

Inverse Gas Chromatographic Characterization of Nanocrystalline Cellulose

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ABSTRACT

Nanocrystalline cellulose (NCC) is an important nanomaterial and the main component of the plant cell walls. NCC is biocompatible, biodegradable and renewable. In the recent years, NCC was the subject of numerous academic and applied researches due to its unique physical and chemical properties. NCC was obtained from acid hydrolysis followed by ultrasound sonication of cellulose fibres. NCC has very high surface area, as well as plenty of hydroxyl groups, which make it suitable for many types of surface modifications. The interaction of NCC with different solutes can provide important information for the improvement of surface properties of NCC.

Inverse gas chromatography (IGC) permits to evaluate the various surface properties of solids materials under test. In this study, Nanocrystalline cellulose (NCC) was isolated using commercial microcrystalline cellulose (MCC). Inverse gas chromatography (IGC) was applied to characterize the surface of NCC. The dispersive component of the surface energy (γ_s^d), and the acid/base character of NCC surface were estimated by using the retention time of different non-polar and polar probes at infinite dilution region. The specific free energy of adsorption (ΔG^{sp}), the specific enthalpy of adsorption (ΔH^{sp}), and the specific entropy of adsorption (ΔS^{sp}) of polar probes on NCC were determined. ΔG^{sp} were correlated with the donor and modified acceptor numbers of the probes to quantify the acidic K_A and the basic K_D parameters of the NCC surface. The values obtained for the parameters K_A and K_D indicated a basic character for NCC surface. The morphology of NCC is investigated by scanning electron microscopy (SEM) images.

Keywords: Nanocrystalline cellulose (NCC); Surface properties, Inverse gas chromatography (IGC); SEM

INTRODUCTION

The need to both avoid wastes and find new renewable resources has led to a new and promising research based on the possibility to revalorize the biomass producing sustainable chemicals and/or materials which may play a major role in replacing systems traditionally obtained from non-renewable sources. In this context, nanocellulose, and in particular cellulose nanocrystals (NCC), have gain considerable attention as nanoreinforcement for polymer matrices, mainly biodegradable. Derived from the most abundant polymeric resource in nature and with inherent biodegradability, nanocellulose is an interesting nanofiller for the development of nanocomposites for industrial, biomedical and agricultural applications. Due to the high amount of hydroxyl groups on their surface, cellulose nanocrystals are easy to functionalize.

Cellulose is one of the most important natural polymers, a sustainable and inexhaustible raw material that represents a key source on an industrial scale. For millennia, cellulose has been used in the form of wood and plant fiber's as an energy source, for building materials, and for clothing. Due to their unique features, cellulose nanostructures and, in particular, cellulose nanocrystals have garnered a tremendous level of attention in the material community, which can be confirmed by the increasing number of scientific publications in the field over the past decades and they found particular attention in the nanocomposite approach. Because of its unique structural properties combined with hydrophilic nature, biocompatibility, transparency and non-toxicity make cellulose structures attractive candidate for a wide range of applications as industrial (packaging), biomedical or agricultural sectors. Nanocellulose, and in particular cellulose nanocrystals, have many positive characteristics for the food packaging industry, for example, and they are considered as the best modifiers for biopolymers since it has shown better mechanical properties than a majority of the commonly used natural reinforcing materials. Moreover, NCC offer additional advantages such as renewability, biodegradability, high stiffness, excellent barrier properties and, low density and cost (Brinchi et al., 2013). Although nanocellulose presents a great potential, the high amount of hydroxyl groups on their surface induces high attraction among them leading to NCC agglomeration (Aranguren et al., 2013). Thus, to improve the processability and performances of nanocellulose based material and, thus, extend its industrial applications, an homogeneous dispersion of NCC in hydrophobic polymer matrices should be achieved. One of the most used methods to favor the nanocellulose dispersion and, therefore, the final properties of the final nanocomposite, is modifying their surface (Habibi, 2014). Another important application of cellulose nanocrystals is those related to biomedical and biotechnology applications (Dahman, 2009). The term biocompatibility is defined as the ability of a material to perform with an appropriated host response in a specific biomedical application. This properties are the most relevant to consider these materials as good candidates for tissue engineering and regenerative medicine applications, both as tridimensional and porous scaffolds or as drug-delivery device. Finally, cellulose nanocrystals have emerged as a novel material for a plethora of important applications as surface coatings and carriers for drug and/or active principles. Their potential applications as stabilizers in chemical reactions were investigated while the terminal OH groups on the glucose-based NCC provide facile surface modification and NCC can be easily functionalized or bio-conjugated, resulting in a rich source of new materials and platforms for diversified applications in biomedical field or as potential new bio-pesticides for plant disease treatment in agricultural sector.

