

Permeability of untreated and atmospheric plasma treated coconut fiber mats

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Abstract

Composites manufactured by resin transfer molding depend on appropriate processing parameters to ensure adequate reinforcement-matrix adhesion. Permeability predicts the fluid flow resistance through reinforcement. The purpose of this work is to evaluate the influence of atmospheric plasma treatment on the permeability of coconut fiber mats. Glycerin solution simulated matrix impregnation of untreated and treated mats. Data from scanning electron microscopy and a decrease in contact angle from 96° to 61° for treated fibers explained the difference in permeability due to etching phenomenon that caused a decrease in permeability value. Kozeny-Carman ratified changes in the permeability of coconut fiber mats. Atmospheric plasma treatment turns fibers more hydrophilic enabling better fluid impregnation in addition to a more regular and slower flow front.

1. Introduction

Environmental concerns combined with waste management issues can explain greater interest in developing and using new environment friendly materials and processes. Within this context, industries and researchers are looking for materials from renewable sources in order to replace traditional materials derived from fossil resources [1–3]. The 2030 Agenda for sustainable development consists of a plan elaborated for governments, societies, companies and academia working in a global partnership to improve people's lives, now and in the future. The 12th Sustainable Development Goal entitled 'Responsible Consumption and Production' aims to achieve economic growth and sustainable development through changes in consumption and production patterns with an efficient management of natural resources and changes in the disposal of toxic and polluting waste [4], as well as the proposed work.

Natural fibers reinforced composites are becoming increasingly common in automotive and construction industries [5–7]. For construction, they are used as low cost housing and seismic resistant building [5]. Automotive companies such as Mercedes Benz, Toyota and DaimlerChrysler have incorporating these lignocellulosic fiber composites into interior and exterior car parts [7]. Lignocellulosic fibers are offered by nature and easily renewable, often considered as natural waste, presenting characteristics as low density, low cost, non-toxicity, biodegradability, turning them a potential substitute for synthetic fibers in composite manufacturing [8, 9]. However, when considered as waste, these fibers are incinerated, sub utilized as low cost energy, wrongly disposed or submitted to composting [10]. Therefore, it is necessary to develop new applications for these waste materials, considering environmental and economic factors [11]. Data from Food and Agriculture Organization of the United Nations indicated that coconut trees occupies around 12 million hectares of total world land and produces around 62 million tons of coconut fruit, totalizing an annual world production around 50 billion fruits [12]. In Brazil, coconut is an important agricultural product with an annual production nearly 2 billion fruits. After its consumption in industries or on the coasts, the shell, which is equivalent to 85% of the total mass of the fruit, is irregularly disposed generating a large amount of waste.

Coconut fibers can be extracted from these are wrongly disposed shells, representing both an economic opportunity and an environmental solution [13–15]. Natural fiber composite manufacturing requires technical knowledge such as degree of polymerization, crystallization, adhesion between fiber and matrix, and processing type. Resin transfer molding (RTM) is a low-cost technique, with low processing time, low waste of material during manufacturing, besides allows high reproducibility and parts with complex geometries [16].

Understanding processing parameters performance, as well as knowing how external factors directly influences it, results in a material with the most appropriate properties. Permeability is an important parameter allowing to estimate the fluid flow behavior through the reinforcement during the process [17], once permeability is the fluid flow resistance through the reinforcement dependent on the fluid viscosity [18, 19]. Essential for low-pressure injection process, depending on the permeability value, it can form voids and the injection time can increase when permeability decreases [18–20]. Manufacturing RTM coconut fiber reinforced composites has an enormous influence on the permeability value, considering that the more compact the mat, the greater is the resistance to the fluid impregnation [21].

