

# INVESTIGATION OF SURFACE PROPERTIES OF CHEMICALLY MODIFIED LIGNOCELLULOSIC FIBRES BY INVERSE GAS CHROMATOGRAPHY

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## **Abstract**

Inverse gas chromatography (IGC) is a suitable method to determine surface energetics of natural fibres when compared to wetting techniques. In the present study, the surface properties of raw and chemically 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 chemical treatments used were 4% NaOH and 2% zein treatment. The uniqueness of zein treatment is that it is bio-based and therefore maintains the biodegradable character of the natural fibres. Fourier Transform Infra-Red Spectroscopy (FTIR) and Environmental Scanning Electron Microscope (ESEM) were also performed to characterize the surface changes in fibres. The surface energy and acid-basic character of fibres were seen to be influenced by the crystalline nature of fibres. Bast fibres exhibited higher surface dispersive energy than leaf fibres which was attributed to the intrinsic chemical composition of fibres. Both alkali and zein treatments were seen to decrease the dispersive surface energy.

Keywords: Natural fibers; Chemical Modification; Alkali treatment; Zein treatment; Inverse Gas Chromatography; Surface characteristics

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## 1. INTRODUCTION

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,  $\gamma_s^D$  and a specific term  $\gamma_s^{SP}$  caused by London forces and polar interactions respectively. As the dispersive component of surface energy is highly sensitive to changes in the surface chemistry,  $\gamma_s^D$  is an appropriate parameter for the characterization of porous materials<sup>1</sup>. The dispersive component of surface energy also gives information of the heterogeneity of the surface<sup>2</sup>.

Inverse Gas Chromatography (IGC) is being widely used in studies of adsorption thermodynamics and the properties of organic and inorganic materials. This technique provides information about the adsorption properties, acid-base characteristics and a better comprehension of surface chemistry. One of the drawbacks of IGC is that the technique computes vapour preservation time of a non-polar solvent and therefore it is not possible to evaluate the polar component of surface energy ( $\gamma_s^{SP}$ ).

Though there is a lot of literature on chemical modification of natural fibres, there are only few studies relating to the characterization and changes in acidity and basicity characteristics of chemically modified natural fibres<sup>3,4</sup>. In the present study, IGC was used to characterize the surface properties of 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 chemical modifications.

### IGC theory

The dispersive component of the surface energy, as well as the specific free energy of sorption, was measured with dispersive (non-polar) and acid-base (polar) probe molecules through pulse technique. The relation between the retention volume and free energy of sorption  $\Delta G_s^0$  is given by the following equation:

$$\Delta G_s^0 = RT \ln V_R^0 + K \quad (1)$$

where R is the gas constant and K is the De Boer or Kemball/Rideal constant depending on the chosen reference state <sup>5,6</sup>.  $\Delta G^0_s$  is also related to the energy of adhesion  $W_A$  (between probe molecule and solid) by the equation:

$$\Delta G^0_s = N_A \cdot a \cdot W_A \quad (2)$$

where a is the cross sectional area of the adsorbate and  $N_A$  the Avogadro constant. According to Fowkes, the dispersive contribution of the work of adhesion  $W_A$  is given by:

$$W_A = 2(\gamma_s^D \cdot \gamma_L^D)^{1/2} \quad (3)$$

with  $\gamma_s^D$  and  $\gamma_L^D$  as the dispersive surface energy of the solid adsorbent and surface tension of the liquid adsorbate respectively<sup>7</sup>. Combining the equations 2 and 3 :

$$RT \ln V_R^0 = 2N_A \cdot (\gamma_s^D)^{1/2} \cdot a(\gamma_L^D)^{1/2} + \text{const} \quad (4)$$

Thus, the dispersive component of the surface tension ( $\gamma_s^D$ ) can be calculated from the plot of  $RT \ln V_R^0$  versus  $a(\gamma_L^D)^{1/2}$ . This parameter is defined as the energy required to form a unit surface under reversible conditions and it is analogue to the surface tension of a liquid and in practical terms, the higher the surface energy the more the reactivity of the surface.

A comprehensive insight in the Lewis acid/base surface interactions can provide better understanding of the influence of the chemical properties of the fibers, as well as their ability to change via chemical modifications, which is of great importance in fibre-matrix interface studies<sup>8</sup>. The presence of acid and base active sites on the fiber surfaces increases the possibility of specific intermolecular interactions with solvents and other polymer matrices<sup>9</sup>.

In order to measure how easily the surface can interact with polar molecules, the specific free energy of sorption,  $\Delta G^0_s$ , is determined. The difference between the measured retention volumes of the polar molecules and the reference line given by the *n*-alkane is used to calculate the specific interaction contribution to the free energy of adsorption. To obtain  $K_a$  and  $K_b$ ,  $\Delta H_s$  must be calculated for probe molecules. Thus, the parameters can be determined by linearising Gutman equation relating the enthalpy ( $\Delta H_s$ ) with the acid-base number equation<sup>10,11</sup>:

$$-\frac{\Delta H_s}{AN^*} = \frac{DN}{AN^*} K_a + K_b \quad (5)$$

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. When IGC is carried out at infinite dilution,  $K_a$  and  $K_b$  relate to the Lewis acidity and Lewis basicity of the highest energy sites. The overall acid/base character of samples can be evaluated from the ratio of  $K_b/K_a$ . At  $K_b/K_a > 1$ , the surface is considered to be basic, while for  $K_b/K_a < 1$ , the surface is considered to be acidic<sup>12</sup>.

## **2. MATERIALS AND METHODS**

### ***2.1. Samples preparation***

Good quality bast and leaf lignocellulosic fibres (flax, hemp, kenaf, agave, agave hybrid pineapple, and sisal) were procured from local sources. Zein was obtained from Scientific Polymer Product Company, Ontario, NY. All other chemical reagents used in this study were of analytical grade.

### ***2.2 Chemical Modification of Fibres***

#### ***2.2.1 Alkali treatment***

The fibres were treated for 3 hours under ambient conditions with 4% NaOH solution. The fibers were further washed with water containing acetic acid. Finally, the fibers 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<sup>13,14,15</sup>. 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 hours. 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.

## **3. MEASUREMENT OF PROPERTIES**

### ***3.1. IGC analysis***

IGC measurements were carried out on a commercial inverse gas chromatograph (*iGC*, Surface Measurements Systems, London, UK) equipped with a flame ionization (FID) and thermal conductivity (TCD) detectors. The *iGC* system is fully automatic with SMS

*iGC* 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 fibers (raw and chemically 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  $\mu$ l gas loop. The retention volume and subsequent data were analyzed using *iGC* 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 and are reported in Table 1. Measurements of the dispersive interaction were made with non polar probes (hexane, heptane, octane, nonane and decane) at 298 K at 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.

