

Urethane Modified Hydrophobic Compact Wood Pulp Paper for Oil Spill Cleanup: A Preliminary Study

Gustavo de Souza, Ricardo K. Kramer and Antonio J. F. Carvalho*

Department of Materials Engineering, Sao Carlos School of Engineering (EESC), University of São Paulo (USP), São Paulo, Brazil

*Corresponding Author: Antonio J. F. Carvalho. Email: toni@sc.usp.br

Received: 04 June 2020; Accepted: 31 July 2020

Abstract: Oil spills and oil/water wastewater are among the great concerns regarding oil pollution. Existing technologies face many limitations and in some cases are responsible for causing secondary pollution, therefore there is as seek for environmental friendly solutions. Biomass, from which celluloses are highlighted, are being employed for oil/water separation or oil absorbents membranes. Usually, these membranes are obtained by freeze drying of CNF (cellulose nano-fibrils) suspensions followed by chemical modification for hydrophobization, which involves expensive process as chemical vapor deposition and expensive reactants as silyanes, turning these processes hardly scalable. Here, we produced a natural porous structure paper from eucalyptus pulp fibers modified by a dipping and heating process in a blocked diisocyanate solution. After the surface treatment, contact angle with water reached 144° and water absorption reduced seven times, keeping the good oil absorbance. The chemical modification process is simple to be performed and use a very low quantity of reactant estimated to be less than 0.1 wt% based on cellulose. The good mechanical properties of the material allows its use in non usual conditions which can be of great importance depending on the environmental conditions.

Keywords: Cellulose; oil removal; hydrophobization; water repellency; blocked isocyanates

1 Introduction

Modern society has achieved great development through the utilization of oil based resources to produce a large amount of goods that have enhanced the easiness of our daily lives. However, this oil based dependency has left human footprints in a diversity of ecosystems mainly due the oil extraction and contaminated wastewater. Oil spills or leakages as well as oil/water (O/W) emulsions in wastewater are the great concerns in regarding oil pollution. Among the existing technologies to deal with oil spills, boomers, skimmers, *in situ* burning, dispersants, bacterial biodegradation and adsorbent are already explored in real situations. However, all these solutions have limitation in working time or cost. Besides, the equipment effectiveness is depending on weather and spill conditions and in some cases secondary pollution may emerge in the cleaning processes. Therefore, new alternatives are demanded [1,2].



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Recently, the production of absorbents based on biomass has attracted the interest of the researchers. Among the possibilities, cellulose has gained most of the attention due its remarkable properties such worldwide availability of raw material, excellent mechanical properties, low density, renewability and biodegradation, which avoid secondary pollution [1,3,4]. There are two main strategies on using cellulose membranes for oil spill or O/W emulsions treatments based on the polarity of the surface. On one side, there are the oleophilic membranes which are main employed for O/W separations under wet conditions, in which they repel the oil and other dyes and let waters passes through its porous structure, cleaning and purifying the collected water [5–9]. On the other hand, there are the so called oil absorbents, which are hydrophobic membranes that collects the oil from the water source by means of capillarity forces and thus the oil is separated from the water and driven to a less pollutant media, which can be recovered by squeezing or solvent treatment [10–13]. The present research focuses on the second alternative.

Nonetheless, the hydrophilic nature of cellulose limits its application in water media as wet environments may cause leaching or swelling of the absorbent material during utilization. Some strategies as chemical modification of the fibers or membrane hydrophobization post-treatment are successfully applied to overcome water plasticizing effect in cellulose absorbents. Chemical vapor deposition (CVD) based on sylanes [11,12], grafting with polystearylmethacrylate [14] and treatment with sodium docecylsulfate [10] are among the most successful and recent approaches. However, some of these treatments, mainly the ones with sylanes have some drawbacks on the cost involved in the membrane production.

One simple and efficient strategy described by our group for surface modification of biopolymers, which was first applied to thermoplastic starch [15], uses blocked isocyanates as a way to modify hydrophilic hydroxyl containing materials without the need of work in anhydrous environment. The method is based on the immersion of the substrate into a blocked isocyanate prepolymer solution; remove it from the solution and then expose the “wet” subtract to drying followed by unblocking and grafting (dip and heating process). The same method was also used to modify cellulosic fiber with the purpose of compatibilize it with polypropylene in thermoplastic composites [16]. The use of blocked isocyanates as prepolymers [15,16] is an interesting way not only to avoid its decomposition in wet environment, leading it to urea and carbon dioxide, but also to make it less toxic since the toxic effects of isocyanates are well known [17]. Phenol was used as blocking agent and at thermal treatment at around 170°C for a few minutes it “de-blocks,” recovering the reactants and releasing the isocyanate group to react with a free primary hydroxyl groups of cellulose fiber, forming stable urethane linkages.

