

2.3. Chemical modifications

The chemical treatment was done following the standard outlined in the TAPPI Test Methods (T 212 om-98). A weighed sample of ground fiber (2 g) was placed in 200 mL beaker, then 1% NaOH solution (100 mL) was added and the mixture stirred with a glass rod. The beaker was placed in a water bath maintained at 97–100 °C for a period of 60 min. At the end of this time, the fibers were transferred to a tared filtering crucible and washed with hot water. A solution of 10% aqueous acetic acid (25 mL) was then added and the extracted fiber allowed to soak for 1 min before filtering. After repeating this stage, the material was finally washed with hot water until acid free. The crucible and contents were oven-dried (for 24 h at 105 ± 3 °C),

and 1% NaOH extractive percent was determined gravimetrically. These results are so-called “NaOH solubles” and listed in Table 1.

2.4. Inverse gas chromatography

IGC measurements were carried out on a commercial inverse gas chromatograph (Surface Measurements Systems, London, UK), that is equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The IGC system is fully automatic with SMS IGC Controller V 1.8 Control Software. Data was analyzed using IGC Standard Analysis Suite V 1.3 and IGC Advanced Analysis Suite V 1.21. The calculation methodology is described and detailed in Cordeiro, Gouveia, and Jacob John (2011). The columns used were standard glass silanized (dymethyldichlorosilane; Repelcote BDH, UK), with 6 mm OD, 300 mm length and an internal diameter of 4 mm.

The columns were packed with about 1 g of the samples (raw and modified) with granulometry lower than 40 mesh. The samples were packed by vertical tapping for 2 h, using the SMS sample packing device. The columns with raw and modified natural fibers were conditioned over-night at 333 K and 10 mL/min of helium flow rate, and then conditioned for 2 h at the temperature of analyses and 0% relative humidity. After conditioning the columns, pulse injections were carried out with 0.25 mL gas loop. Methane was the tracer molecule used to calculate the dead time.

Five *n*-alkanes (hexane, heptane, octane, nonane and decane) were used to measure the dispersive component of the surface energy at four different temperatures; 293, 296, 298, and 300 K. Four polar probes; tetrahydrofuran (THF), ethyl acetate, ethanol, and acetonitrile were used at the same conditions, to study Gibbs specific free energy and acid–base surface character. The permeability and the isotherm experiments were done using the *n*-octane as the probe molecule at 298 K. All the experiments were performed at 0% RH. The experiments were done in duplicate and the presented results are the average values. The experimental error due to the temperature variation, flow rate and retention time measurement was estimated to be below 3%.

2.5. Infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR), Tensor™ 27, Bruker Optics, Billerica, was used to identify the raw and modified fibers by measuring the transmitted radiation of various infrared light wavelengths. Powdered samples were mixed with KBr (sample/KBr ratio, 6/94) to prepare pastilles. FTIR spectra were recorded in a spectral range of 4000–400 cm⁻¹ with a resolution of 4 cm⁻¹ and with 32 scans.

2.6. X-ray diffraction

The crystallinity of raw and modified natural fibers (in powder shape) was evaluated by X-ray diffraction (XRD). X-ray patterns were obtained with a PHILIPS X-ray diffractometer model PW 1800 under the following conditions: CuK α radiation, 30 kV and 17.5 mA. A step size of 0.02° and a step scan of 2.5 s were used for the entire reading range (4–60°).

The degree of crystallinity was expressed by the crystallinity index (CI), using Eq. (1), where I_{002} is the maximum peak intensity at a 2θ angle around 22°, representing crystalline part, and I_{101} is the maximum peak intensity at 2θ angle around 18°, representing amorphous part. This method developed by Segal, Creely, Martin, and Conrad (1959) has been widely applied to study natural fibers.

$$CI = \left(1 - \frac{I_{101}}{I_{002}}\right) \times 100 \quad (1)$$

3. Results and discussion

In their natural state, and before chemical extraction, the fibers surface is covered with a layer of substances such as oils, waxes and other encrusting substances, as hemicelluloses, lignin and pectin that form a tick outer layer to protect the cellulose inside. In general, during chemical treatment of the fibers, most of the surface waxes and other non-cellulosic substances are removed. When agro-based fibers are used as reinforcing fibers for composites, the removal of surface waxes and encrusting substances makes the fiber surface rough and improves the adhesion of fibers and polymer matrix (Eichhorn, Bailie, Zafeiropoulos, & Mwaikambo, 2001).

Chemical, biological and physical treatments are used to improve the morphological features, processability and utility of the fibers (Eichhorn et al., 2001; Gañán, Cruz, Garbizu, Arbelaz, & Mondragon, 2004; Nourbakhsh et al., 2010; Reddy & Yang, 2005). In recent years, some research work has been conducted on surface characteristics of natural fiber modified by different methods, the alkaline treatment being one of the most used (Cordeiro, Gouveia, & Jacob John, 2011; Mills, Gardner, & Wimmer, 2008). The physico-chemical properties of natural fibers usually changed significantly, depending on the concentration of the chemical agent and duration of processing time.