Concerning composite materials, synthetic fibers such as glass and carbon fibers for example, have chemical, mechanical and microstructural properties different from natural fibers, resulting in different surface interaction characteristics with the matrix, which influences some process parameters such as permeability [22]. Reinforcement-matrix interface interaction is also an important factor for mechanical properties [21], which can be improved through several types of surface treatments [23]. Chemical and physical treatments can be applied to the surface of these natural fibers by removing some of the amorphous components such as hemicellulose and lignin, besides waxes and impurities with the purpose of improving interfacial adhesion between reinforcement and matrix [14]. The most commonly surface treatment applied to natural fibers are chemical treatments such as mercerization, bleaching and acetylation, which aim to react with them, allowing greater interaction between the constituents of the composite, providing partial removal of lignin and hemicellulose [24]. From literature is common to observe the use of this kind of treatment to change natural fibers surfaces [25–29]. However, physical treatments has gained attention due to its purpose in improve the interfacial adhesion of the composite, guaranteeing mechanical properties without using chemicals reagents such as sodium hydroxide and hydrogen peroxide, which are commonly used [9]. Plasma is an interesting, versatile and promising technique, considered as the highest level of private and public investment technology [30], that turns natural fibers surface rougher and activated [31], improving reinforcement-matrix surface interaction and consequently its permeability properties [32]. Natural fiber surface become hydrophilic and has better wetting and adhesion properties with other materials [33, 34]. To induce plasma, different conditions can be chosen, especially pressure, type of gas (air, oxygen, nitrogen, helium, argon, etc) and the way to discharge [35, 36]. Atmospheric plasma treatment is considered as a clean and high-efficient surface modification method [32], and also a less aggressive process that minimizes polluting waste generation, replacing more costly and polluting treatment techniques [37]. Improving permeability properties of natural reinforcements by plasma treatment requires understanding the mechanisms present in natural fibers impregnation like mechanical interlocking and chemical interaction, which can improve fiber-matrix adhesion. By etching coconut fibers surface with plasma, these results are expected. Li [22] observed that, by hybridizing jute fabrics with ramie fabrics, the permeability of reinforcements showed a shorter infusion time and higher permeability. Francucci [18] studied saturated and unsaturated permeability for natural fibers and observed that both values decreases due to fluid absorption and swelling. Nguyen [38] investigated the fluid type influence on the permeability of flax fiber in liquid composite molding process concluding that permeability values were different for each one.

Based on advantages of plasma treatment and the characteristics of coconut fibers, the purpose of this paper is to evaluate the influence of atmospheric plasma treatment on the permeability of coconut fiber mats in order to remove surface lignin and improve fiber-matrix adhesion, thus improve natural fiber composite RTM processing and consequently enhancing the composites mechanical properties. Therefore, coconut fibers morphology and contact angle measurement before and after plasma treatment were performed in order to understand its influences. Furthermore, untreated coconut fiber mats (UCM) and treated coconut fiber mats (TCM) permeability was calculated for RTM process by Darcy's law (DL) and modified Kozeny-Carman (KC) model was used to predict an analytical relationship between permeability and porosity results.

2. Experimental

2.1. Materials

Coconut fibers were manually molded in order to produce non-woven mats. Tangled coconut fibers were immerse in boiling water inside a glass dish to easier handle and remove some residual impurity. Between two shape glass plates, wetted coconut fibers were arranged, clip pressed and oven dried at 60 °C for 24 h.

Rectangular mats 210 mm long, 165 mm wide and 3 mm thick were cut according to RTM mould chamber dimensions.

2.2. Atmospheric plasma treatment

Atmospheric plasma jet device used for coconut fiber mats treatment consists of a high voltage electrode centered inside a vertical glass syringe with 11 mm diameter coupled with an insulating cap through which argon gas was admitted to the system at controllable flow rate of $1.2 \text{ L}\cdot\text{min}^{-1}$. A second grounded electrode (aluminum platform) under a 4 mm thick glass plate supporting the mats and avoiding accidental arcing were located above the syringe nozzle 9 mm gap, both coupled in a sliding table with controllable x-y displacement ensuring full mat coverage. Plasma was generated using a low frequency AC generator composed of high voltage power supply generating 16 kV peak-to-peak with 19 kHz frequency, displayed on a digital oscilloscope. Coconut fiber mats, oven dried at 100°C for 1 h, were arranged in the glass plate 2 mm distant from the nozzle and moved at a rate of $2 \text{ mm}\cdot\text{s}^{-1}$, with a stationary treatment time equivalent to 7.0 s covering 132 mm^2 circular area. Treatment were performed at room temperature and 65% relative humidity.