Another concerning about cellulose oil absorbents is regarding to the physical characteristics of the membranes. It is desired that an absorbent material has some degree of porosity so the oil can be absorbed by capillary effect. However, a balance between porosity and mechanical integrity has to be achieved aiming at better effectiveness of the absorbing material [1]. The majority of the studies present a top down strategy, i.e., fibrillation of cellulose fibers until nanoscale in order to produce CNF (cellulose nanofibrilated) followed by a production of an aerogel by freeze-drying [10–12,14]. The obtained porous material, after been hydrophobized by any given method, has outstanding absorbent properties but this strategy stucks on the scalability of the process. Although there are protocols of high yield to lead cellulose fibers to a nanoscale length, it is still a relative expensive process. Besides, freeze-drying is a time and energy consuming process that is hardly scalable in real life absorbent applications [1,4].

Papers produced by dewatering of a cellulose fiber suspension lead to a natural porous structure that can replace the need of CNF aerogels in oil absorbent applications. Here, we produced a porous cellulose pulp paper by a vacuum dewatering process, followed by drying in a hydraulic press. The produced hydrophilic paper was further hydrophobized by dipping in a blocked isocyanate solution followed by a thermal treatment at 170°C for surface modification—dipping and heating processing. The modified paper was

evaluated regarding to its ability of water resistance and oil removal from aqueous media focusing on its application in wastewater and oil spills treatment.

2 Materials and Methods

2.1 Materials

Bleached Kraft wood pulp fibers from eucalyptus (never dried with 33% solid content) were kindly supplied by Suzano S.A. Brazil (fiber diameter of 15 μm). 4,4-Methylenebis (phenyl isocyanate) (MDI), as well as phenol and dodecanol were all purchased from Sigma–Aldrich and used as received in conjunction with commercial dibutyltin dilaurate, DBTL, and zinc octoate as catalyst. Reagent grade butyl acetate, xylene, methylene chloride were also supplied by Sigma–Aldrich were dried by storing with 4Å molecular sieves at least 36 h before use.

2.2 Paper Preparation

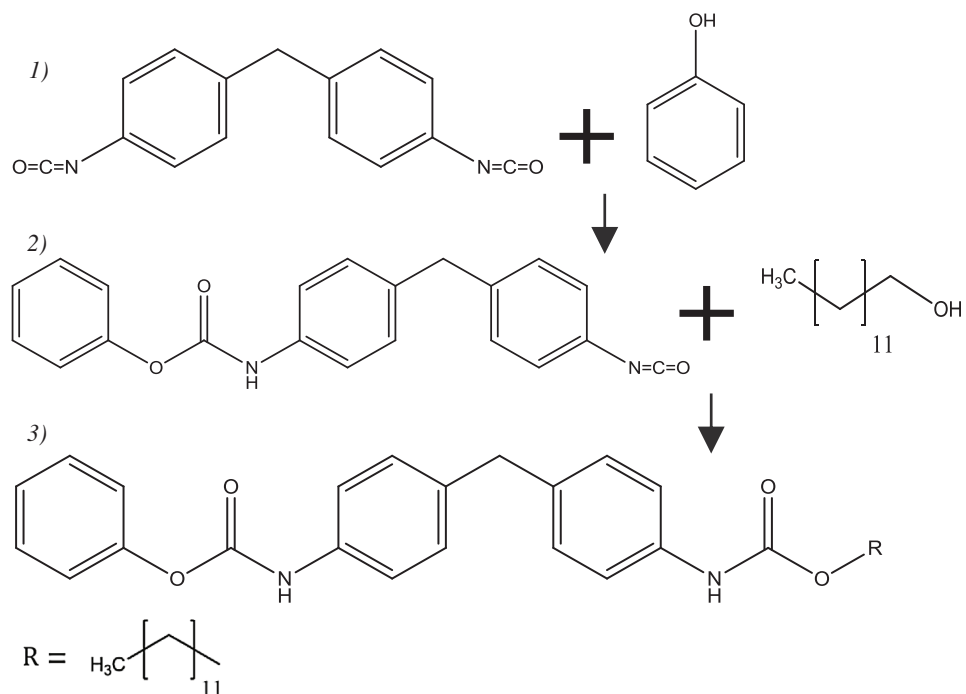
Never-dried Kraft wood pulp was suspended in water (0.1 wt%) using an Ultra-Turrax IKA model T25 operating at 20,000 rpm for 5 min. The suspension was filtrated with a Buchner funnel with 90 mm diameter aided by vacuum pump using a qualitative filter paper as fiber holder. The wet fiber cake was carefully removed from the filter paper and sandwiched between two fresh filter papers to remove the excess of water. In sequence, the system was pressed between two metal plates with a 1 mm thickness metal separator and heated at 120°C for 30 min under a weight of 100 kg in a hydraulic press. After production the paper was stored in desiccator containing dried silica gel.