In the present study, a chemical treatment was used – the alkaline treatment or mercerization – to improve the adhesion between the fibers and matrix. The effect of alkali on cellulosic fibers is a swelling reaction, during which the native cellulose can be changed into different polymorphous forms. The type of alkali (KOH, LiOH, NaOH) and its concentration will influence the degree of swelling, and hence, the degree of lattice transformation of the cellulose (Fengel & Wegener, 1983). The alkali solution influences not only the cellulosic components inside the plant fiber but also the non-cellulosic components (hemicelluloses, lignin, and pectin) (Van de Weyenberg, Chi Truong, Vangrimde, & Verpoest, 2006).

3.1. Chemical characterization

As the main components of the lignocellulosic fibers are cellulose, lignin and hemicelluloses, the obtained FTIR spectral bands was attributed mainly to these components. Fig. 1(a) shows as example the FTIR spectra of the raw spruce and wheat straw fibers. Identification reveals lines representing the hydrogen bonded stretching bands of OH groups in the region of 3400 cm^{-1} and in the region of $1030\text{--}1150\text{ cm}^{-1}$, the absorptions can be attributed mainly to the carbohydrates, including C–O–C and C–O stretch (primary and secondary hydroxide groups) and bonds belonging to the glucoside linkage and possibly to lignin, since lignin has hydroxyphenyl, guaiacyl and syringyl groups, which are aromatic OH compounds. The peaks in the region of 2900 cm^{-1} are due to the aliphatic saturated C–H stretching vibration in lignin/polysaccharides complex. The peaks in the region at 1740 cm^{-1} in the raw (unmodified) fibers are attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic and *p*-coumeric acids of lignin and/or hemicelluloses (Alemdar & Sain, 2008; Cherian et al., 2008). The bands in the region $1250\text{--}1056\text{ cm}^{-1}$ involve the C–O stretching vibrations of aliphatic primary and secondary alcohols in cellulose, hemicelluloses, lignin and extractives (El-Zawawy, 2006). The peak at 897 cm^{-1} is due to β -glycosidic linkages of glucose ring of cellulose (Gañán et al., 2004).

The quantification of the main components of the fibers under study was made by standard methods and the results were resumed in Table 1. These analyses show that the wheat straw fibers have the higher content in lignin (28.6%) and a lesser content in cellulose

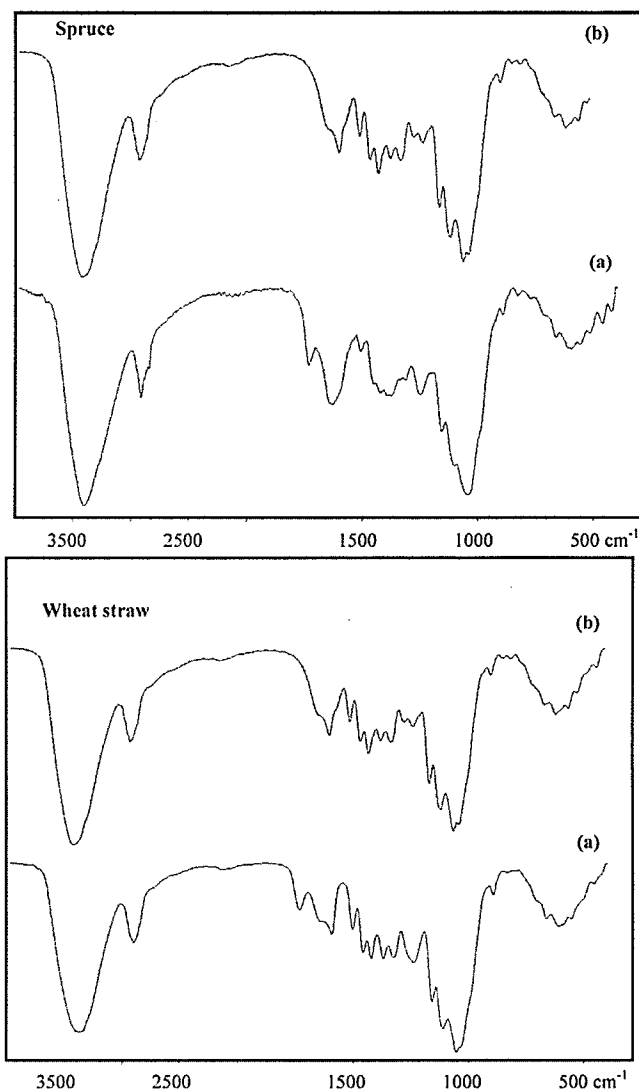


Fig. 1. FTIR spectra of spruce and wheat straw, before (a) and after (b) NaOH treatment.

(37.5%). On the other hand, spruce presents the smaller content in lignin (19.0%) and the Eucalyptus has the higher content in cellulose (55.5%).

Native cellulose (i.e. cellulose as it occurs in nature), the main component of all the samples under study, can be found in the crystalline or amorphous form and can be observed by X-ray diffractograms. X-ray patterns were obtained for all the samples and are shown in Fig. 2 for the eucalyptus and wheat straw fibers. The occurrence of two more intense peaks, close to the values of $2\theta = 16^\circ$ and $2\theta = 22^\circ$, representing the cellulose crystallographic planes I_{101} and I_{002} , respectively, can be observed. These peaks can be attributed to crystalline scattering and the diffuse background associated with disordered regions. The samples show similar X-ray diagrams to wood fibers with a more intense peak at $2\theta = 22^\circ$, which is indicative of a more amount of crystalline cellulose in the raw wood fibers. The crystallinity index (CI), calculated according to Eq. (1) and presented in Table 2, collaborated with this observation: raw wood fibers have the higher CI (54%) and agro-fibers the less CI (45–49%). This smaller CI in the agro-fibers is due to the higher presence of non-crystalline extractive free components.