Cellulose is a natural linear polymer consisting of D-anhydroglucose ($C_6H_{11}O_5$) repeating units joined by 1,4 β -D-glycosidic linkages at the C1 and C4 positions. The degree of polymerization is around 10,000 and each repeating unit contains three hydroxyl (OH) groups. The ability of these groups to make hydrogen bonds plays a major role in the crystalline packing of cellulose and also governs its physical properties. Solid cellulose comprises a microcrystalline structure with higher (crystalline) and lower order (amorphous) regions. The crystal nature (monoclinic sphenodic) of naturally occurring cellulose is known as cellulose I (Chakraborty et al., 2005).

Cellulose is the most abundant chemical compound on earth and its natural affinity for self-adhesion has long been recognized. The ease of adhesion that occurs in cellulose has contributed to its use in paper and other fiber-based composite materials. Cellulose adhesion, which has received considerable attention over the past half century, occurs over a practical length scale ranging from the nanoscale to millimeters. Adhesion theories that have been examined in the bonding of cellulose fibers include: mechanical interlocking, adsorption or wetting theory, diffusion theory, and the theory of weak boundary layers. Structure and properties of nanocellulose that are important include: morphology, crystalline structure,

surface properties, chemical and physical properties, and properties in liquid suspension. Cellulosic nanofibers present a very high surface area which makes the adhesion properties the most important parameter to control for nanocomposite applications.

Fundamentally, the surface energy of a solid can be defined as the reversible work required to form a unit area of new surface under constant temperature, pressure, mass and volume (Lang and Kohn, 1970). This can be measured directly using techniques such as the brittle fracture method (Lawn, 1993), however, the particulate nature of most pharmaceutical materials precludes them from such direct surface energy measurement. As an alternative, the definition that the surface energy is equal to the sum of the energy of all adsorption sites over a unit area may be exploited (Jacob and Berg, 1994). Clearly, such a definition may be more useful than the previously described classic definition, particularly where surface energy measurements are to be used for absorption-related studies. Several methods for calculating the total surface energy and the respective contributions of polar and disperse components to the total surface energy of a solid have been published (Gindl et al., 2001; Sharma and Rao, 2002). However, the generally preferred method, also used in this study, is based on the acid–base approach (Good, 1992), since it has been shown to produce results with improved internal consistency compared with equation of state methods (Volpe and Siboni, 1998).

The specific surface energy of a solid may be calculated from contact angle measurements using liquids which exhibit different and known polar and disperse components. The dynamics between the specific interactions produce a stable surface contact angle between the surface and the liquid which can be attributed to a composite of the dispersive (Lifschitz-van der Waals, γ_L^{LW}), acid–base (γ_L^{AB}) and individual positive and negative polar (γ_L^+ , γ_L^-) components of the solid's surface energy and the surface tension of the liquid. As previously stated, contact angle goniometry usually requires the solid under investigation to be a flat non-porous surface. Although compacts of powders have been used for contact angle measurements (Planinsek, 2001), the general utility of compacts for surface contact angle measurements is questionable since a certain level of surface roughness must be expected, complicating angle measurement. Furthermore, for many powder compacts, the contact angle measurements may be complicated by the action of surface-accessible pores, thereby decreasing the droplet volume by capillary action during measurement. In addition, the compaction of powder particulates may affect the material solid state, for example via pressure-induced crystallography changes (Kumar and Kothari, 1999) or inducing material anisotropy, for example in compacted MCC (Edge et al., 2011), leading to orientation-specific results after compaction. In part, such observations have been confirmed via variation in the surface energy properties as a function of compaction force (Khan et al., 2011; Buckton and Newton, 1986). To address the potential 'pitfalls' that exist in measuring surface energy values from compacted particulates, alternative methods of measuring the surface energy of uncompacted systems must be developed. Two of the most common methods are capillary intrusion of liquid analytes into the powder sample and analyte adsorption onto a powder bed at infinite dilution using inverse gas chromatography (IGC).