2.3 Blocked Isocyanate Preparation

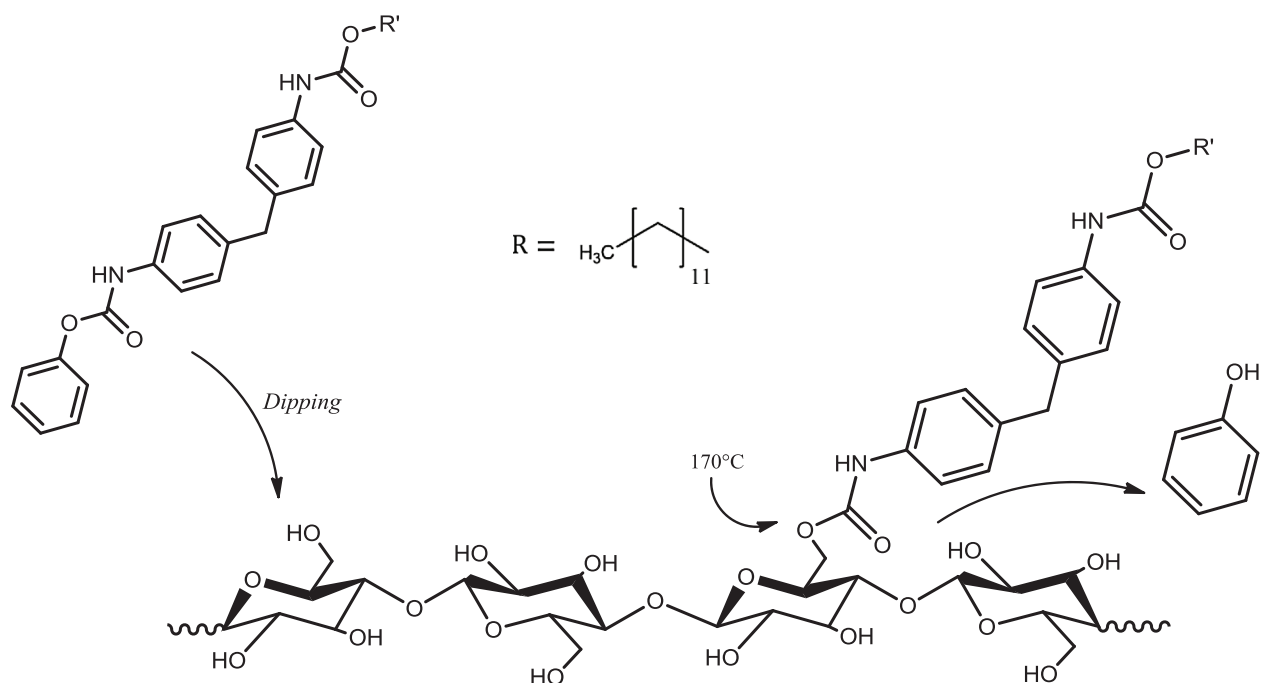
5 g (20 mmol) of 4,4'-Methylene diphenyl diisocyanate (MDI) was dissolved in 100 ml of anhydrous butyl acetate into a 3 neck round bottom flask equipped with an addition funnel under nitrogen atmosphere and immersed in a water bath at 40–45°C. Then 1.88 g (20 mmol) of phenol (blocking agent) and 0.1 ml of DBTL (dibutyltin dilaurate) diluted in 30 ml of butyl acetate at 50°C was added dropwise during 15 min into the three neck bottom flask under vigorous magnetic stirring at inert N_2 atmosphere. In sequence, 20 mmol of dodecanol alcohol was dropwise added and agitation was kept for 2 h. The products were recovered by solvent evaporation at room temperature using a rotary evaporator. Non-reacted moieties were eliminated by washing the product powder was with 2-propanol and after that the powder was dried in an oven at 60°C. The urethane formation was confirmed by FTIR [18]. [Scheme 1](#) illustrates a possible path for the adduct synthesis in an idealized situation in which one NCO group from MDI reacts with one phenol and the other reacts with dodecanol to form Phenol-MDI-Dodecanol (Ph-MDI-D). Other molecules as phenol-MDI- phenol (Ph-MDI-Ph) and dodecanol-MDI-dodecanol (D-MDI-D) could also be formed as there was no control about the reaction yield. Moreover, other concurrent moieties such as urea, alophanates and biurets could also be formed if any residual water is present in the system [19].

2.4 Paper Modification by Dipping and Heating

1.6 g of blocked MDI adduct (Ph-MDI-D) was mixed with 0.25 g of zinc octaoate dissolved in 75 ml of xylene and 25 ml of butyl acetate at 60°C using a magnetic stirrer. Paper samples were cut in squares of 5 × 2.5 cm, dipped for 60 s into the solution, dried under a nitrogen flow and then placed in an oven for 10 min at 170°C. They were subsequently washed twice with hot xylene and butyl acetate (75/25v) and rinsed several times with methylene chloride to remove the non-reacted Ph-MDI-D. Finally, paper samples were dried at 60°C for 1 h. [Scheme 2](#) shows simplified possible path for the deblocking reaction followed by the formation of urethane linkage with cellulose. The blocking agent (phenol) is released. Other side-reactions not showed can also occur forming for example ureas and alophanates [19].