To improve the adhesion between the fibers and matrix, the four different fibers under study were subjected to chemical treatment

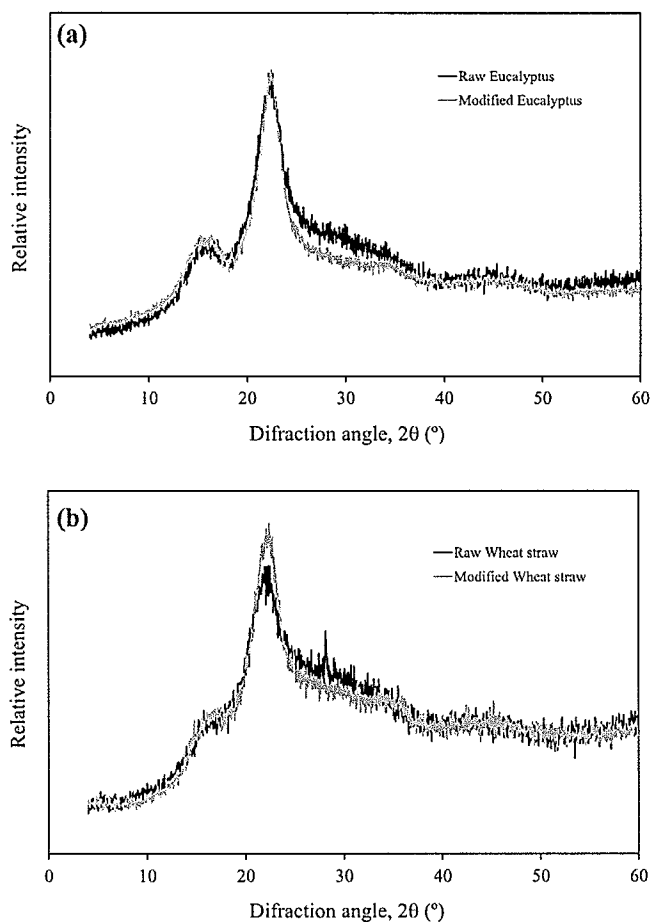


Fig. 2. X-ray diffractogram of eucalyptus (a) and wheat straw (b) raw and treated with NaOH.

with 1% NaOH following the TAPPI Test Methods (T 212 om-98). The treatment extracted a significant amount of fibers components. The results are summarized in Table 1. Based on previous studies, this chemical treatment removes extractives, waxes, oil, etc., from fibers surfaces, and depending on the alkali process, it can also extract lignin, hemicellulose and pectin (Le Troedec et al., 2008; Sun, Xu, Sun, Fowler, & Baird, 2005). The extraction of these components can be observed in FTIR spectrum, exemplified by the spectra of wheat straw fibers after alkaline treatment (Fig. 1). The peaks in the region at 1740 cm^{-1} , in the raw fibers attributed to either the acetyl and uronic ester groups of the hemicelluloses or the ester linkage of carboxylic group of the ferulic and *p*-coumaric acids of lignin (Alemdar & Sain, 2008; Cherian et al., 2008), disappeared in the spectra of the chemically modified fibers, which indicates a complete cleavage of these ester bonds. The intensity of the peaks attributed to C=C of aromatic skeletal vibrations in lignin, in the region of $1500\text{--}1600\text{ cm}^{-1}$, has decreased in chemically modified fibers reflecting partial removal of lignin. Also, the disappearance of the peak around 1260 cm^{-1} after alkalization indicates the preferential removal of hemicelluloses materials rather than lignin (Mwaikambo & Ansell, 2002).

Table 2
Crystallinity index (%) of the raw and modified fibers.

Fibers	Raw	Modified
Eucalyptus	54.48	57.64
Spruce	54.43	55.98
Bagasse	45.23	62.87
Wheat straw	49.95	58.29

Although this chemical transformation in the composition of the fibers, the alkalization of lignocellulosic plant fibers changes the surface topography and their crystallographic structure. Abraham and Pothen (2010) investigated the effect of alkali treatment on different natural fibers by XRD and observed an increase in the crystallinity index of the natural fibers upon mercerization. Similar results were observed in present study. An increase in the crystallinity was observed and can be seen by the example given in Fig. 2 for eucalyptus and wheat straw fibers. The X-ray diffractograms show that the intensity of the I_{002} crystallographic peak was increased by alkali treatment of the fibers with more relevance to the agro-fibers. This increase in the crystallinity can be attributed to the removal of extractives and cementing amorphous components like lignin, hemicellulose and pectin. The CI results (Table 2) confirm this observation, and show a higher crystallinity of agro-fibers in the opposition to the observed raw samples. The alkaline treatment has a more strong effect in the bagasse fiber, increasing the CI by 39%, followed by the wheat straw with an increase of 17%. In the case of wood fibers the CI increases by less than 6%.

3.2. Surface characterization

In order to study the influence of the alkaline treatment on the surface characteristics of the fibers, the raw and the modified fibers were studied by inverse gas chromatography (IGC). In this work, the dispersive component of the surface energy, γ_S^D , was obtained by the application of the method of Schultz, Lavielle, and Martin (1989):

$$\Delta G_{\text{ads}}^D = RT \ln V_N = 2N_A(\gamma_S^D)^{1/2} a(\gamma_L^D)^{1/2} + \text{const.} \quad (2)$$

where ΔG_{ads}^D is the dispersive free energy of adsorption, V_N is the net retention volume, γ_S^D and γ_L^D the dispersive component of the surface tension of the solid material and the probe molecule, respectively, a is the cross sectional area of the probe molecule and N_A the Avogadro constant.

