CELLULOSE CHEMISTRY AND TECHNOLOGY

CELLULOSE NANOFIBERS MODIFIED WITH ALKYL KETENE DIMER FOR OIL ABSORBENT AEROGELS

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Nanofibrillated cellulose consists of interconnected cellulose nanofibers, isolated from wood or agricultural byproducts, which leads to a three dimensional, porous and flexible structure. In this sense, the present work aims to develop hydrophobic aerogels for oil absorbing. Different percentages of alkyl ketene dimer (AKD) were added to the cellulose nanofiber (CNF) gel in order to partially hydrophobize the surface thereof. After mechanical stirring in an Ultraturrax and two cycles of sonication at 80 watts for 2 minutes, the CNF gel was poured into aluminum dishes and frozen at -80ºC for two hours. Then, the samples were freeze-dried for 48 hours. Water and oil absorption capacity was determined both under static and dynamic conditions in an oil-water mixture.

Keywords: aerogel, cellulose nanofibers, sugarcane bagasse, oil absorption

INTRODUCTION

Cleaning oil spills in a marine environment is a challenging task. Nowadays, several methods are used, such as the collection of the oil on the water surface (taking advantage of their different densities), dispersing oil in water easing its natural degradation or *in situ* burning.[1]None of the above-mentioned methods seems to be efficient nor environment-friendly. In this sense, many efforts have been made to solve this issue, such as depositing sawdust on the water-oil mix surface with the purpose of removing the hydrophobic component. However, sawdust also absorbs water, which makes its reusequite difficult.[2] More recently, silica aerogels,[3,4] carbon nanotubes and even carbon nanotube aerogels,[5,6] manganese oxide fiber membranes,[7] among other materials, have been used for oil removal. However, the above-mentioned materials still present the drawback of their non-renewable nature and their presence is incipient.

Cellulose nanofibers (CNFs) have become one of the main topics of research among cellulose and polymer scientists and techniciansin recent years. Nanocellulose offers a wide range of applications, such as in paper reinforcement,[8-11] films,[12,13] biomedicine,[14-16] among others. Moreover, nanocellulose is also attractive because it is based on renewable and abundant resources and can be processed on large scale using well-established pulp, paper and wood industry methods. Among all the explored applications, aerogels made of CNF are a product of interest due to their lightweight, great specific surface and their high porosity. Moreover, CNF aerogels present great mechanical properties, which gives them remarkable dimensional stability. CNF, in its native form, has a highly hydrophilic character (even greater than that of sawdust), whichalso makesits use for oil removaldifficult. In this sense, methods for CNF modification areunder study and are mainly focused on the hydrophobization of its surface. There is some literature available reporting on themodification of CNF through silanation[17] and acetylationtechniques.[18] The main drawback of these methods is the use of organic solvents, which at first sight, makes difficult their implementation on a large scale mainly because of the strict safety regulations that these products are forced to comply with.

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Alkyl ketene dimer (AKD) is a product broadly used in the papermaking industry with the purpose of hydrophobizing papers that are supposed to be used under wet conditions or for applications where it is imperative that the dimensional stability should remain constant in the presence of water, such as outdoor banners. The main mechanism of AKD is based on blocking the OH groups present on the cellulose surface and, thus, avoiding any hydrogen bond with water.

On the other hand, environmental concernsurge research to take advantage of the by-productsobtained from other activities, such is the case of sugarcane bagasse. Sugarcane bagasse is produced in large quantities by the sugar and alcohol industries in Brazil, China, Indonesia, Mexico, Colombia and other South-American countries.[19]After extracting the juice from sugarcane for biofuel production, what remains is called bagasse. The resulting stalks are commonly used for the production of pulp, paper, board and feed as a substitute for wood.

With these considerations, the present work aims to develop hydrophobic aerogels (made of TEMPO oxidized CNF and mechanical LCNF from bagasse) modified with alkyl ketene dimer (AKD) for use as oil remover. In addition, the present work suggests a possible application of these products for environmental purposes, such as oil discharges in the high seas.

EXPERIMENTAL

The experimental procedure followed in this work is reflected in Figure 1.