Scheme 1: A possible path for blocked diisocyanates synthesis



Scheme 2: Deblocking and the reaction of the *in situ* generated isocyanate with cellulose chains. For the purpose of illustration the reaction with primary alcohol is shown, however the other hydroxyl groups can also form urethane linkages with the free isocyanate generated due to deblocking of the Ph-MDI-R

2.5 Paper Substrate Characterization

2.5.1 Scanning Electron Microscopy (SEM)

SE images were acquired in the mode of secondary electrons (SE) using an Inspect F-50 (FEI) microscope with voltages of 2.0 and 4.0 kV and working distances from 7.0 to 9.0 mm. Kraft pulp fibers were diluted to a 0.01 %wt and a droplet of 20 μl was deposited in a slice of silicon wafer that was dried under high vacuum. Paper samples were prepared by bonding squares of the material in a double side carbon tape. Sample stubs were metalized in a sputtering of type scancoat six, from Edwards[®], using a platinum target with 90 s of exposure.

2.5.2 Atomic Force Microscopy (AFM)

An AFM model Flex-Axiom (Nanosurf) working in tapping air mode was used. Samples with 5×2.5 cm previously dried at 60°C for 2 h, were bonded in a double side tape and pressed in the sample holder. The silicon scanning probe used was a Tap190Al-G with a maximum radius of curvature of 10 nm. The images were obtained using resonance frequencies of the cantilever in the range of 150 kHz. Images processing were performed using the freeware software Gwyddion[®]. For the measurements, five horizontal lines of 30 μm in length were parallel drawn, spaced 5 μm along the edge of the image. For each line, the mean value of the said roughness parameter, calculated by the simple arithmetic mean of the five lines, was calculated. The measured roughness parameters were the average roughness (Ra), which is an arithmetic mean of the roughness profile deviations; the mean square root roughness (Rq), which is the mean value of the deviation of heights, and the maximum profile height (Rt), which is the measure of the absolute value of the largest peak minus the smallest valley of the measurement line. All parameters are set by ASME B46.1-1995 and calculated on software interface.

2.5.3 Tensile Test

Tensile tests were performed in an Instron3365 with a load cell of 5 kN using miniaturized rectangular testing specimens (35×5 mm) with extension rate of 0.5 mm min^{-1} and 25 mm of distance between the grips [20]. Temperature and relative humidity were controlled at 23°C and 48 % RH during all tests. The specimens were conditioned in the test room for at least 24 h before loading.

2.5.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were measured using a PerkinElmer Spectrum 100 with an attenuated total reflection (ATR) accessory. The spectroscopy was performed on the films in the range of mid-infrared from 4000 cm^{-1} to 650 cm^{-1} , where each spectrum is an average of 32 measurements. Spectra were normalized in relation to their characteristic bands, where reactants were first normalized dividing the curves by the maximum peak value and then normalized to [0–1]. The synthesized adduct was normalized dividing values by the band at 1410 cm^{-1} , a distinct and homogeneous band that appears clearly in the spectra, and then normalized to [0–1]. In this way the pressure factor is eliminated from the different ATR measurements and bands from the various spectra can be compared among each other in the same scale.

2.5.5 Thermogravimetric Analysis (TG)

TG analysis were acquired using a Thermogravimetric Analyser Pyris I (Perkin Elmer) under constant N_2 flow of 20 mL \cdot min⁻¹, at a temperature ranging from 25 to 700°C and heating rate of 10°C \cdot min⁻¹.

2.5.6 Water Contact Angle

A contact angle device from KSV, model CAM 101 system was used to measure the static contact angle of the modified paper. Specimens were cut into rectangular shapes with a width of 5 mm and length of 30 mm. Five droplets of distilled water with ~ 5 μl in volume were dropped on each specimen and 40 pictures with 16ms of interval were taken for each experiment. The static contact angles were obtained

by plotting the contact angle vs. time, where the equilibrium value (static) was determined. Measurements were performed at 23°C and 30 % RH.

2.5.7 Oil/Water Absorption Test and Oil Separation

The previously dried sample was put into separated beakers with distilled water and soy oil and the weight gain was measured at 1 h and at 24 h. The experiment was conducted at 25°C and three experiments were performed for each sample. For the determination of oil separation, two drops of a solution of methylene blue solubilized in ethanol was poured into a beaker with 50 ml of distilled water along with five drops of soy oil. Isocyanate modified paper specimen of 5×2.5 cm length was hold with a tweezers and placed into the beaker with circular movements for one minute.

3 Results and Discussion

3.1 Paper Preparation and Characterization

Good compaction and an adequate network of porosity are essential for a permeable and separation membrane and the images from macro to microscale (photos and SEM images) on Fig. 1 shows that both features are present on paper structure after hot pressing. The grammage of papers was 190 g/m², which resulted in good mechanical properties as is observed in Fig. 2, with elastic modulus near 1 GPa and tensile strength above 10 MPa.