Fig. 3 shows, as example, the plot of $RT \ln V_N$ versus $a(\gamma_L^D)^{1/2}$ for the *n*-alkanes series in raw and modified fibers at 298 K. In the present study, excellent linear corrections (0.994–0.9996) were obtained for the *n*-alkanes series in all samples undertaken for analysis. γ_S^D was determined at four different temperatures (293, 296, 298, and 300 K). The results are listed in Table 3. It was observed that the γ_S^D decreases linearly with increase in temperature. The γ_S^D decrease with the temperature is frequently observed in lignocellulosic materials (Cordeiro, Gouveia, & Jacob John, 2011a).

On the surface of lignocellulosic fibers, polar groups (such as hydroxyl and carboxylate) are located that are able to exchange dispersive, but also specific interactions with polar probes. Therefore, the surface interaction with polar probes was also studied for all the samples. The specific free energy of adsorption, $\Delta G_{\text{ads}}^{\text{sp}}$, is calculated by the difference between the surface acid–base parameters using the Gutmann (1978) concept:

$$-\frac{\Delta G_{\text{ads}}^{\text{sp}}}{AN^*} = K_a \frac{DN}{AN^*} + K_b \quad (3)$$

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 sample to accept or to donate electrons, and were determined from graphic representation of $-\Delta G_{\text{ads}}^{\text{sp}}/AN^*$ versus DN/AN^* (Fig. 4; Table 4). The correlation coefficients determined by the linear fitting of the data for all samples under study, were in the range 0.96–0.99, showing that the Gutmann's acid–base concept is valid for the studied samples, and that the specific interactions may be considered to be of the electron donor–acceptor type.

Table 3
Dispersive component of the surface tension (mJ/m²) of the raw and modified fibers surfaces.

	γ_s^D (mJ/m ²)				Correlation coefficient
	293 K	296 K	298 K	300 K	
Eucalyptus					
Raw	44.39	43.60	43.20	42.41	0.984
Modified	44.00	43.05	42.72	42.22	0.985
Spruce					
Raw	43.26	42.23	41.61	41.19	0.990
Modified	45.92	44.63	44.18	43.27	0.988
Bagasse					
Raw	46.39	44.90	44.24	43.15	0.994
Modified	44.16	43.18	42.82	42.12	0.989
Wheat straw					
Raw	47.57	45.91	45.06	44.47	0.982
Modified	52.13	50.27	48.82	48.02	0.991

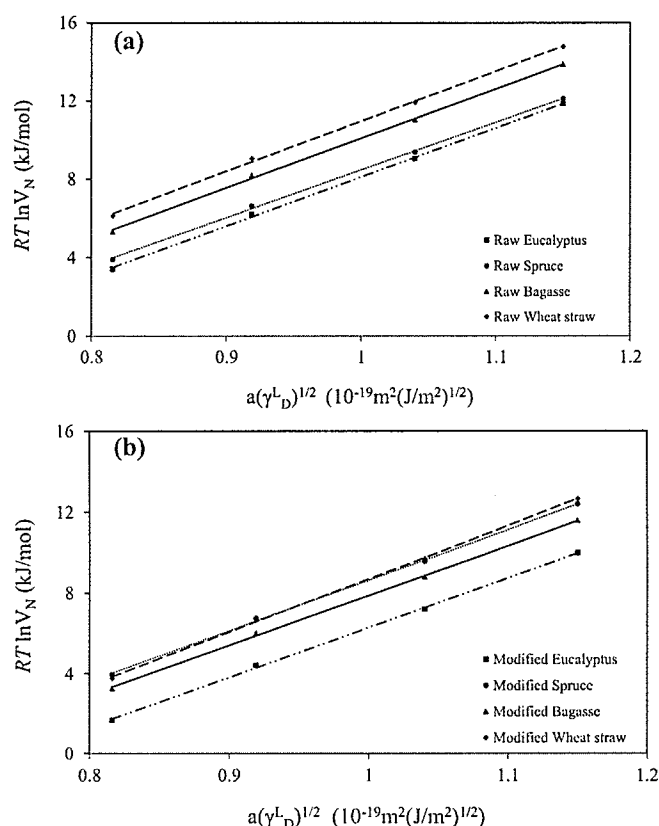


Fig. 3. Plot of $RT \ln V_N$ versus $a(\gamma_D^L)^{1/2}$ for the *n*-alkanes onto raw (a) and modified (b) fibers at different temperatures.

Table 4
Acid/base constants obtained for the raw and modified fibers at 298 K.