### **3.2 FTIR**

Infrared spectra of the untreated and treated fibres were recorded with an FT-IR spectrometer (Perkin Elmer FTIR). The spectra were analyzed over the range of 4000 – 650  $\text{cm}^{-1}$ .

### **3.3 Environmental scanning electron microscope (ESEM)**

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.

## **4. RESULTS AND DISCUSSION**

### **4.1 Dispersive surface energy ( $\gamma_s^D$ )**

#### **Untreated fibres**

A series of n-alkanes was used to determine the dispersive surface energy of the different fibres. The dispersive surface energy of natural fibres is dependent on

microstructure as well as its chemical composition (See Table 2<sup>16</sup>). It is also related to the crystalline and amorphous regions within the fibres. Figure 1 (a) and (b) shows the plot of  $RT\ln V_R^0$  versus  $aN_A(\gamma_L^D)^{1/2}$  (Eq. 4) for the *n*-alkanes series for agave fibers and agave hybrid fibres respectively. Excellent linear corrections (0.9991-0.9996) were obtained for the *n*-alkanes series for all samples analyzed. The calculated dispersive surface energy ( $\gamma_S^D$ ) values of the different fibres are summarized in Table 3. Flax fiber presents the highest surface energy while agave hybrid exhibited the lowest. It is quite apparent (from Table 3) that the bast fibres exhibit higher dispersive surface energy than the leaf fibres. This can be attributed to differences in concentration of cellulose and crystallinity of the fibres. Similar values for ( $\gamma_S^D$ ) in raw fibres were observed by Mills et al<sup>17</sup> who studied the dispersive surface energy of several lignocellulosic fibers at different temperatures by IGC. They also observed a proportional co-relation between surface dispersive energy and percentage of cellulose. Such a clear association was not found in our studies as pineapple fibre which has the highest percentage of cellulose (~80%) exhibited lower  $\gamma_S^D$ .

### **Alkali treatment**

It can be observed that there has been a significant change in  $\gamma_S^D$  when the fibres were subjected to 4% NaOH treatment. While the  $\gamma_S^D$  of all the fibres decreased upon alkaline treatment, mercerized pineapple fibres registered an increase. Alkaline treatment is one of the most commonly used chemical treatments for natural fibers. Treatment of the cellulose fibers with alkali results in swelling, during which the natural crystalline structure of the cellulose –cellulose I- changes to cellulose II. The degree of swelling can be influenced by the concentration, the type of alkali, the temperature and the time of treatment<sup>18</sup>.

In order to understand changes in surface energy, one must look at the supramolecular chemistry of cellulose which is indeed a complex issue. Cellulose exists mainly in four different polymorphs, named cellulose I, II, III and IV. Cellulose I is found in nature and it occurs in two allomorphs  $I_\alpha$  and  $I_\beta$ . Cellulose II is the crystalline form formed after re-crystallization. Figure 2 shows the structures of cellulose I and II. 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<sup>19</sup>. During mercerization, cellulose I is converted to cellulose II which is thermodynamically the more stable configuration and hence will exhibit lower surface dispersive energy.

The extent of transformation from cellulose I to cellulose II depends on experimental conditions and nature of fibres. Amongst all the natural fibres in the study, pineapple fibre has the maximum cellulose content (~80%). As the amount of cellulose is significantly higher in pineapple fibres, some of the swollen cellulose may not recrystallize into cellulose II, resulting in large fraction of disordered amorphous cellulose which might account for the higher  $\gamma_S^D$ .

#### 4.1.3 Zein treatment

For the zein treated fibres, it can be observed that  $\gamma_S^D$  values have decreased for all the fibres except pineapple fibre. The amino acid composition in zein<sup>20</sup> 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 proportional 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  $\gamma_S^D$  has been co-related to the polarizability of the system<sup>1</sup>.

#### 4.2 Specific Free Energy of Desorption ( $\Delta G_o^{SP}$ ) and Acid-Base Characteristics

A series of polar probes were used to determine the ( $\Delta G_o^{SP}$ ) of all the fibres. Figure 3a and b presents the plot of  $RT \ln V_R^0$  versus  $aN_A (\gamma_L^D)^{1/2}$  of the kenaf fibres before and after alkaline treatment respectively. The specific free energy of desorption was calculated using the difference between the desorption energy of the polar probe and its dispersive increment, as shown in Figure 3(b) and the results are presented in Table 4. All the raw fibers exhibited maximum interaction with acetonitrile which is an amphoteric compound that can interact both with acidic and basic constituents. Similar results were found in studies by Heng et al. who did an extensive investigation into determination of surface energies of natural fibres<sup>19</sup>. Alkali treated fibres present an

acidic nature evident from the greater interaction with basic probes compared to acidic probes.

The specific free energies of desorption 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 from the slope and intercept of the respective linear regression line of  $\Delta H/AN$  as a function of  $DN/AN$ . These values are summarized in Table 5. Due to space constraints all 21 graphs are not shown. The linearity of the plots (Figure 4a and b) 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 fibers in the study presented a Lewis base character as seen in Table 5. Similar results were observed by other researchers for hemp fibres<sup>21</sup> 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 results. Another reason could be the inter and intra hydrogen bonding between hydroxyl groups, that result in free ether linkages which could contribute to the basic character of natural fibres<sup>22</sup>. Amongst all natural fibres, agave fiber presents the lowest  $K_b/K_a$  ratio 1.33, while agave hybrid exhibited the highest ratio 3.83.

After alkaline treatment, basic character was found to decrease for all fibres except kenaf. Alkalization cleans the fiber surface by dissolving extractives and hemicellulose. This would increase the acidic character of the fibres due to exposure of cellulose, which is predominantly acidic. Kenaf fibres showed a surprising increase of  $K_b/K_a$  ratio which at this point cannot be interpreted. More systematic investigation is necessary. Another reason for the anomalous results can be attributed to the fact that adsorption of probes onto the fibres is largely affected by the presence of waxes leading to gas-liquid interaction between probes and waxes rather than gas-solid interactions.

Zein treatment resulted in increase in basic character for agave, kenaf and hemp fibres when compared to raw fibres. The increase in basicity was due to reduction of the accessible hydroxyl groups in the natural fibres and presence of amino groups. The alkaline treated fibres were found to be more acidic than the zein coated fibres.