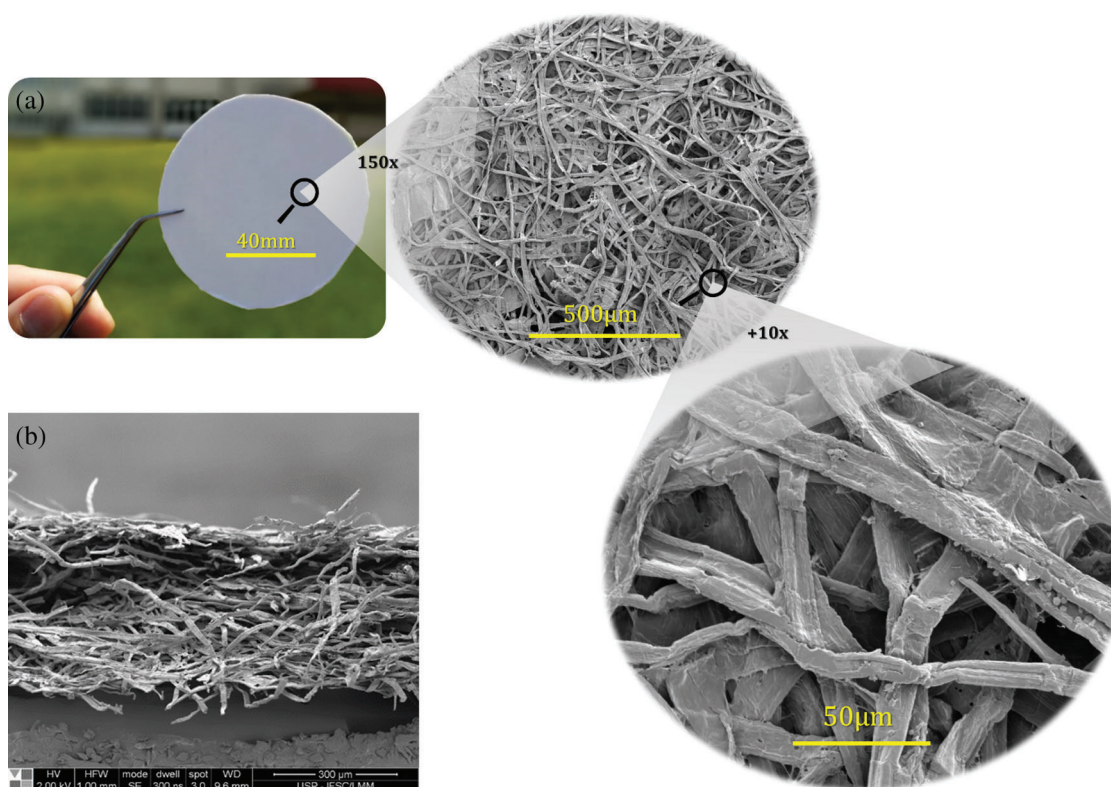


Figure 1: (a) Digital photography of a sample of paper as prepared and SEM images of the pulp paper. Details in SEM images show the porous structure of the paper at microscale. (b) The cryogenic fracture on the right side shows that the porous structure remains present in the bulk section

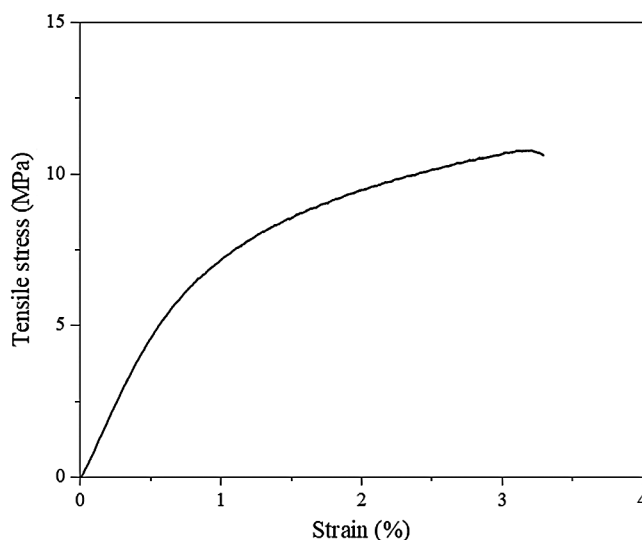


Figure 2: Tensile stress vs. strain curve for the hot pressed pulp paper

For a film passing by a surface hydrophobization treatment, the roughness plays a big role as, following Wenzel or Cassie-Baxter models, the higher the surface area of contact, more the hydrophobic effect is amplified. Fig. 3 shows AFM images and perspective view on the right side presents a maximum height of the surface as being $9.3 \mu\text{m}$, approximating the dimension of a single fiber. From the topographic data on AFM three parameters of roughness were calculated and are also presented in the figure, with R_a of 75 nm . A porous and rough surface present the ability of encompassing air bubbles and contributes significantly to a more hydrophobic surface or even super-hydrophobic [21].