Fibers	K_a	K_b	K_b/K_a	Correlation coefficient
Eucalyptus				
Raw	0.09	0.31	3.44	0.963
Modified	0.08	0.43	5.37	0.972
Spruce				
Raw	0.08	0.33	4.13	0.956
Modified	0.08	0.45	5.63	0.972
Bagasse				
Raw	0.10	0.13	1.30	0.992
Modified	0.09	0.28	3.11	0.986
Wheat straw				
Raw	0.12	0.12	1.09	0.995
Modified	0.11	0.28	2.54	0.988

The strength of the interaction between the surface of a solid and a gas molecules adsorbed on the surface can be directly measured by the heat of adsorption, Q :

$$Q = R \frac{d(\ln V_N)}{d(1/T)} \quad (4)$$

In this study, Q was determined with a non-polar probe, *n*-octane, and with the four polar probes: tetrahydrofuran, ethyl acetate, acetonitrile and ethanol, at 293, 296, 298, and 300 K (Fig. 2). Excellent linearity's was obtained (>0.98). Although Q is dependent on the probe molecule and the surface properties, its study allows the understanding of the variations in surface acid–base characteristics of a material during a transformation process. In the present work, the interaction between the different fibers and all polar probes (Fig. 5) indicates the presence of both acidic and basic sites on the fibers surface.

The isotherm experimental, done with the *n*-octane probe, shows symmetrical peaks for all the studied fibers, typical of linear adsorption isotherms described by Henry's Law, and highlights that *n*-octane interacts only with the surface of the fibers (Fig. 6).

Using the BET approach, the monolayer capacity, n_m , and the surface area, S_{BET} , were determined, as explained in detail by Condor and Young (1979). The results are presented in Table 5.

The examination of the surface properties of the fibers using IGC at finite concentration conditions, gives also access to information on the surface heterogeneity (Cordeiro, Gouveia, Moraes, et al., 2011). In the present work, the surface heterogeneity was determined by the variation of the *n*-octane concentration. For all the samples the curves (Fig. 7) have only one peak maximum, A_{max} , with energies between 10 and 14 kJ/mol.

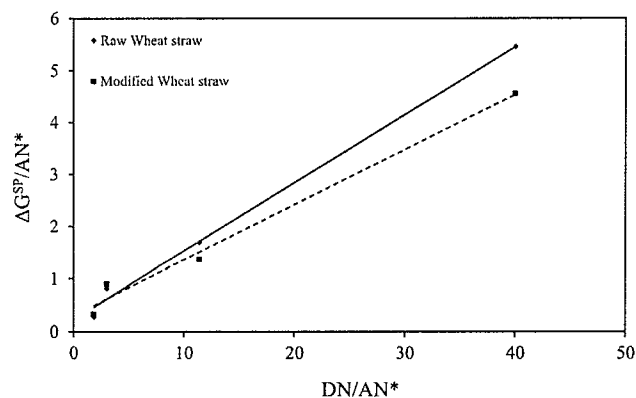


Fig. 4. Plot of $\Delta G_{ads}^{sp}/AN^*$ versus DN/AN^* for wheat straw before and after NaOH treatment.

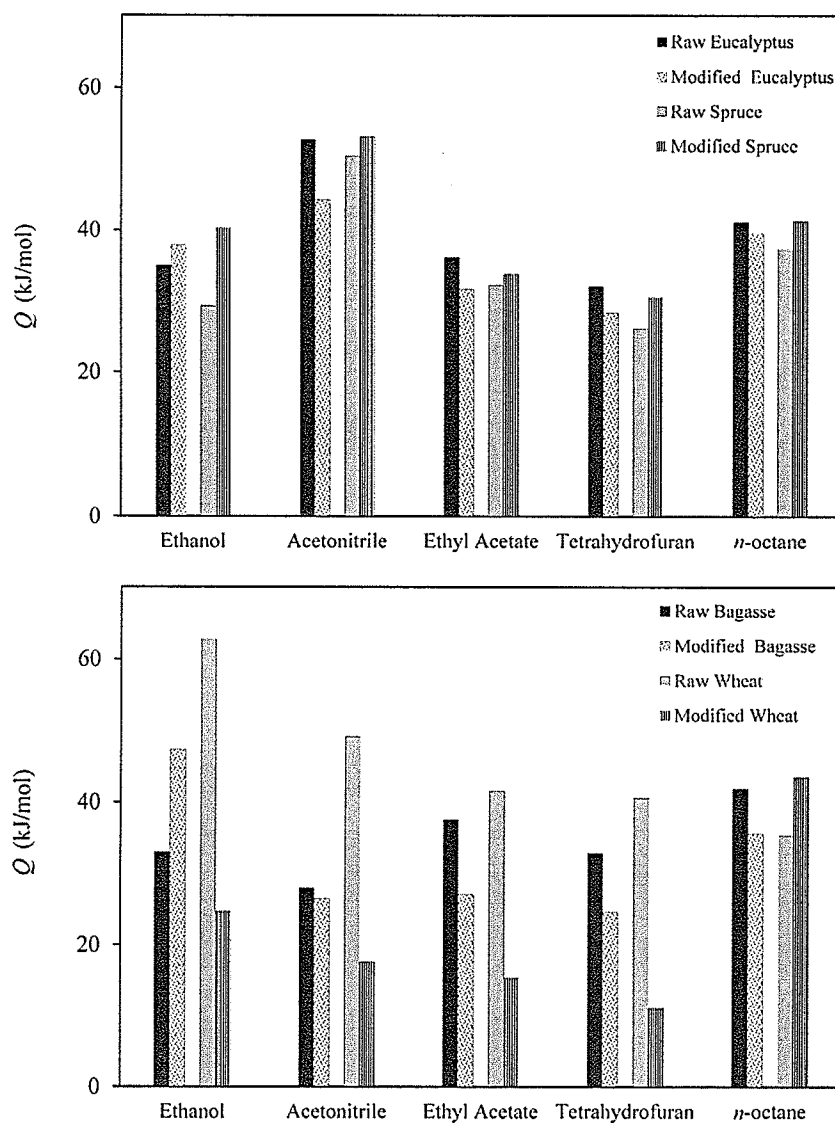


Fig. 5. Heat of adsorption obtained for raw and modified fibers at 298 K.