## 4.2 FTIR and ESEM

The FTIR spectra of untreated and alkali treated pineapple and hemp fibres are given in Figure 5 a & b respectively. In the untreated sisal and pineapple fibres, the peaks around  $3329\text{ cm}^{-1}$  and  $1050.98\text{ cm}^{-1}$  are assigned to  $-\text{OH}$  stretching, and  $-\text{C}-\text{O} / \text{C}-\text{C}$  stretching vibrations respectively. The peaks ranging from  $1200\text{-}1400\text{ cm}^{-1}$  are assigned to  $\text{C}-\text{H}$  and  $\text{CH}_2$  stretching vibrations. The peak at  $1731\text{ cm}^{-1}$  present in raw pineapple and sisal fibre corresponds to  $\text{C}=\text{O}$  in acids and esters of p-coumaric and uronic acids which are the main constituents of hemicellulose<sup>23,24</sup>. This peak is absent in NaOH treated fibres due to the removal of hemicellulose by alkali treatment. The intense peak around  $1300\text{ cm}^{-1}$  is reflects the In the FTIR spectra of zein treated pineapple and sisal fibres, the peak at  $1071\text{ cm}^{-1}$  assigned to  $\text{C}-\text{O}$  stretching is less intense in the treated fibres indicating interactions between functional groups. The emergence of new bands on the zein coated kenaf fibres around  $1530\text{ cm}^{-1}$  are assigned to  $\text{C}-\text{N}$  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  $3300\text{ cm}^{-1}$  which is attributed to the presence of amide group in zein treated fibres. Figure 6 (a), (b) and (c) presents the SEM of untreated, alkali treated and 2% zein treated sisal fibres. The untreated fibres show the unidirectional structure of the fibre while alkali treated fibre presents a rough surface due to removal of non-cellulosic constituents. Fibre fibrillation is also evident. The presence of zein coating on fibres is clearly seen by the presence of macrospheres on the fibre surface (Figure 6 c).

## CONCLUSIONS

The surface properties of untreated and chemically modified lignocellulosic fibres were analysed by inverse gas chromatography measurements. The dispersive surface energy of natural fibres was found to be dependent on chemical composition and crystallinity of natural fibres. Bast fibres exhibited higher surface energy than leaf fibres. Alkali treatment resulted in a decrease for all natural fibres. This was attributed to the conversion of cellulose I to cellulose II which being more stable had a lower  $\gamma_s^D$ . The lowering of  $\gamma_s^D$  in zein coated fibres was attributed to interactions between hydroxyl groups and amino groups which led to decrease in free polar groups and subsequently total polarizability of the fibres. All the natural fibres were found to have a predominant basic character due to the ether linkages present in the cellulosic structure. It

is quite apparent that IGC coupled with EDS is a successful technique for characterizing surface properties of natural fibres.

## **ACKNOWLEDGMENT**

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## **TABLES CAPTIONS**

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

**Table 2.** Chemical composition of fibres

**Table 3.** Dispersive component of the surface tension ( $\text{mJ/m}^2$ ) and of the fibers surfaces before and after treatments.

**Table 4** Specific free energy of desorption of untreated and treated fibres

**Table 5** Acid-base constants ( $K_a$ ,  $K_b$ ) of the fibers surfaces before and after treatments.

**Table 1**

Probe	Cross-sectional área ( $10^{-19}\text{m}^2$ )	Surface tension ( $\gamma^d_1$ ) (mJ/m <sup>2</sup> )	DN (kcal/mol)	AN* (kcal/mol)	Specific characteristic
<i>n</i> -Hexane	5.15	18.4	-	-	Neutral
<i>n</i> -Heptane	5.73	20.3	-	-	Neutral
<i>n</i> -Octane	6.30	21.3	-	-	Neutral
<i>n</i> -Nonane	6.90	22.7	-	-	Neutral
<i>n</i> -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

**Table 2**

	Cellulose	Hemicellulose	Lignin	Pectin	Waxes
Fibres	(%)	(%)	(%)	(%)	(%)
Flax	71	18.6-20.6	2.2	2.3	1.7
Hemp	70-74	17.9-22.4	3.7-5.7	0.9	0.8
Sisal	66-78	10-14	10-14	1.9	0.3
Kenaf	45-57	21.5	8-13	3-5	-
Agave	59	37.4	2.5	-	-
Agave hybrid	62	23	5.6	-	-
Pineapple	70-82	10-12	3-4	-	-

**Table 3**

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**Dispersive surface energy ( $\gamma_s^D$ )**

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Fibre	Raw material	Alkaline Treatment	Zein Treatment
Agave	42.01	34.69	38.01
Agave Hybrid	37.17	29.72	35.17
Flax	51.37	43.23	43.38
Hemp	46.68	41.92	40.54
Kenaf	42.83	35.50	38.01
Pineapple	39.58	41.74	42.19
Sisal	37.49	35.09	36.78

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**Table 4**

Fibre	Specific free energy of desorption $\Delta G^{SP}$ (kJ mol <sup>-1</sup> )														
	Acetonitrile			Ethyl acetate			Acetone			THF			DCM		
	Raw	4% NaOH	Zein	Raw	4% NaOH	Zein	Raw	4% NaOH	Zein	Raw	4% NaOH	Zein	Raw	4% NaOH	Zein
Flax	17.666	13.354	8.228	9.468	7.186	8.241	7.622	5.582	6.830	10.50	7.992	9.178	10.836	8.344	9.560
Hemp	18.627	11.830	19.285	8.892	7.088	7.172	7.445	5.496	5.870	9.809	8.858	8.327	9.100	8.634	7.326
Kenaf	11.673	5.754	18.632	7.515	5.879	7.132	6.285	5.830	6.147	8.161	3.431	4.830	7.382	5.519	9.481
Sisal	18.597	9.140	15.637	6.614	6.237	6.773	5.287	4.502	5.460	7.753	6.831	8.088	6.712	5.998	14.947
Pineapple	16.305	11.879	8.583	8.067	7.415	9.033	7.653	5.951	9.590	8.749	8.251	9.011	8.531	7.765	10.676
Agave	16.550	7.060	9.547	7.806	6.286	6.335	6.624	4.687	4.799	9.683	7.060	7.125	8.126	6.205	6.525
Agave hybrid	18.793	9.708	8.583	7.459	5.148	6.335	6.402	3.420	4.799	8.018	6.411	7.125	7.589	4.264	10.676

**Table 5**

Fibre	Raw			Alkaline Treatment			Zein Treatment		
	$K_a$	$K_b$	$K_b/K_a$	$K_a$	$K_b$	$K_b/K_a$	$K_a$	$K_b$	$K_b/K_a$
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
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
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

## FIGURES CAPTIONS

**Figure 1:** Plot of  $RT\ln V_R^0$  versus  $aN_A(\gamma_L^D)^{1/2}$  for the n-alkanes series onto (a) Agave fibers and (b) Agave Hybrid fibers

**Figure 2:** Hydrogen bonding pattern for (a) cellulose I and (b) cellulose II

**Figure 3:** Plot of  $RT\ln V_R^0$  versus  $aN_A(\gamma_L^D)^{1/2}$  for polar probes in kenaf fiber, (a) before and (b) after 4% NaOH treatments.