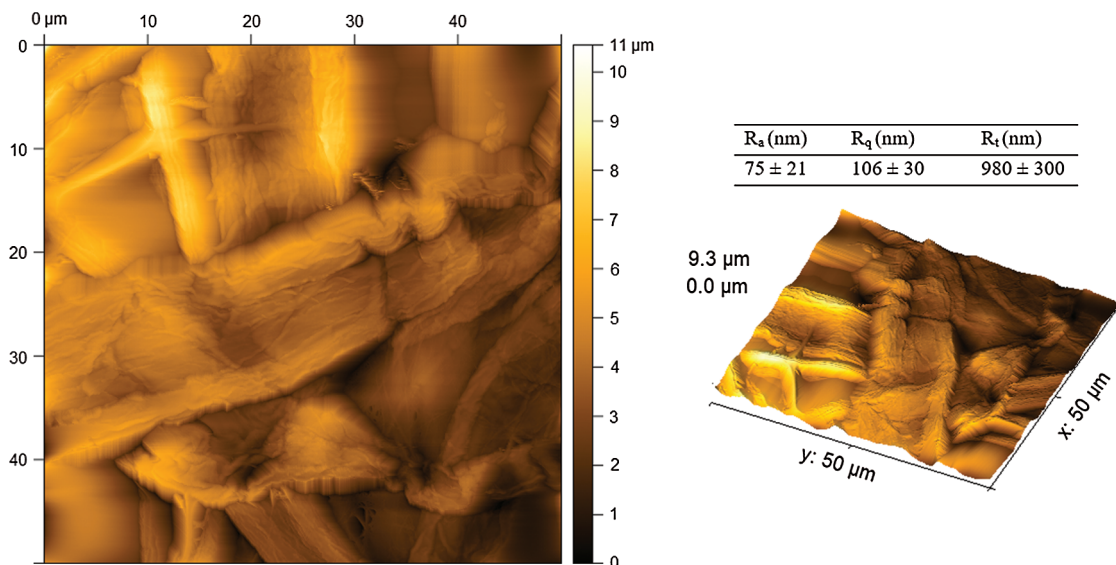


Figure 3: AFM images of the topography and perspective of the non treated paper

3.2 MDI Adduct Preparation

Fig. 4 shows FTIR spectra of the reactants and the resulting blocked diisocyanate (Ph-MDI-D). As can be observed, the hydroxyl groups vibration of the blocking agents (phenol and dodecanol) at 3330 cm^{-1} give

place after reaction to a sharp vibration related to -NH from urethane bonds. Vibrations at 1720 cm^{-1} and 1700 cm^{-1} are ascribed to carbonyl from phenyl-carbamates and alquil-carbamates, respectively [18]. Urethane formation is also evidenced by the presence of -HNCO vibration at 1535 cm^{-1} . The presence of the vibration at 1640 cm^{-1} indicates the formation of urea. However, its relative small size in relation to the alquil/phenyl urethane bands indicates the reactants yielded mainly the aimed products.

The thermal decomposition of Ph-MDI-D as a function of temperature is presented in the Fig. 5a and its derivate (dTG) in Fig. 5b. By the deconvolution of the thermal events in the dTG graph using Origin[®] software, four different thermal events were found. The first occurs in the range of $170\text{--}180^\circ\text{C}$ and is related to the de-blocking temperature of phenyl-urethane bond, followed by the elimination of phenol. Events 2 and 3 take place in the range $250\text{--}300^\circ\text{C}$ and are related to the dissociation of alquil-carbamate with elimination of dodecanol. Event 4, starting at 312°C , is due the decomposition of the regenerated MDI [18]. The expected mass loss at event 1, for the structure proposed in Scheme 1 should be around 17%. TG data provided a close empirical loss of 17.28% suggesting the desired adduct as the main product of the reaction.

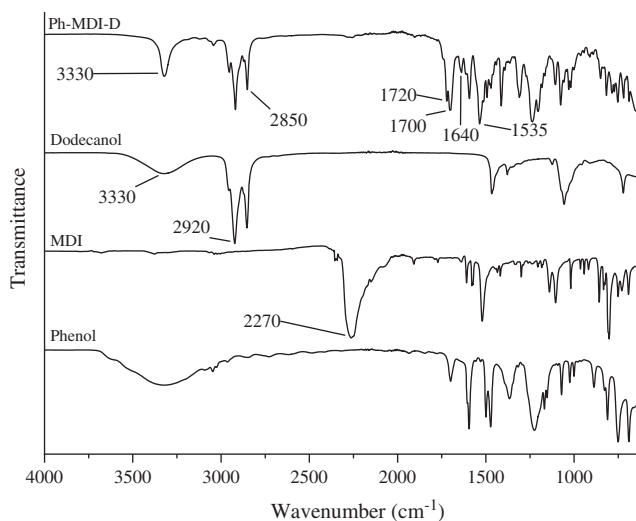


Figure 4: FTIR spectra of the blocking agents, MDI and the synthesized blocked diisocyanate (Ph-MDI-D)

3.3 Treated Paper Characterization

Before the hydrophobization treatment, paper samples were placed in a circular oven at 60°C for three days for mass stabilization and weighted with a four-digit balance. After the dipping and heating process, samples were weighted again and mass gain was below the method limit (less than 0.1%).