3.2.1. Dispersive surface energy

Among the studied raw fibers, the non-wood samples present the highest value of the γ_S^D when compared with the wood fibers (Table 3). Wheat straw presented the highest value of the γ_S^D (47.57 mJ/m², at 293 K) while spruce fiber exhibited the lowest value of γ_S^D (43.26 mJ/m², at 293 K). These values are close to those reported in the literature for similar materials. Mills et al. (2008) reported a dispersive surface energy for wheat straw of 40.9 mJ/m² at 293 K. Walinder and Gardner (2000) reported a dispersive energy for Norway spruce wood of 42 mJ/m² at 293 K and Aquino et al. (2002) reported a dispersive energy, for eucalyptus of 41.3 mJ/m² at 313 K. Cordeiro, Gouveia, and Jacob John (2011), Cordeiro, Gouveia,

Moraes, et al. (2011), found γ_S^D ranged from 37.17 to 51.37 mJ/m², at 298 K, for various lignocellulosic fibers, namely piassava, jute, sorghum, ramie, pita Mexicana, curaua, sisal, flax, hemp, kenaf, agave, agave hybrid and pineapple.

The variation in surface energy can be explained by the chemical composition of lignocellulosic fibers which depends on various factors such as species, variety, farming type of soil, weather conditions, plant part from which the fibers are extracted, age of the plant, etc. (Rowell et al., 2000; Satyanarayana & Wypych, 2007).

Previous works (Mills et al., 2008; Cordeiro, Gouveia, & Jacob John, 2011; Cordeiro, Gouveia, Moraes, et al., 2011) associate the γ_S^D increase with lignin decrease and cellulose increase content of

Table 5

Adsorption potential distribution maximum, specific surface area and monolayer capacity for the raw and modified fibers at 298 K.

Fibers	Raw			Modified		
	A_{max} (kJ/mol)	S_{BET} (m ² /g)	n_m (μ mol/g)	A_{max} (kJ/mol)	S_{BET} (m ² /g)	n_m (μ mol/g)
Eucalyptus	11.89	0.81	2.13	10.08	0.48	1.26
Spruce	11.20	1.19	3.15	10.97	0.82	2.15
Bagasse	14.15	1.07	2.82	11.34	0.96	2.52
Wheat straw	14.13	0.95	2.50	14.20	0.60	1.58

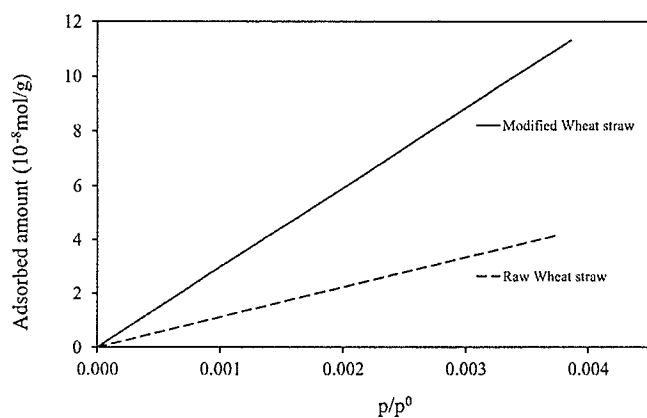


Fig. 6. *n*-octane isotherms obtained for fibers before and after NaOH treatment.

the analyzed material. However, the retention of the probes, and consequent IGC data, could be influenced by other parameters such as crystallinity and the arrangement and orientation of chemical groups in the surface (Belgacem, Blayo, & Gandini, 1996; Papirer, Brendle, Balard, & Vergelati, 2000).

As concluded by the chemical characterization, the alkaline treatments modify the composition of the samples, which results in γ_S^D changes (Table 3). The modified fibers, wheat straw and spruce fibers, show higher γ_S^D , than the respective raw fibers. On the contrary, the modified eucalyptus and bagasse show lower γ_S^D , than the respective raw fibers. The change in the dispersive component of the fiber surface can be also evaluated by Q parameter