**Figure 4:** Plot of  $\Delta H_s/AN^*$  versus  $DN/AN^*$  for Flax (a) and for hemp (b), before and after treatment.

**Figure 5:** FTIR spectra of untreated and treated pineapple fibres

**Figure 6:** ESEM of (a) untreated (b) 4% NaOH and (c) 2% zein sisal fibres.



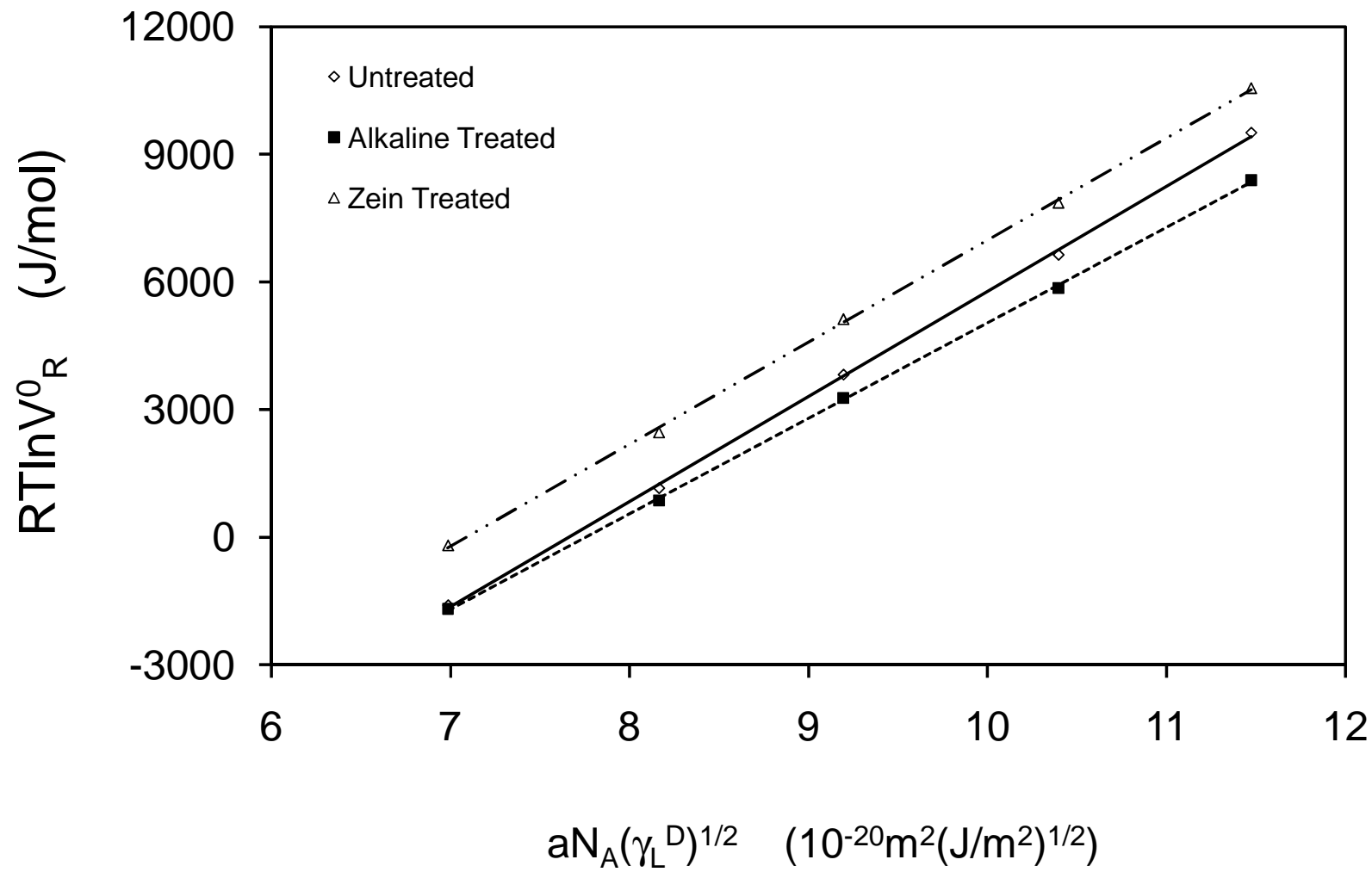


Figure 1 (a)