Fig. 6 shows the FTIR spectra of the non-treated and treated papers. Absorption bands at 1700 cm^{-1} from alquil-carbamates and at 1538 cm^{-1} relative to -HNCO bond, indicate the surface chemical modification. Also, steep vibrations at $2900\text{--}2800\text{ cm}^{-1}$ ascribed to -CH_2 from dodecanol are observed in the modified paper spectra, indicating that the thermal treatment at 170°C only caused the deblocking of the phenyl-carbamate, keeping the alquil-carbamate unchanged, as indicated on TG analysis (Fig. 5). The vibration bands observed on the spectrum of the modified paper are in the following regions; $1720\text{--}1695\text{ cm}^{-1}$ from C=O stretch (Amide: -NH-CO-O-), $1660\text{--}1640\text{ cm}^{-1}$ from C=O stretching (probably, urea: -NH-CO-NH-), $1650\text{--}1635\text{ cm}^{-1}$ from absorbed water, 1600 cm^{-1} from C=C aromatic stretching, $1535\text{--}1540\text{ cm}^{-1}$ from -HNCO- symmetric stretching, 1425 cm^{-1} from -CH_2 of cellulose and $1230\text{--}1250\text{ cm}^{-1}$ from C-N stretching. These regions of absorption are in accordance with the literature [19].

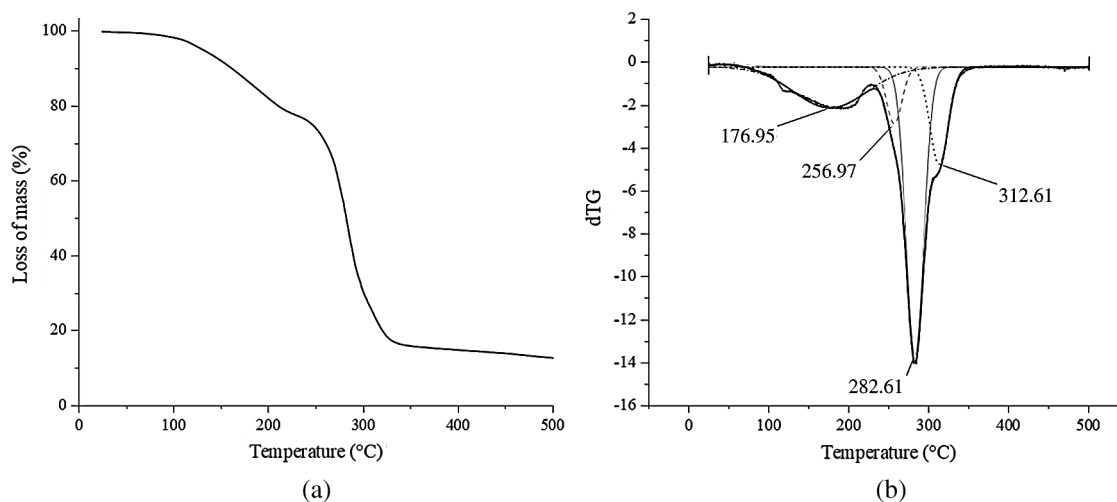


Figure 5: (a) TGA profile with loss of mass as a function of temperature for the synthesized adduct (Ph-MDI-D). (b) Deconvolution of the derivate curve of loss of mass from Ph-MDI-D showing four main thermal events

Fig. 7 shows the water contact angle (WCA) of the paper treated with Ph-MDI-D (40 measurements during and interval of 16 ms). An equilibrium value of 144° on average evidenced that the surface chemical modification was effective to hydrophobized the paper surface. The high value of WCA, near the superhydrophobic state, is ascribed to a combination of both chemical treatment and high surface roughness. Oil drop was readily absorbed by the modified paper, being not possible to measured properly the oil contact angle with the proposed experimental setup.

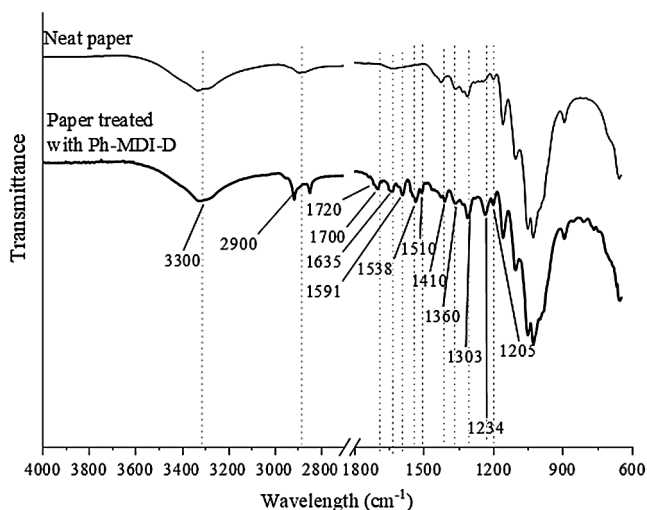


Figure 6: FTIR spectra of the pulp fiber paper (neat paper) and the modified pulp fiber paper with Ph-MDI-D

Fig. 8(a) shows the water and oil uptake data for the pristine and surface hydrophobized paper. Despite the fact that the modified and non modified paper absorbs the same quantity of oil, the treated paper absorb a proportion of water very low when compared to the non modified paper (218% and 30% for non-treated and treated, respectively). Moreover, in addition to the water repellent property, the modified paper became

resistant to disintegration in the presence of water which makes its application suited for oil removal in wet environments. The test shows that despite the drastically reduction on water absorption, the oil absorption still has to be improved and changes in the drying parameters as the pressure and time in which the paper pass inside the hot press device can be optimized to produce a more porous but still compact network of fibers, increasing the ability of the structure to absorb more oil. Other oils are worth to be investigated as well. Fig. 8b shows images in sequence of the oil/water separation test where the hydrophobized pulp paper was able to collect the soy oil spilled in the methylene blue colored distilled water without losing its shape or swelling. Besides, after chemical modification the paper possess a lower energy surface and floats above the water. The oil absorption capacity is still lower compared to other proposed studies in literature [21]. It is noteworthy that the compact papers used, although absorbing a relatively low amount of oil, exhibit good mechanical resistance which is necessary for several applications.