At infinite dilution conditions of appropriate gas probes, IGC may provide important parameters including the dispersive component of the surface energy of the material under analysis, thermodynamic data on the adsorption of specific probes, and Lewis acid–base interaction parameters between the matrix and the filler of composite materials. Emphasis will be put into the cellulose and nanocellulose surface properties, changes in the surface properties of cellulose and lignocellulosic materials after chemical and physical modifications, and in the context of papermaking, textile area and, particularly, in the production of composites with polymeric matrices (Dorris and Gray 1980; Belgacem et al. 1995, 1996; Tshabalala 1997; Papirer et al. 2000; Borges et al. 2001; Steele et al. 2008).

Regarding the dispersive component of the surface energy (γ_s^d) the majority of the reported values fall within the range of 40–50 mJ m⁻², although other values have been published. For instance, at 40 °C, cotton cellulose was reported to have a γ_s^d value of 49.9 mJ m⁻² (Dorris and Gray 1980), purified hardwood α -cellulose showed a γ_s^d value of 47.4 mJ/m² (Belgacem et al. 1995, 1996), and cellulose powder presented a γ_s^d of 48 mJ/m² (Tshabalala 1997). Recently, the dispersive component of the surface energy of microcrystalline celluloses was assessed by IGC at 0 and 44 % relative humidity (RH) (Steele et al. 2008). Values were in the range of 41–46 mJ/m² for the determinations carried out at 44 % RH. Interestingly, the results obtained under these conditions were in reasonable agreement with those obtained by capillary intrusion method. Somewhat larger values of γ_s^d (5–10 mJ/m² higher) were obtained at 0 % RH suggesting the inhibition of high-energy adsorption sites by water molecules at 44 % RH. Although cellulose has a well-defined molecular structure, the fact that this material is difficult to obtain in pure chemical form (i.e., without surface contaminants) should greatly account for some variety of the reported IGC results. It has been proposed that, besides the chemical composition of the cellulose surface, other factors such as crystallinity, diffusion of probes into the bulk volume and surface morphology also play an important role in the interaction between the probes and the cellulose surfaces and thus influence the IGC data (Chtourou et al. 1995; Papirer et al. 2000). Concerning crystallinity, it has been reported that microcrystalline cellulose shows a significantly higher γ_s^d value at 50 °C (40.9 mJ/m²) than that calculated by an empirical method for “amorphous” cellulose (27.4 mJ/m²) (Belgacem et al. 1996; Papirer et al. 2000).

The adhesion and surface properties of nanocellulose are a very important issue due to the increasing interest in this nanomaterial (Gardner et al. 2008). The surface properties of nanofibers obtained by enzymatic treatments were analyzed by IGC (Siddiqui et al. 2011). The authors reported γ_s^d values in the range of 37–45 mJ/m² (at 40 °C), which are not very different from those expected for cellulose fibers. A γ_s^d value of 42 mJ/m², comprised in the same range, was also reported for hemp cellulose nanofibers (Wang and Sain 2007). Bacterial cellulose was found to have a relatively high γ_s^d value, i.e., 61 mJ/m² in comparison to other cellulose types (Pommet et al. 2008). The authors proposed that this could be due to its high degree of crystallinity compared to plant derived cellulose. Several researchers have studied the effect of organic solvent extraction on the surface properties of cellulose and lignocellulosic materials. For instance, Belgacem et al. (1995, 1996) reported that the acetone extraction of α -cellulose fibers increased the dispersive component of the surface energy from 31.9 to 47.4 mJ/m² (at 40 °C). This was attributed mainly to the removal of low molecular weight components at the fiber surface, such as fatty acids, which possess lower γ_s^d values than cellulose. Similar results have been obtained after extraction of microcrystalline cellulose (Avicel) cellulose fibers with acetone or dichloromethane (Borges et al., 2001).