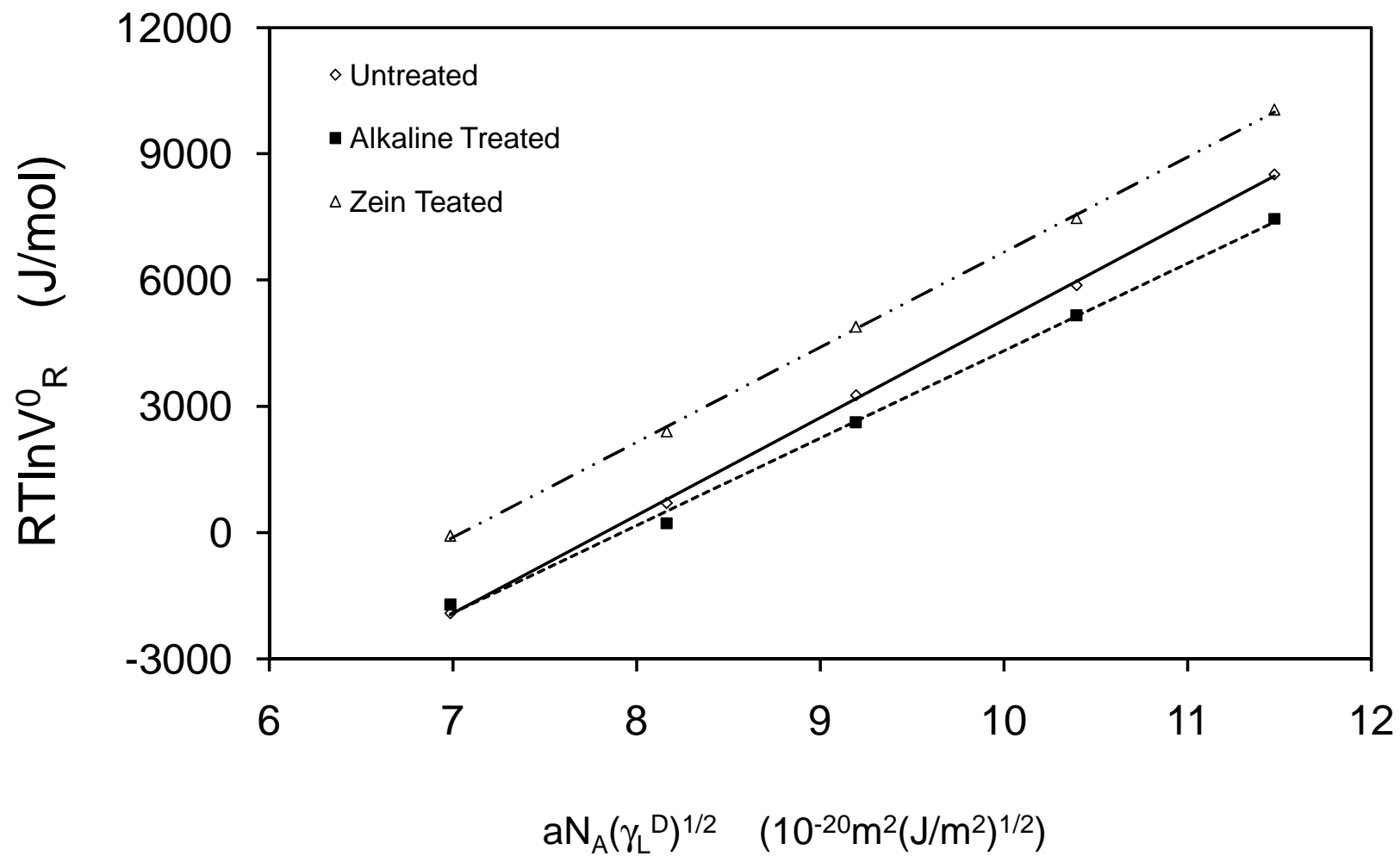
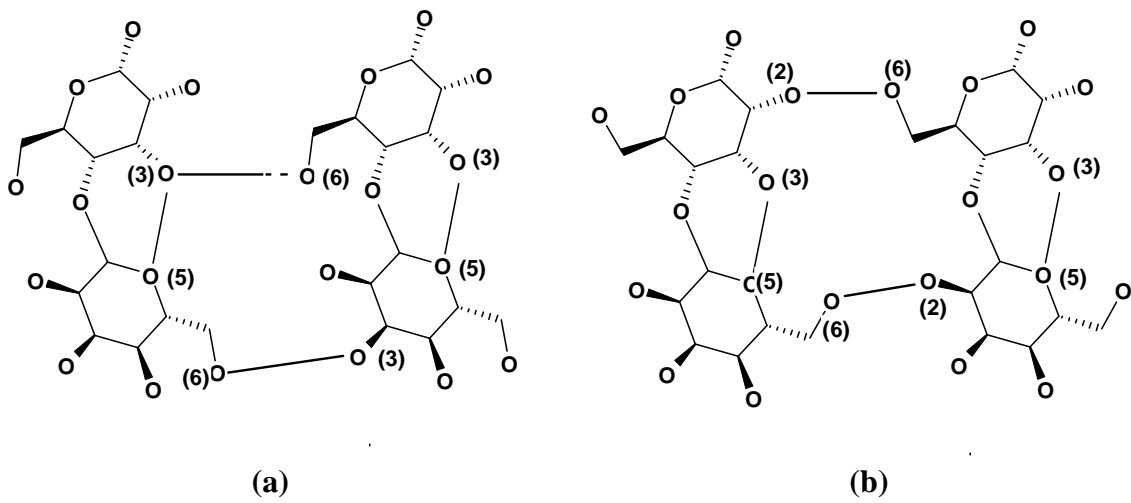


Figure 1(b)



**Figure 2: Hydrogen bonding pattern for (a) cellulose I and (b) cellulose II**

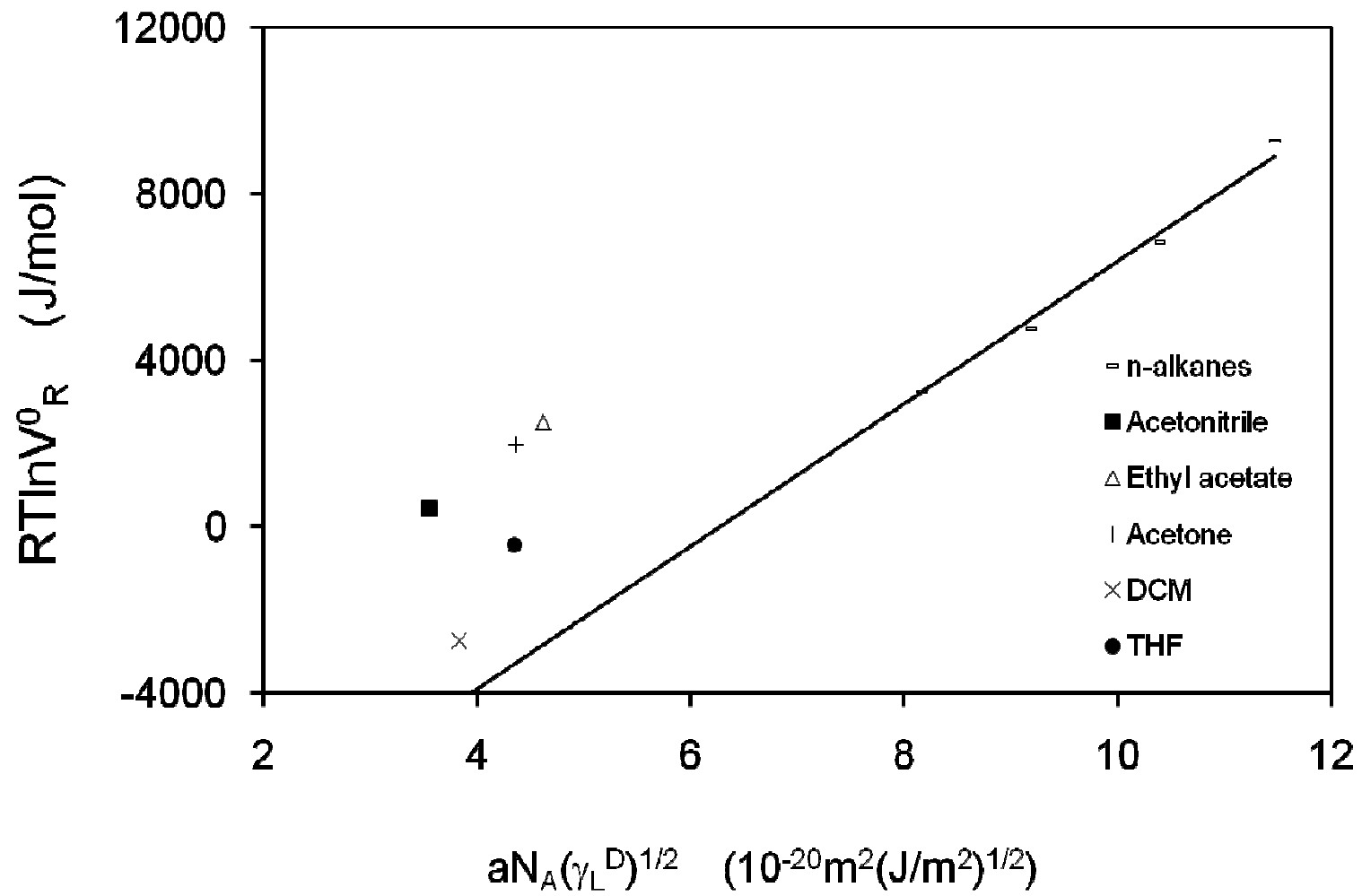


Figure 3(a)