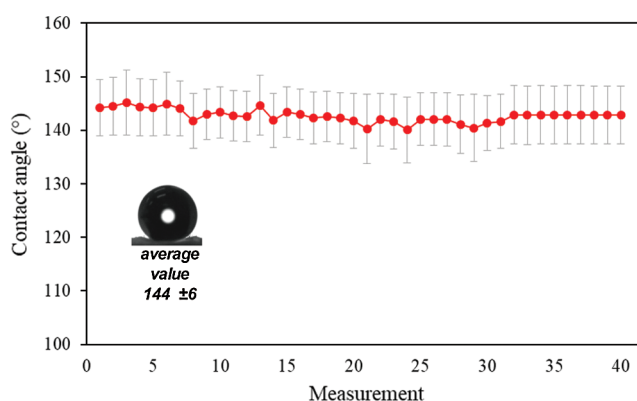


Figure 7: Water contact angle (WCA) of the pulp paper surface hydrophobized with Ph-MDI-D

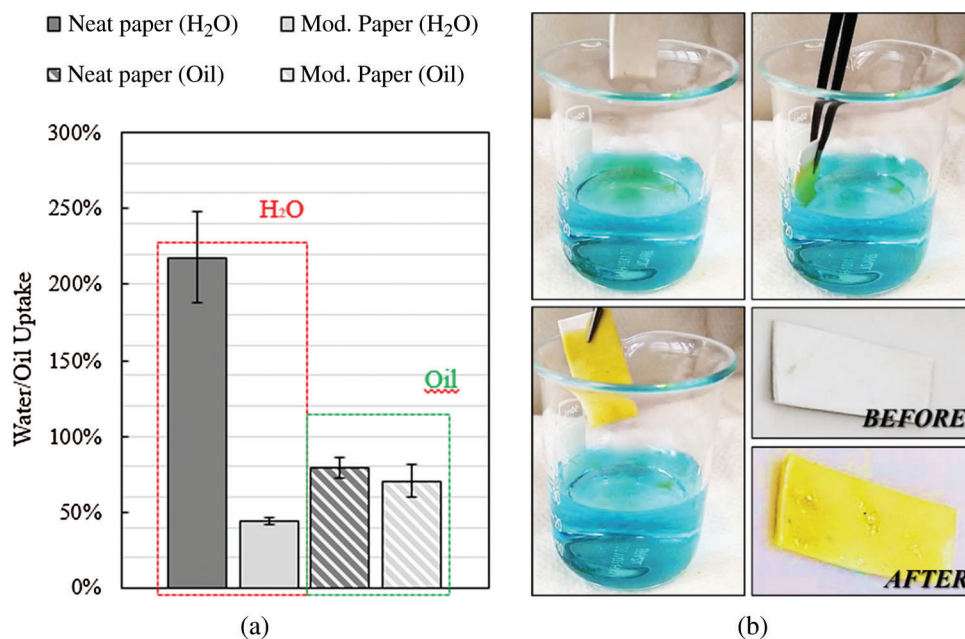


Figure 8: (a) Water and oil absorption for the neat paper and for paper surface modified with Ph-MDI-D. (b) Sequence of pictures showing the ability of the modified pulp fiber paper on removing soy oil spills from a beaker filled with water dyed with methylene blue without swelling or leaching

4 Conclusion

In the present research porous cellulose pulp paper was produced by a filtration/hot pressing procedure followed by modification by dipping and thermal treatment with a solution of blocked diisocyanates. The hydrophobization process was confirmed by FTIR and water contact angle with an almost superhydrophobic value of 144° . Oil/water uptake tests showed the reduction of water absorption by a factor of seven though keeping the oil absorption feature. The hydrophobic paper was used to successfully remove oil spills from water. Modified paper also presented swelling and disintegration resistance in contact with water. Besides, the treatment lowered its surfaces energy, which started to floats over water, an important feature for absorbent material dealing with oil spills. In summary, the presented results show the potential of using hydrophobized cellulose pulp sheets for oil/water separation in a cost effective and scalable process creating an alternative over common freeze-drying methods of CNF suspensions. The oil absorption can be increased changing the morphology of the paper and will be subject of future research.

Funding Statement: This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior—Brasil (CAPES)—Finance Code 001. Authors also acknowledge CNPq for financial support in special for the doctoral fellowship granted to G.S (CNPq Proc. 140249/2017-6). AJFC acknowledge CNPq for research funding project # 03847/2019-0.

Conflicts of Interest: The authors declare that they have no conflicts of interest to report regarding the present study.

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