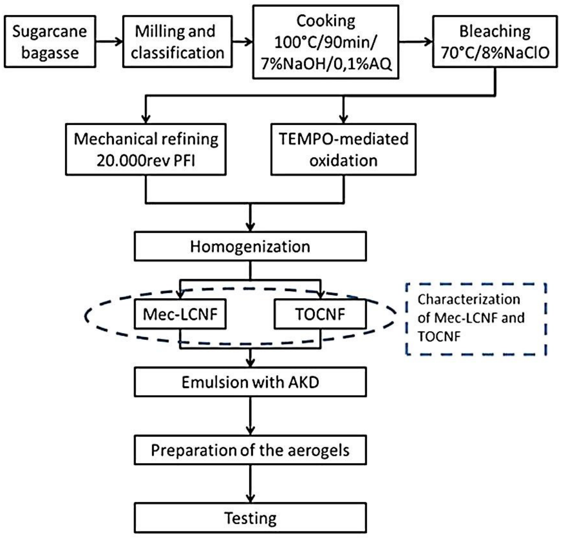

Figure 1: Experimental procedure of the present work

Preparation of chemical-thermomechanical pulp

Bagasse biomass, provided by the Pontifical Bolivarian University (Medellín, Colombia), was ground and classified in a knife mill with a 5mm pore size sieve at the bottom. The biomass was treated in an atmospheric reactor at 100 ºC for 90 minutes, with a NaOH charge of 7 wt% over dry weight of fiber and 0.1% of antraquinone. The liquor ratio was 10:1 with regard to the amount of fiber (dry weight).

Pulp bleaching

The pulp was subjected to a bleaching process with a sodium hypochlorite charge of 8 wt% over dry weight of fiber at 10 wt% consistency and 70 ºC for six hours; a kappa number of 4was obtained.

Preparation of CNF

Mechanical LCNF (Mec-LCNF): the unbleached pulp was refined in a PFI refiner (IDM) at 20.000 revolutions and then passed through a high-pressure homogenizer (NS1001L PANDA 2 K-GEA) for three and seven times at 300 and 600 bar, respectively. The operating consistency was 1 wt%.

TEMPO oxidized CNF (TOCNF): the bleached pulp was oxidized following a method reported elsewhere,[20] varying the oxidation degree. In a typical experiment, 15 g of cellulose fibres was dispersed in distilled water containing TEMPO (0.016 g per g of fibre) and NaBr (0.1 g per g of fibre). The mixture was stirred for 15 min in order to assure good dispersion of all the substances. After this, a 15% sodium hypochlorite solution was added drop by drop to the slurry. The volume of NaClO was calculated to add 15 mmol per gram of cellulose. The pH was kept at 10 by adding a 0.5 M NaOH solution dropwise. The oxidation was considered finished when the pH remained constant at 10. The oxidized fibres were then filtered and washed five times with distilled water. Finally, the pulp was passed through a high-pressure homogenizer (NS1001L PANDA 2 K-GEA) for three and seven times at 300 and 600bar, respectively. The operating consistency was 1 wt%.

The water retention value (WRV) was measured by separating a determined volume of CNF gel into two equal portions, which were then centrifuged in a Sigma Laborzentrifugen model 6K15 (7 cm radius of rotation) at 2,400 rpm for 30 min to eliminate non-bonded water. In order to retain the CNF, a nitrocellulose membrane with a pore diameter of 0.65 µm was used at the bottom of the centrifuge bottles. Once centrifuged, only the CNF in contact with the membrane was removed, weighed and then dried at 105 ± 2 ºC for 24 h in containers of previously measured weight. This method is based on TAPPI UM 256. The average WRV value was then calculated according to the following equation:

$$WRV(\%) = \frac{W_w - W_d}{W_d} x100$$

where W_w is the wet weight (g) and W_d the dry weight (g). The carboxyl content (CC) of TEMPOoxidised cellulose was calculated by conductometric titration. A dried sample (50-100 mg) was suspended in 15 mL of 0.01 M HCl solution; this exchanges Na cations bound to the COOH group by H ions. After 10 min of magnetic stirring, the suspensions were titrated with 0.01 M NaOH, 0.1 mL of NaOH was added to the suspensions and then the conductivity was recorded in mS/cm; this process was repeated until a reduction, stabilisation and increase in the conductivitywere observed. From the conductometric titration curve, the presence of strong and weak acid is observed. The CC is given by the following equation:

$$CC = 162(V_2 - V_1)c[w - 36(V_2 - V_1)c]^{-1}$$

where V1 and V2 are the equivalent volumes of added NaOH solution (l), c is the NaOH concentration (mol/L) and w the weight of oven-dried sample (g). The results indicate the average mmols of –COOH groups per gram of CNF.