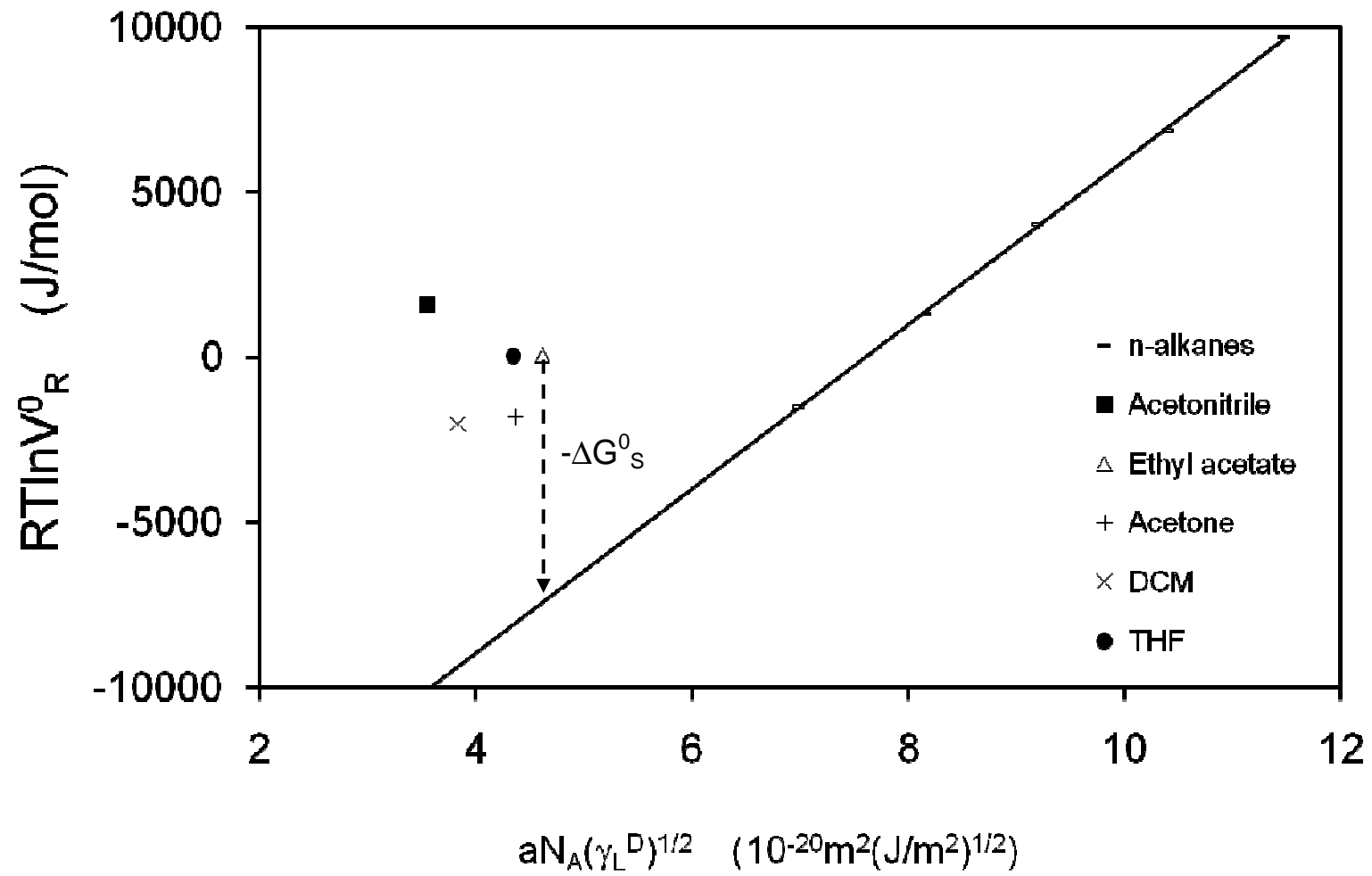


Figure 3(b)