The main objective here is to give of the surface characteristics of NCC that impact its properties and application in nanomaterials. For this reason, applied IGC method at infinite dilution to the investigation of surface properties of NCC. The objectives of this study were, (a) to estimate the dispersive (London) component of the surface energy, (b) to determine the degree of acidity/ basicity of the NCC surface, and (c) to demonstrate that the IGC method provides a convenient way to evaluate surface properties of cellulose.

MATERIALS AND METHODS

Materials

Extra pure microcrystalline cellulose (MCC, average particle size 90 μm) from Acros Organics (NJ, USA) was used as reference material for the analyses and will be referred to as NCC. Nanocrystalline cellulose was isolated from commercial cellulose by means of sulfuric acid hydrolysis. Six grams of commercial cellulose were added into 90 mL sulfuric acid (60 wt%) solution and stirred at 40°C and 110 rpm by using laboratory shaking water bath (Nüve ST 30, Ankara, Turkey) for 40 min. Hydrolysis reaction was terminated by adding 10-fold cold water. The resulted dispersion was centrifuged at 7000 rpm for 15 min at 10°C (SL 8R Thermo Centrifuge, International Equipment Company, Waltham, MA) and then dialyzed with cellulose dialysis membranes against water until the dialysate became neutral. Following the dialysis step, the suspension was sonicated in an ice bath for 30 min and then freeze-dried. The collected nanocrystalline cellulose products were stored under vacuum. Scanning electron microscopy (SEM) observation of the NCC sample was done by a Jeol JSM-5600 LV (Tokyo, Japan). Prior to SEM observation, all samples were coated with a thin layer of gold using a Polaron SC7620 (Quorum Technologies Ltd., East Sussex, UK).

For the IGC analysis, the polar probes used were, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane. The polar probes used were tetrahydrofuran (THF), diethyleter (DEE), dichloromethane (DCM), Acetone (AC) and ethyl acetate (Et. Ac.). All of these chemicals were analytical reagent grade and used without further purification. Properties were taken from literature of the probes (Cordeiro et al., 2011). These probes are commonly used for solid surface characterizations by IGC method. The chromatographic experiments were performed with Agilent 7890 gas chromatography equipped with a flame ionization detector (FID). A vacuum pump was used for packing the solids into the columns. High purity nitrogen was used as the carrier gas with a flow rate of about 40 mL/min. The flow rate of carrier gas was corrected for pressure drop and temperature change in the column using James-Martin gas compressibility factor. A stainless steel column (2.00 m long, 5.35 mm I.D.) previously washed with methanol and acetone was packed with NCC powders. The column was stabilized overnight in stream of nitrogen at 260°C. The dead volumes of the columns were determined by injecting methane. At least three replicate determinations were used in averaging the net retention volume (V_N).

IGC theory

Inverse gas chromatography (IGC) is a derivation of conventional gas chromatography. However, unlike analytical chromatography, the material being investigated is the solid in the gas chromatography column. The retention volume of the mobile phase (probe) indicates the interaction between the probe and the surface of the material in the column (Cordeiro et al., 2011; Santos et al., 2002; Matsushita et al., 2006). IGC provides an excellent method to measure the surface energy of rough and porous powders (Hole et al., 2011). The surface energy is the result of the unbalanced molecular forces at the surface of the solid. It can be considered to be formed by two different contributions: dispersive and specific (Perez-Mendoza et al., 2008). The retention time of a series of homologous *n*-alkanes is used to determine the dispersive component of the surface free energy (γ_S^d) of NCC. In IGC literature, γ_S^d is commonly determined from the following equation, which was introduced by Lavielle and Schultz (Lavielle and Schultz 1991):