The cationic demand of CNF was also determined by means of a Mütek PCD 04 particle charge detector. First, 0.04 g of CNF (dried weight) was diluted in 1 L distilled water and dispersed with a pulp disintegrator for 10 min at 3,000 rpm. Afterwards, 10 mL was taken and mixed with 25 mL of cationic polymer polydiallyl dimethylammonium chloride (poly DADMAC) for 5 min with magnetic stirring. Then, the mixture was centrifuged in a Sigma Laborzentrifugen model 6 K 15 for 90 min at 4,000 rpm. Then, 10 mL of the supernatant was taken to the Mütek equipment. Anionic polymer (Pes-Na) was then added to the sample drop by drop with a pipette until the equipment reached 0 mV. The volume of the anionic polymer consumed was used to calculate the cationic demand by the equation below:

$$CD = -\frac{(C_{PolyD} \cdot V_{PolyD}) - (V_{Pes-Na} \cdot C_{Pes-Na})}{W_{sample}}$$

where CD is the cationic demand (leq/L), C_{PolyD} = cationic polymer concentration (g/L), V_{PolyD}= used volume of cationic polymer (mL), C_{Pes-Na} = anionic polymer concentration (g/L), V_{Pes-Na} = used volume of anionic polymer (mL) and W_{sample} = sample's dry weight (g). The yield of CNF was also determined; a CNF suspension with 0.2% solid content was centrifuged at 4,500 rpm for 20 min in order to isolate the nanofibrillated fraction (contained in the supernatant) from the non-fibrillated and partially fibrillated one retained in the sediment fraction, which was recovered, weighed and oven-dried at 90 ºC until constant weight. The yield of nanofibrillation was then calculated from the following equation:

$$CD = -\frac{(C_{PolyD} \cdot V_{PolyD}) - (V_{Pes-Na} \cdot C_{Pes-Na})}{W_{sample}}$$

where % Sc represents the solid content of the diluted gel sample.

Specific surface (σ) and diameter (d) were calculated as reported by Delgado-Aguilar *et al.*[22]

Emulsion of CNF

Alkyl ketene dimer was dispersed in a CNF suspension (0.2wt%) using an Ultraturrax dispersing instrument at 17000 rpm for 2 minutes. After that, the solution was sonicated in a sonicator in order to remove any air bubble into the suspension. The percentages of AKD added to the CNF suspensions were 0, 7.5 and 15%.

Preparation of the aerogels

CNF suspensions were poured into a metallic dish and frozen at -80ºC for 3 hours. After that, the frozen suspensions were freeze-dried in a lyophilizer for 48 h (until constant weight). The obtained aerogels had a basis weight of 50 g/m^{2}on average. The aerogels that contained AKD were then cured at 105 ºC in an oven for 10 minutes in order to enhance the bonds between the dimer and CNF.

Determination of the physical properties

Density and porosity were calculated as reported elsewhere,[17] but considering the density of AKD of 1.18 g/cm^3, which was calculated for an AKD suspension in water at 17.85wt% consistency. Basis weight was also calculated taking into account the surface of the aerogel and its weight.

Preliminary tests

In order to have a preliminary idea of the character of the aerogels, a drop of colored water (with disulfine blue) and a drop of motor oil wereput on the aerogel surface. Moreover, a mixture of oil and colored water was prepared on a Petri dish and a modified and unmodified aerogel was placed on the liquid surface.

Determination of the oil absorption potential

Two different experiments were carried out in order to bear out the oil absorption capacity of the produced aerogels: (i) under static conditions and (ii) under dynamic conditions.

Static conditions: 100mL of oil was added to 900mL of water, having a total volume of 1L. Aerogels were suspended in the liquid mixture for 10 minutes.

Dynamic conditions: 100mL of oil was added to 900mL of water, having a total volume of 1L. The mixture was stirred at 500rpm during the entire test. Aerogels were suspended in the liquid mixture for 10 minutes.

Aerogels were weighed and then dried at 105ºC in order to evaporate the water. Finally, the aerogels were weighed again in order to assess the amount of water evaporated.

RESULTS AND DISCUSSION

Table 1 shows the results of the characterization of Mec-LCNF and TOCNF.

TOCNF presented a lower degree of polymerization than Mec-LCNF. This is mainly due to the introduction of carboxylic groups into the cellulose chains during TEMPO-mediated oxidation. However, Mec-LCNF also presenteda low degree of polymerization in comparison with cellulose, that is about 2000 on average.[23] This indicates that the mechanical treatment (homogenization) also causes depolymerization and thus reduction of (nano)fiber length.