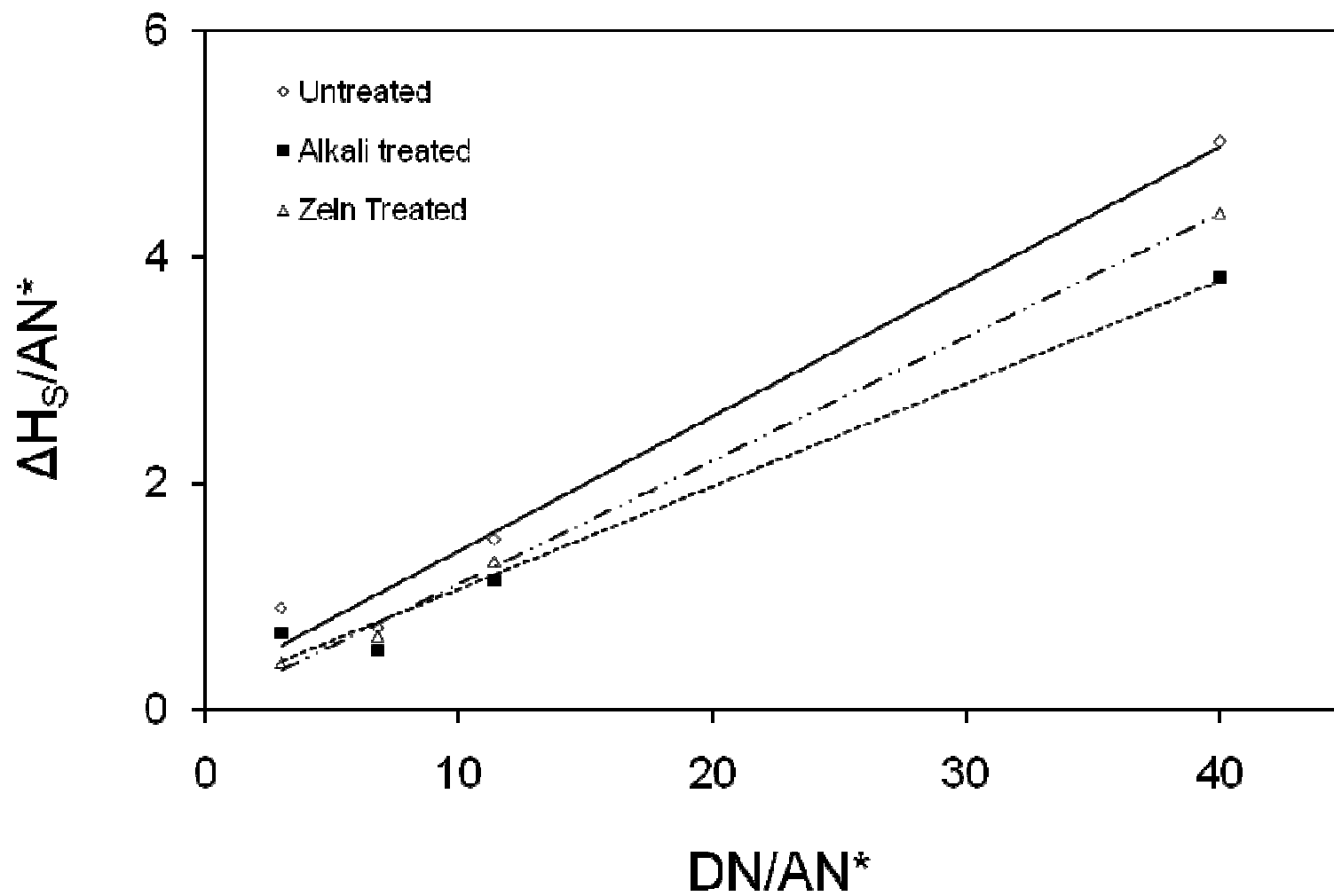


Figure 4 (a)

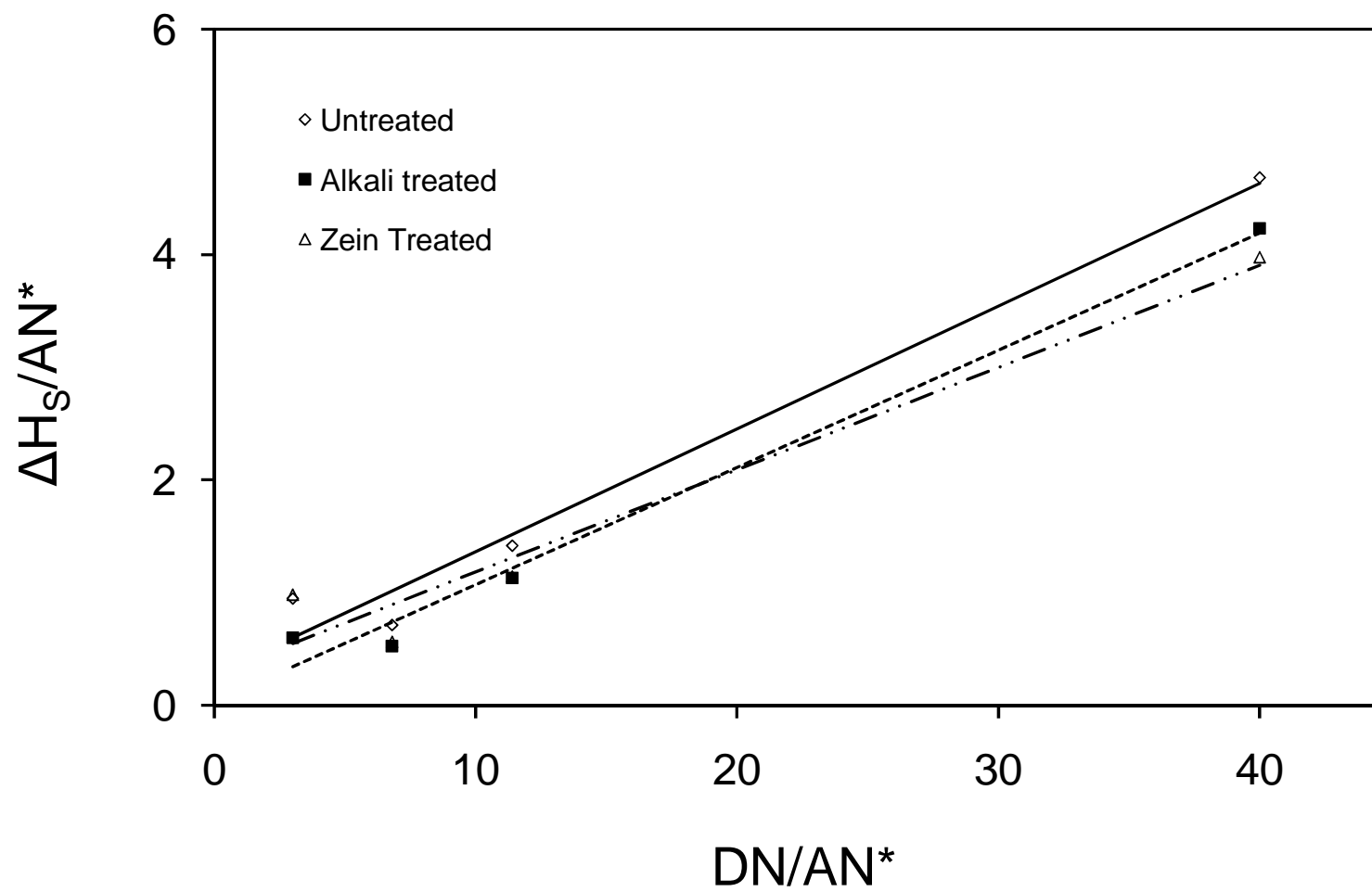
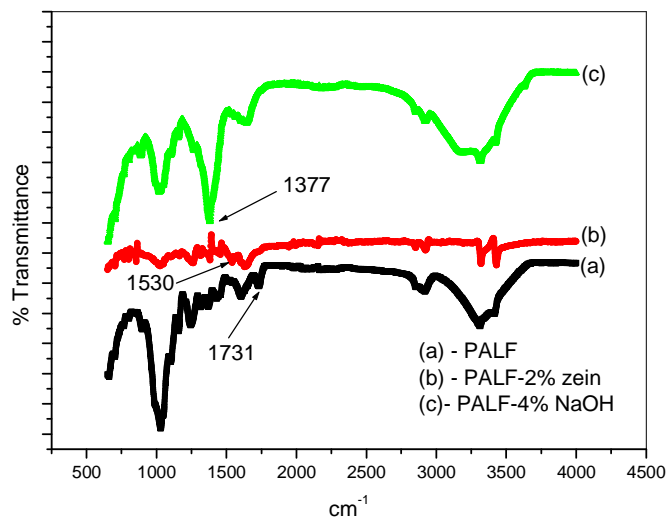
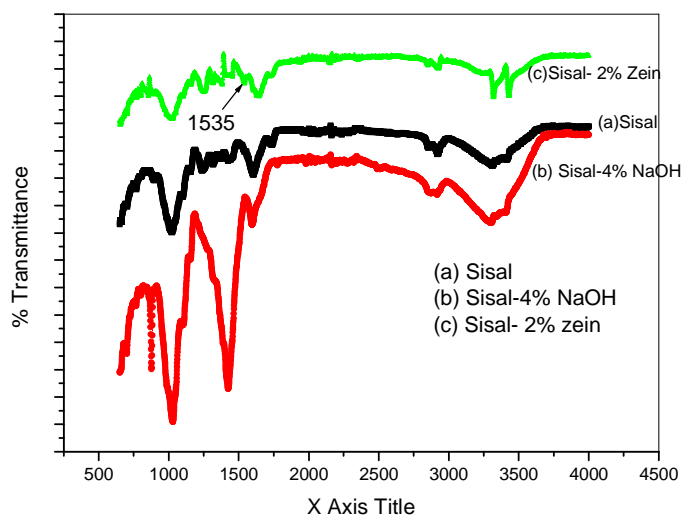