$$RTLnV_N = 2N.(\gamma_S^d)^{1/2}.a.(\gamma_L^d)^{1/2} + C \quad (2.1)$$

Here, R is the gas constant, T is the absolute column temperature, a is the molecular surface area coated with a kind of adsorbed alkane, N is the Avogadro's number, γ_L^d is the dispersive component of the surface free energy of the probe, C is a constant, and V_N is the net retention volume of the n -alkane probe. The net retention volume (V_N) is calculated using the equation below (Thielmann 2004) :

$$V_N = F_o \frac{T}{T_o} \frac{3}{2} \left[\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1} \right] (t_A - t_0) \quad (2.2)$$

Here, t_A is the retention time of the probe, while t_0 is the retention time of the probe which has no interaction with the solid in the column (marker). P_i and P_o are, respectively, the inlet and outlet pressures of the carrier gas, while the T/T_o ratio is used in order to get the value of the flow rate at the column temperature (T) from the measurement of the flow rate at ambient temperature (T_o). The flow rate of the carrier gas which is measured at the column outlet and at ambient temperature is expressed as F_o . According to the following equation, specific components of the adsorption enthalpy (ΔH^{sp}) and entropy (ΔS^{sp}) can be determined from ΔG^{sp} 's relationship with the temperature:

$$\frac{\Delta G^{sp}}{T} = \frac{\Delta H^{sp}}{T} - \Delta S^{sp} \quad (2.3)$$

A plot of $\Delta G^{sp}/T$ versus $1/T$ should yield a straight line with slope ΔH^{sp} and intercept ΔS^{sp} . The acidic–basic parameters can be obtained from the calculated ΔH^{sp} values using the following equation (Lazarevic et al., 2009). The values of K_A and K_D were calculated using Equation (2.4):

$$-\frac{\Delta H^{sp}}{AN^*} = K_A \frac{DN}{AN^*} + K_D \quad (2.4)$$

Here, ΔH^{sp} is the specific component of the adsorption enthalpy and the K_A and K_D parameters define acid and base constants of the analyzed surface, respectively, AN^* shows the acceptor number of the adsorbed probe while DN shows the donor number. The K_A and K_D values can be calculated with the aid of probes which have acidic, basic, and amphoteric properties. According to the above equation, representing the $(\Delta H^{sp}/AN^*)$ versus (DN/AN^*) , one gets K_A as the slope and K_D as the intercept (Santos et al., 2002). Finally, K_D/K_A is known as S_C . According to the values obtained from these parameters, it is accepted that $S_C \leq 0.9$ means the surface is acidic, $S_C \geq 1.1$ means basic, and if it is between 0.9 and 1.1, the surface is amphoteric (Cava et al., 2007).

RESULTS AND DISCUSSION

The adsorption runs were performed at infinite dilution conditions. The chromatographic peaks of n -alkanes on NCC were symmetrical. So retention time is independent of the amount of injected. The value of γ_S^d represents the interaction of the surface with n -alkanes and hence is a measure of how easily the surface can polarize the probe (Price and Ansari 2003).

The dispersive component of the surface free energy, γ_S^d , was determined by injection of a homologous series of n-alkanes having between 7 and 10 carbon atoms. One of the most commonly measured parameters for the description of the energy situation on the surface of a solid is the surface energy. The surface energy can affect, e.g. catalytic activity or the strength of particle-particle interaction. The dispersive components of NNC at experimental temperatures were calculated from Eq. (2.1). Plotting $RT \ln V_N$ against $a(\gamma_L^d)^{1/2}$ yields a straight line with the slope of γ_S^d , which can be seen for NNC in Figure 1. Table 1 shows the dispersive component of the surface free energy, γ_S^d , of NNC. It was observed that γ_S^d values decrease with increasing temperature.

A comprehensive insight into the Lewis acid-base surface interactions provides a better understanding of the influence of the catalytic and sorption capabilities of NNC, as well as their ability to change via chemical modifications, which is of great importance for their applications. The application of the Schultz's method to our experimental results (Fig.1 and 2) gave us the value of ΔG^{sp} . The variation of free energy of specific interactions, ΔG^{sp} , NNC and polar probes for different temperatures is given Table 2. The average $-\Delta G^{sp}$ values of polar probes and kaolinite in the following order: DCM < THF < Et. Ac < DEE < Acetone.