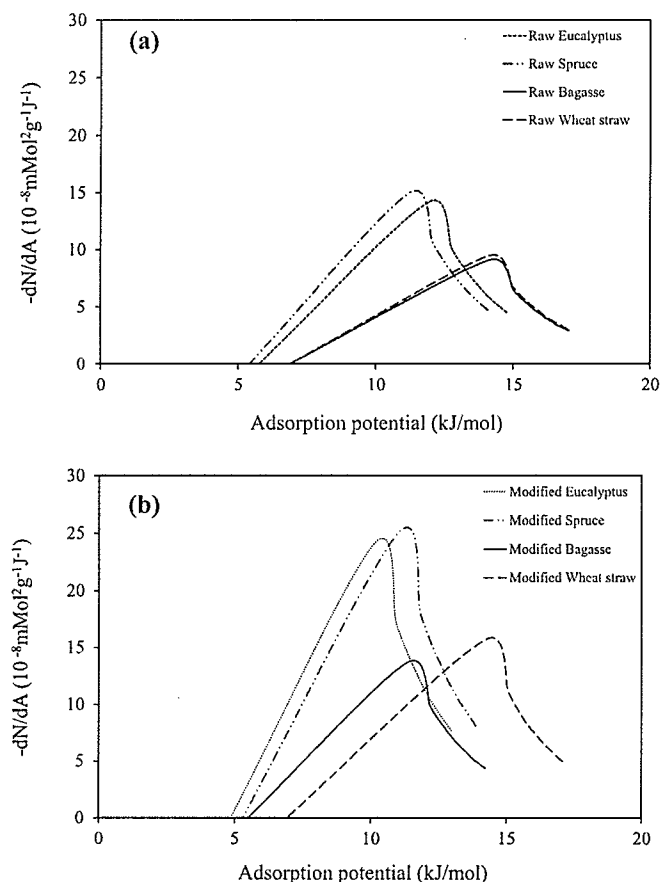


Fig. 7. Heterogeneity profiles obtained with *n*-octane at 298 K for (a) before NaOH treatment and (b) after NaOH treatment.

using a non-polar probe. The Q values obtained for the *n*-octane in the raw fibers were 35.39 and 37.47 kJ/mol, and they increased to 43.53 and 41.36 kJ/mol after treatment, for wheat straw and spruce fibers, respectively (Fig. 5). In the case of the γ_S^D decrease, a similar tendency is observed in Q values.

Since *n*-alkane probes are able to interact only through dispersion interactions, the increased γ_S^D for modified fibers was an indication that the fibers became with more hydrophobic active sites (Matuana, Balatinecz, Park, & Woodhams, 1999). This increase can be due to the increase in number and/or in the energy of the active sites. As example, the energetic profile show that the modified wheat straw fibers (Fig. 7b) present active sites more energetic (A_{max} at 15.20 kJ/mol) than in raw material (A_{max} at 14.13 kJ/mol). On the other hand, the energetic profile of the modified bagasse (Fig. 7b) shows the presence in their surface of less energetic active sites (A_{max} at 11.34 kJ/mol) than in the raw material (A_{max} at 14.15 kJ/mol). As referred above, a decrease in the γ_S^D can be also due to the reduction in the number of the non-polar sites on the surface. In the present case, the mercerization can remove waxy material (small non-polar molecules) and thus should leave the surface richer in cellulose, with polar hydroxyl groups in a more exposed conformation lowering the γ_S^D (Ass, Belgacem, & Follini, 2006). The reduction in the γ_S^D values can be due also to the protective coating formed by the moieties created by the partial depolymerisation of lignin. The FTIR and the XRD analyses have confirmed the increased cellulose content of the fibers after NaOH treatment (Table 2; Fig. 2), due to the dissolution of the extractives, hemicelluloses and lignin components in the fiber. Li, Tabil, and Satyanarayan (2007) found that the alkaline treatment used in chemical treatment of vegetable fibers causes disruption of hydrogen bonds and removal of amorphous portions (hemicellulose, lignin and pectins) and impurities, raising the content of exposed cellulose on the fiber.

3.2.2. Acid–base surface characteristics

FTIR spectra indicate that alkaline treatment removes some components but how this affects the acid–base surface properties? Can these alterations have impact on their adhesive bond quality?

As referred above, using different polar probes (acetonitrile, ethanol, ethyl acetate and tetrahydrofuran) the Q values were obtained. Greater changes in Q values were observed for all the polar probes (Fig. 5), which is indicative of modifications in acid and base active sites during the alkaline treatment. The highest increase in Q was observed for the ethanol, probe with lower DN/AN^* , when compared to the probe with higher DN/AN^* , in the case of bagasse fiber, suggesting that the alkaline treatment increased predominantly the basic groups in the fiber surfaces. The decrease in Q values for the THF (the more acid probe) for all the fibers, supports the indication given by the FTIR spectra about the removal of acidic groups by alkaline treatment. In the case of spruce fibers, the Q decreases for all the polar probes. This indicates that the alkaline treatment changes significantly the surface with a decrease in the polar active sites used in the specific interactions.

Relative to specific free energy of adsorption, ΔG_{ads}^{SP} , calculated according to Eq. (2), the data at 298 K are shown in Fig. 8. All the raw and modified fibers exhibited maximum interaction with acetonitrile, which is an amphoteric compound that can interact with both the acidic and basic groups, which is indicative of both groups in the fibers surface. Fig. 8 shows increase in ethanol ΔG_{ads}^{SP} (16–143%) with the alkaline treatment for all the fibers, clearly indicating that the alkaline treatment creates new basic active sites for specific interactions. On the other hand, the ΔG_{ads}^{SP} decrease in the THF probe can be due to acid active sites removal.