Figure 4(b)



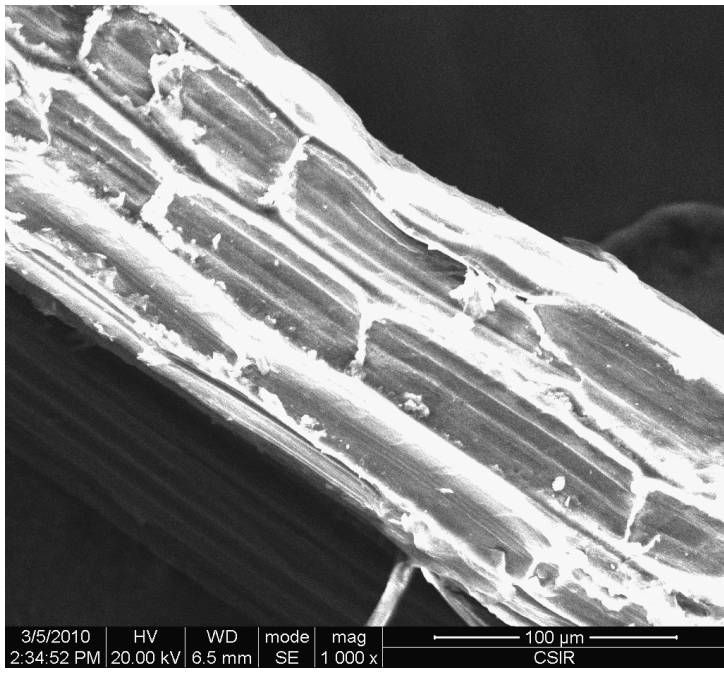
(a)



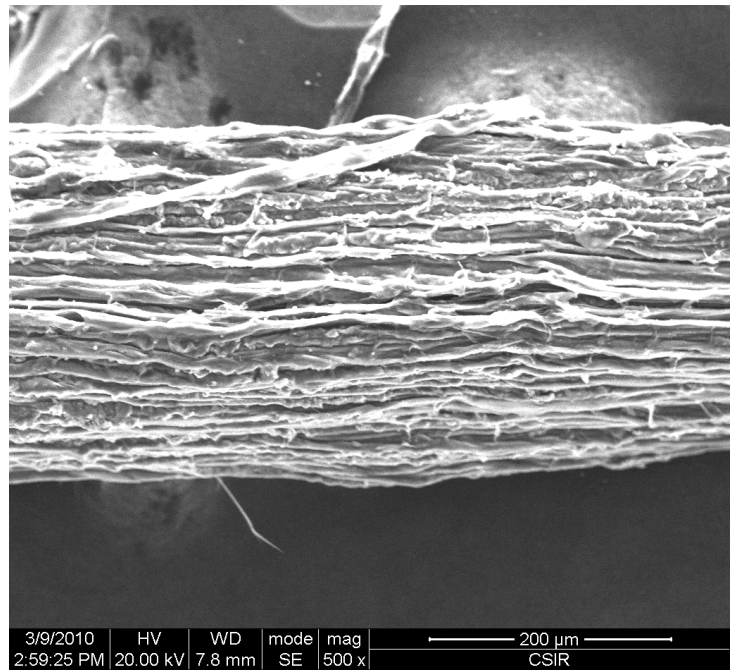
(b)

**Figure 5**

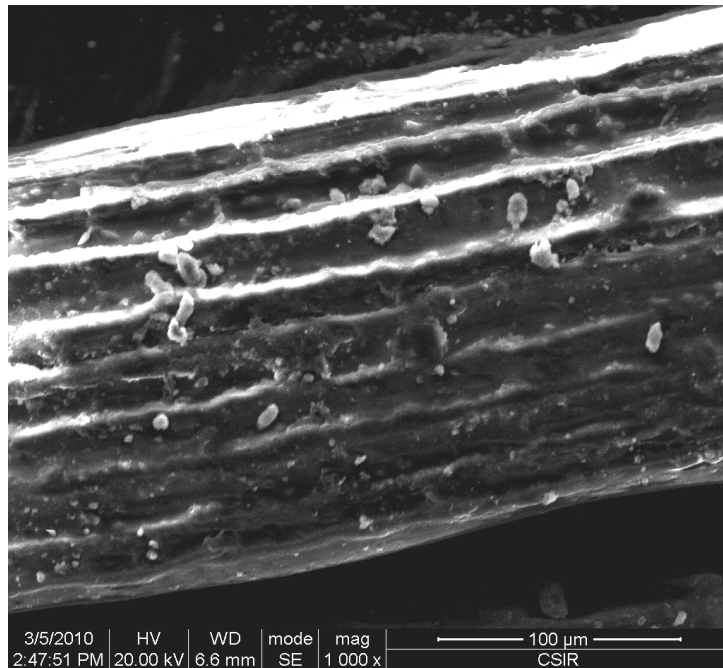




(a)



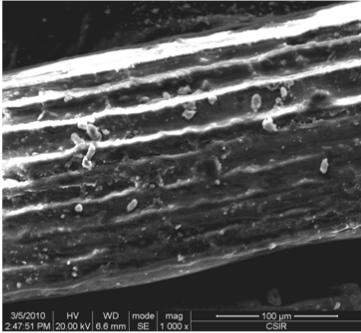
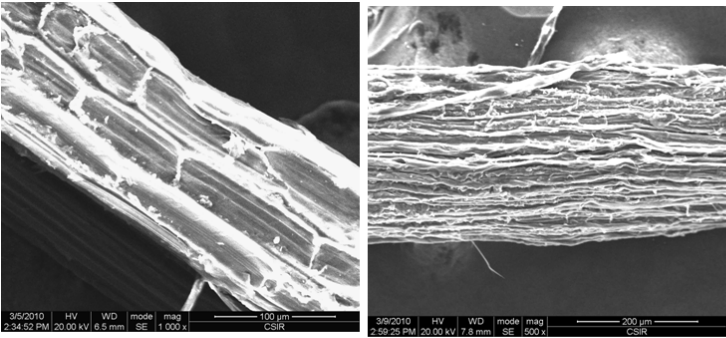
(b)



(c)

Figure 6

**TABLE OF CONTENTS GRAPHIC**



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