The values of K_A and K_D were calculated using Eq. (2.4). Representing $-\Delta H^{sp} / AN^*$ versus DN / AN^* , one gets K_A as the slope and K_D as the intercept. The values of K_A and K_D for NNC found to be 0.048 and 0.230 with the correlation coefficient of 0.9768. The overall acid-base character of NNC can be evaluated from K_D / K_A ratio. According to the values obtained for of K_A and K_D , the surface of exhibits largely basic character with the ratio of $K_D / K_A = 4.82$.

Table 1. Values of dispersive component of the surface energy measured on NNC at various temperatures.

T (°C)	30	40	50	60
γ_S^d (mJ/m ²)	51.74	47.60	44.50	37.41

The interpretation of the IGC results obtained on cellulose is all but simple, due principally to the very complex nature of the cellulose surface. Indeed, from a chemical point of view, different functional groups exist on the surface; also from a morphological point, the surface texture and surface morphology at the molecular scale are complex and difficult to evaluate. Furthermore, in the presence of water, the cellulose surface will acquire electrical surface charges and possibly undergo local swelling, giving rise to additional complication. Several papers recommend the use of IGC for the evaluation of the dispersive component (γ_S^d) that describes the potential of cellulose to exchange London type interactions, starting from the retention data of a series of n-alkanes and applying the theoretical treatment developed by Dorris and Gray, 1980. These authors studied a cotton cellulose (Whatman paper No. 1) and recorded at 40 °C a value of 49.9 mJ /m² for γ_S^d , a value that is in close agreement with the one (48 ± 3 mJ/m² at 20 °C) that they calculated from the spreading pressure, at saturation, determined from the adsorption isotherms of alkanes. Chtourou *et al.*, 1995; examined wood pulp fiber (DuPont Co.) and samples modified by ozone or fluorinated gases, using both electron spectroscopy for chemical analysis (ESCA) and IGC techniques. They noted a rather

low (9.8 mJ/m^2) and unrealistic value for γ_S^d on non-modified cellulose. Moreover, they could not find a clear correlation between surface energy characteristics (γ_S^d) and acid–base surface properties. The acid–base properties were determined by replacing the nonpolar n-alkane probes by probes of known acid–base characteristics in the IGC experiment. They observed a very strong interaction of cellulose with acetone and ethyl acetate, molecules that can be considered amphoteric (being able to exchange both acid and base interactions). They also pointed out that the retention of the probes could not be simply accounted for by pure enthalpic effects, but that other parameters such as crystallinity, the diffusion of the probes in the bulk of cellulose, and the surface arrangement and orientation of chemical groups influenced the chromatographic process and thus were likely to influence the IGC data. Belgacem *et al.*, 1995, 1996; demonstrated the influence of crystallinity, since microcrystalline cellulose showed a significantly higher (γ_S^d) value (40.9 mJ/m^2) than did amorphous cellulose (27.4 mJ/m^2). These authors performed surface modifications either by corona treatments or by the grafting of polystyrene on the cellulose surface, but the measurement of γ_S^d only, even though it indicates tendencies, is unable to actually unravel the importance of the treatments as evidenced by ESCA. Czeremuszkin *et al.*, 1997; examined the applicability of IGC for the surface evaluation of cellulose by checking if the entire amount of injected solute probes was really eluted as it should be, which the case was not always.

To investigate the surface morphology at the micron level, SEM observations were carried out in the NNC (Fig. 3). It should be noted that, coating with gold would broaden the nano-sized structure and NCC particles aggregated to some extent during the long freeze drying process. The structure is very rare and composed of particles with small pores. This image reminds the capillary structure of cellulosic fibers at the macromolecular level. The nanofibrils were not pulled out from the cell wall.