Water retention value results (WRV) indicatedthat TOCNF can chemically retain more water than Mec-LCNF, and this property influences the results of the static and dynamic tests on oil and water absorption of the aerogels. The percentage is expressed as the amount of water that the aerogels can retain per gram of (L)CNF, which means that TOCNF can retain 17 gH_2O/g, whereas Mec-LCNF can retain about 8.5 gH_2O/g. The cationic demand and carboxyl content are parameters related to the specific surface area of (L)CNF (σ). TOCNF presented higher carboxyl content due to the TEMPO-mediated oxidation process, which introducesthis negatively-charged group in the primary alcohol of carbon 6 atom of the cellulose chain. TEMPO-mediated oxidation of cellulose fibres allows obtaining nanofibre suspensions with yields of nanofibrillation higher than 90% after passing the suspension through high pressure homogenization/microfluidization; this means that most of the fibres have diametres within thenanometric scale. On the other hand, Mec-LCNF presented a lower yieldof nanofibrillation (about 30%). Overall results show thatTOCNF has better water affinity, bonding capacity and homogeneity than its mechanicallyproduced counterparts.

Table 1
Characterization of the obtained (L)CNF

CNF type	DP	WRV (%)	CC (μeq-g/g)	CD (μeq-g/g)	Yield (%)	σ (m^2/g)	d (nm)
TOCNF	488	1706	881.3	1235	95.1	172.61	14.47
Mec-LCNF	803.6	847	76.6	216.38	31.0	68.18	36.67

Table 2
Density and porosity of the aerogels produced in this study

CNF type	AKD (%)	Nomenclature	Density (g/cm^3)	Porosity (%)
TOCNF	0	TOCNF-0	0.0031	99.79
	7.5	TOCNF-7,5	0.0043	99.73
	15	TOCNF-15	0.0050	99.67
Mec-LCNF	0	Mec-LCNF-0	0.0089	99.40
	7.5	Mec-LCNF-7,5	0.0097	99.35
	15	Mec-LCNF-15	0.0107	99.29

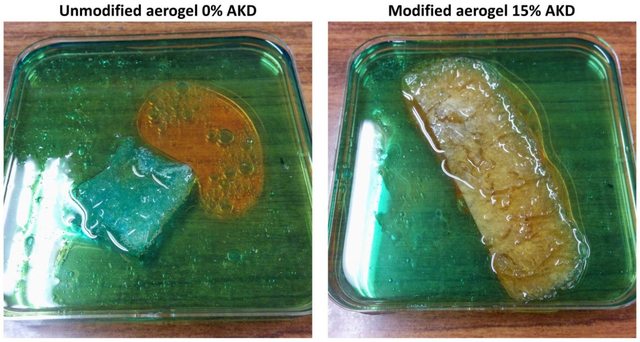

Figure 2: Different affinity of aerogels when suspended in an oil-water mixture

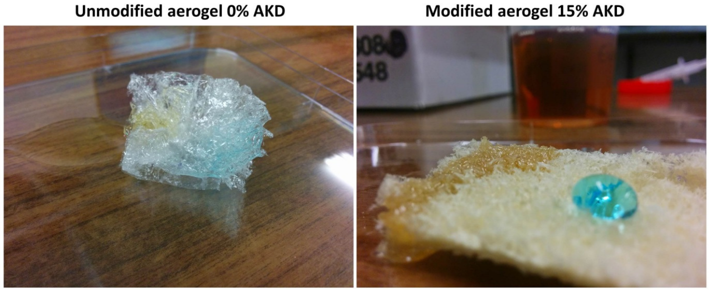

Figure 3: Drop shape for unmodified and AKD modified aerogels

Table 2 shows both parameters for the aerogels produced in the present study. Cellulose aerogels are characterized by their high porosity and low density, which make them an interesting absorbing material. The samples made of Mec-LCNF were denser than those produced from TOCNF. The main reason for this is that TOCNF has higher yield of nanofibrillation and specific surface area than Mec-LCNF; consequently, it has a better ability to create more expanded, highly porous three-dimensional networks that absorb liquids better. However, porosity was close to 100% in all aerogel samples produced, regardless of the CNF grade.

Aerogel density increased after AKD treatment and this increase was in relation to the amount of AKD added. Since the amount of CNF remained always constant for all types of aerogels, an increase in the AKD content produced denser samples. On the other hand, porosity remained without significant variations throughout the whole set of samples. The result seems to indicate that the presence of AKD did not affect the aerogel formation. However, by blocking the OH groups on the CNF surface, AKD reduces nanofibres water affinity, which enables aerogels to absorb mainly oil. Figure 2 shows how the unmodified aerogel prefers water against oil, while the one modified with 15% AKD has a greater affinity for oil.