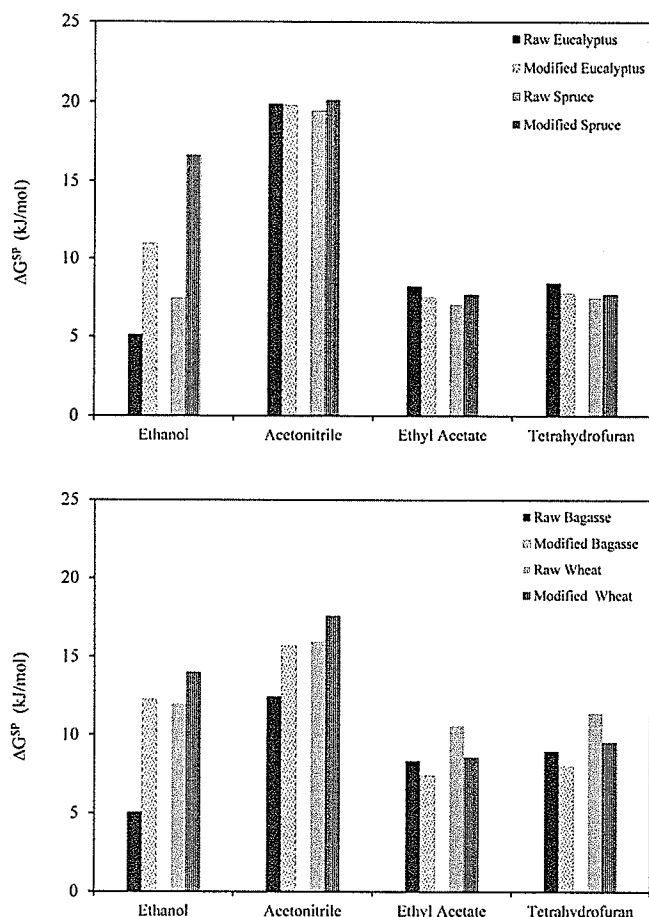


Fig. 8. Specific free energy of adsorption ($\Delta G_{\text{ads}}^{\text{SP}}$) obtained for raw and modified fibers at 298 K.

In terms of acid–base constants (calculated by $\Delta G_{\text{ads}}^{\text{SP}}$ using Eq. (3)) the K_a is lower than the K_b for all the samples (Table 4), which means that all the samples show stronger basicity. This property can be attributed to the strong basicity and weak acidity of cellulose and hemicelluloses. Bagasse fibers exhibited the lowest ratio of K_b/K_a (1.09) and the spruce fiber exhibited the highest ratio of K_b/K_a (4.13). The same Lewis basic predominant characters were also found by Cordeiro, Gouveia, Moraes, et al., (2011) in the piassava (0.09 to K_a and 0.15 to K_b), jute (0.10 to K_a and 0.17 to K_b), sorghum (0.10 to K_a and 0.15 to K_b), ramie (0.10 to K_a and 0.18 to K_b), pita Mexicana (0.09 to K_a and 0.36 to K_b), curaua (0.11 to K_a and 0.14 to K_b) and sisal (0.09 to K_a and 0.12 to K_b). Mills et al. (2008) also reported basic character onto the surface of bast fibers, namely for hemp (0.16 to K_a and 0.49 to K_b), flax (0.17 to K_a and 0.49 to K_b) and kenaf (0.07 to K_a and 0.32 to K_b).

For the modified fibers, the wheat straw exhibited the lowest ratio of K_b/K_a (2.54) and the spruce exhibited the highest ratio of K_b/K_a (5.37). This increase in K_b/K_a ratio was higher for the agro-fibers (133–139%) compared to the wood-fibers (36–56%) due principally to the K_b increase.

After alkaline treatment, basic character was found to increase for all fibers. To conclude: the alkaline treatment increases the basic surface character for all the modified samples with more relevance to the agro-fibers.

3.2.3. Isotherm measurements

The BET model was used to determine the values of surface area and monolayer capacity (Table 5). The surface area of the raw fibers

were found to range between 0.81 and 1.19 m^2/g , corresponding to eucalyptus and spruce fibers, respectively.

A parameter that can be undoubtedly related to surface area is monolayer capacity. The *n*-octane monolayer capacity of the raw fibers was found to vary between 2.13 $\mu\text{mol}/\text{g}$ for eucalyptus and 3.15 $\mu\text{mol}/\text{g}$ for the spruce fiber. Cordeiro, Gouveia, Moraes, et al. (2011) found for agro-materials S_{BET} values between 0.382 and 2.793 m^2/g and n_m values between 0.3 and 7.4 $\mu\text{mol}/\text{g}$.

After alkaline treatment, the modified fibers show values for the surface area ranging between 0.48 and 0.96 m^2/g , and to monolayer capacity between 1.26 $\mu\text{mol}/\text{g}$ and 2.52 $\mu\text{mol}/\text{g}$, corresponding to eucalyptus and bagasse, respectively. This can be indicative of fibers aggregation during the alkaline treatment or/and indicative of less rough or/and perforated samples.

4. Conclusions

This study investigated the effects of alkaline treatment on surface properties of Iranian cultivated natural fibers that may have impact on their adhesive bond quality. The following conclusions can be drawn from this study:

1. Alkaline treatment removes some chemical components on the surface of raw fibers, namely uranic acid (hemicellulose), non-polar molecules (extractives) and aromatic moieties from the partial lignin depolymerisation. The treatment has a higher impact on chemical components of non-wood fibers;
2. Alkaline treatment enhances the crystallinity of non-wood fibers, while in the softwood fibers produces only a slight increase;
3. Alkaline treatment can remarkably improve the specific interaction of the fibers, namely in the interaction with acids agents. This improvement was more significant in the agro-fibers;
4. Alkaline treatment achieves the best overall improvement in the properties evaluated for the agro-fibers when compared to the wood fibers;
5. In general, alkaline treatment can improve wettability of the fibers and reduce the need for coupling agent in wood plastic composite process.

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