Table 2. The variation of ΔG^{sp} with temperature, and ΔH^{sp} and ΔS^{sp} values of polar probes on NNC

Adsorbent	Polar probes	$-\Delta G^{sp} \text{ (kJ mol}^{-1}\text{)}$				$-\Delta H^{sp} \text{ (kJ mol}^{-1}\text{)}$	$-\Delta S^{sp} 10^3 \text{ (kJ mol}^{-1}\text{K}^{-1}\text{)}$
		30 °C	40 °C	50 °C	60 °C		
NNC	DCM	2.13	2.10	2.06	2.07	-2.88	2.48
	DEE	4.80	4.87	4.91	4.79	-4.74	-0.30
	Acetone	7.15	7.26	7.44	7.01	-7.67	1.40
	THF	3.81	3.83	3.86	3.72	-4.46	2.06
	Et. Ac	4.54	4.65	4.83	4.48	-4.47	-0.47

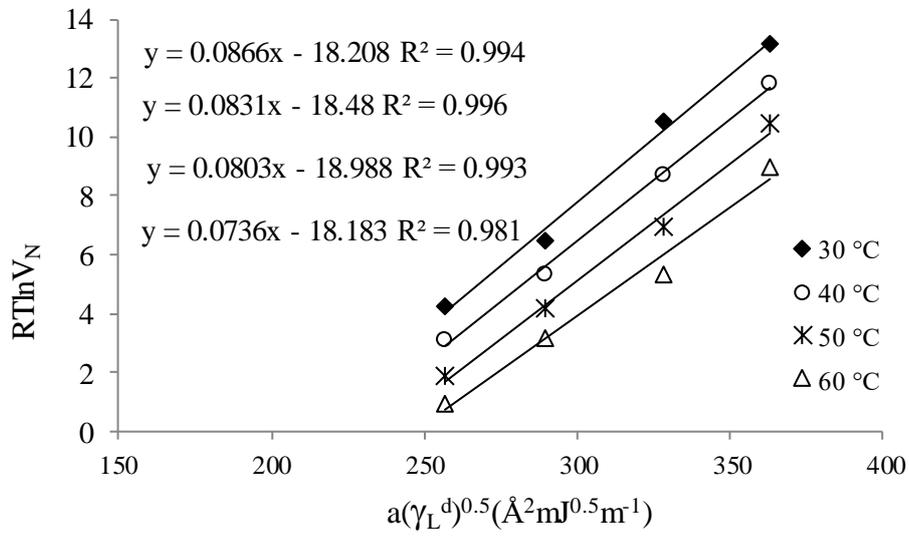


Figure 1. The $RT \ln(V_N) - a(\gamma_L^d)^{1/2}$ graphs for NNC

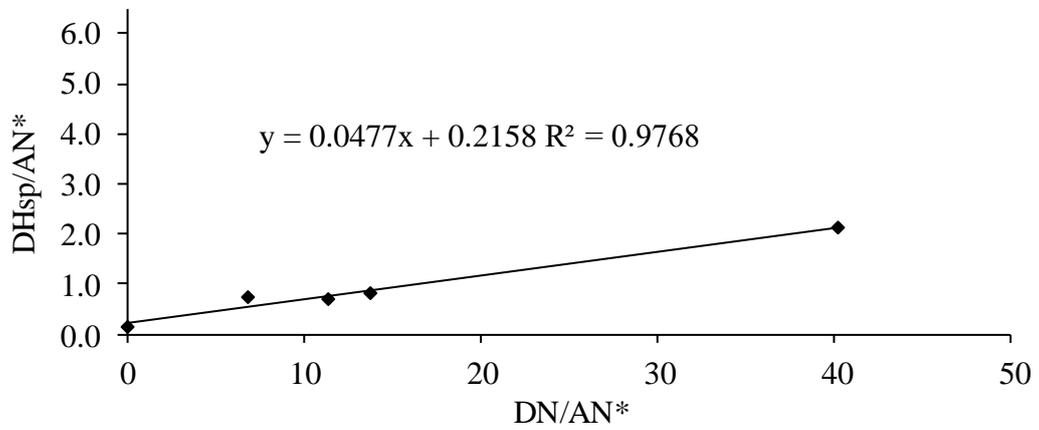


Figure 2. Plots of $\Delta H^{sp}/AN^*$ versus (DN/AN^*) for NNC

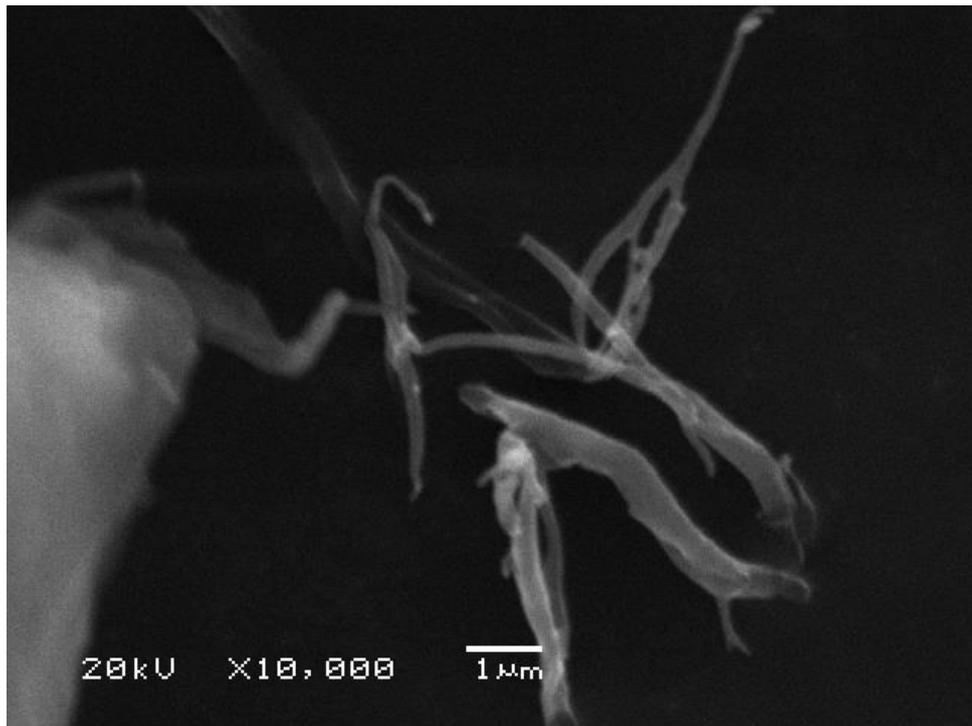


Figure 3. SEM image of NCC

CONCLUSION

IGC under infinite dilution conditions explores only the most active part of the solid surface and, consequently, is unable to describe fully the surface characteristics of cellulose of different origins or structures. However, it gives valuable qualitative information on the trends induced, for instance, by surface treatment and thus allows us to monitor the induced modifications. Knowledge of the surface properties of cellulose is of great interest for a number of applications. IGC readily provides information, not only on the reversible interaction capacity of cellulose, but also on its surface nanomorphology. It allows us to demonstrate the consequences of adsorbed water. However, the interpretation of the results provided by IGC is anything but simple, since the adsorption processes are dependent on the morphology of the partners in contact besides the interaction capacities.

In this study, IGC is a powerful analytical technique very useful for studying the surface properties of NNC and for monitoring adsorption processes. Thermodynamic information on adsorption was obtained from the temperature variation of the partition coefficients for probes at zero coverage. The high value of the dispersive component of free energy of adsorption γ_s^d probably was related to structural heterogeneities on the lateral surfaces, as well as to the channels and pores present at 30–60 °C. The values of K_A and K_D indicated that NNC surface is basic.

The morphology of NNC is investigated by SEM, which give supporting evidence for the formation of NNCs. From morphological studies, the SEM image showed that there the effects of chemical treatments on the surface of samples due to removal of the non-cellulosic materials and producing white and clean surfaces of cellulose. Isolation of cellulose nanocrystal from commercial microcrystalline cellulose were successfully carried out.

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