The degree of hydrophobicity can be qualitatively assessed by the deposition of one drop of water (coloured) and one drop of oil on the aerogel surface (Figure 3).The left picture shows that both water and oil are absorbed into the structure of an untreated aerogel, probably by capillarity and, in the case of water, also by chemical affinity. However, the AKD-treated samples clearly show that hydrophobicity was successfully attained by reducing the chemical affinity between CNF and water.

Figure 4 shows that, both under static and dynamic conditions, aerogels made of TOCNF absorbed more water than those made of Mec-LCNF, mainly due to the higher water affinity that TOCNF develops after TEMPO oxidation. Overall unmodified aerogels absorbedmuch more water than oil under static conditions. This is mainly due to the water's lower viscosity, which allows water to penetrate the aerogel's porous structure; besides, during the experiment the samples stayed mainly floating on the top of the mixture and, due to the differences in density between oil and water, oil remained also on top, whichdid not allow better contactbetween the aerogel and the water.

On the other hand, for the aerogels modified with 7.5% AKD, water absorption decreased, whereas oil absorption was improved. Finally, for the aerogels modified with 15% AKD, water absorption was very low for Mec-LCNF and close to zero for TOCNF-15%AKD. Another important property that AKD provided to aerogels was dimensional stability: unmodified aerogels were almost completely disintegrated when they were submitted to dynamic conditions, a phenomenon that was not observed in the treated samples. It is interesting to point out that modified aerogels absorbed more water under dynamic conditions than under static ones; probably turbulences eased the entrance of water into the aerogel structure. The performance of the AKD-treated aerogels under dynamic conditions indicated that they could suitable for applications under harsh environmental conditions, such as strong waves in the open sea.

Even though the aerogels made of TOCNF seem to have a higher absorbing capacity due to their larger specific surface area, it should be underlined that TOCNF is about 150 times more expensive that Mec-LCNF.[21]Considering both economic and technological aspects and thinking of a near-future application, Mec-LCNF appears as the best option against TOCNF in economic terms, despite its lower oil absorption capacity.

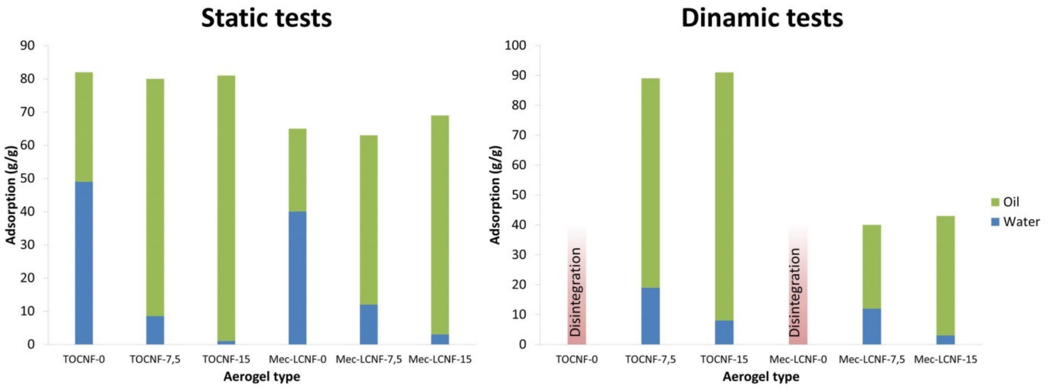

Figure 4: Oil and water absorption of each aerogel, under static and dynamic conditions

CONCLUSION

The present work explored the fabrication of aerogels modified with AKD from TEMPO oxidized CNF and mechanical LCNF.It has been demonstrated that AKD promotes the hydrophobization of CNF surface (both types of CNF) without the use of any organic solvent. Moreover, the oil absorption tests (both under dynamic and static conditions) showed a good behaviour with regard to selectivity of oil against water. This hydrophobization has also been checked qualitatively by adding drops of water and oil on the aerogel surface. TOCNF presented a slightly higher oil absorption capacity than Mec-LCNF. Even though the performance of both types of CNF was not significantly different, the cost of Mec-LCNF is about 150 times lower than that of TOCNF, as reported in the literature. Oil absorption experiments under dynamic conditions also indicated that, with a proper structure design, modified aerogels could be easily used for oil removal (or petroleum, where appropriate).

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