2.3. Coconut fiber characterization

2.3.1. Scanning electron microscopy (SEM)

It was used a scanning electron microscope Zeiss EVO LS-15, with EDS/EBDS Oxford INCA Energy 250 system to analyze UCM and TCM morphology. SEM operates under 10 kV and variable pressure mode with a secondary electron detector. An adhesive tape fixed specimens in a support, which were coated with a thin layer of gold to create an electrical conductible surface.

2.3.2. Contact angle

A Ramé-Hart goniometer model 300-F1 coupled with a camera and the DROPimage Standard software was used for contact angle measurements. Therefore, $5.0 \mu\text{l}$ droplets of glycerin solution were deposited on the surface of a single stretched coconut fiber before and after the plasma treatment. To allow good statistical control, in each specimen, 8 drops were placed and each drop processed 20 times.

2.4. Glycerin solution viscosity

A Brookfield DV-II + PRO model RV viscometer, SC4-27 spindle type, measured glycerin solution viscosity. The analysis was performed with a specimen vessel filled with 10 ml of glycerin solution, at room temperature until reaches a maximum torque of 90% at 200 rpm.

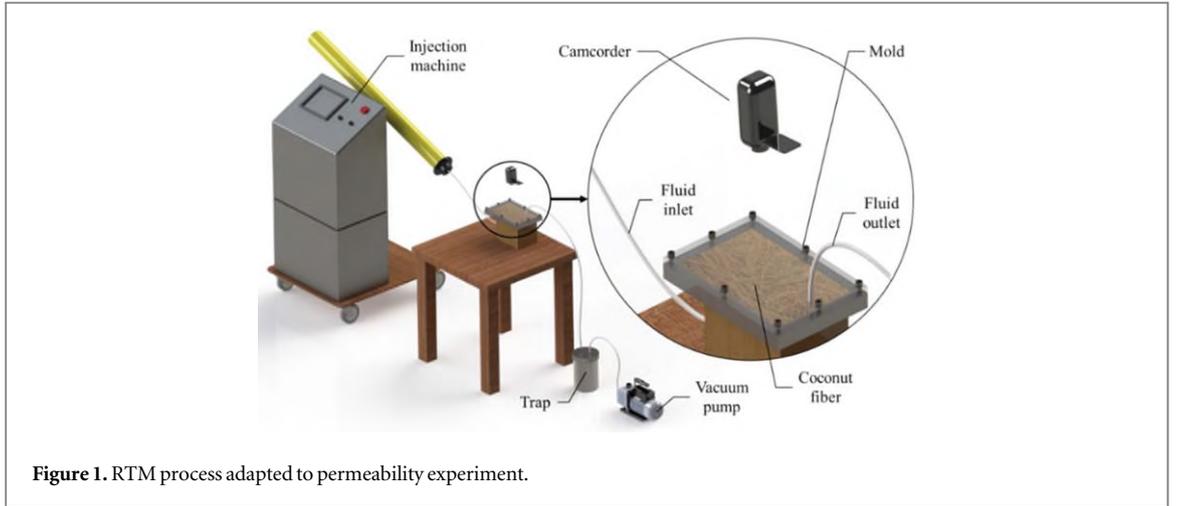
2.5. Permeability experiment

In order to verify the fluid flow behavior through UCM and TCM, a RTM Radius 2100 cc Injection machine with a controlled pneumatic system coupled with a vacuum system, was used. Vacuum was applied before processing to remove volatiles from the inside of the mold. Horizontal unidirectional flow experiments at room temperature and constant pressure (145 kPa) were performed in a rectangular mold with the coconut fiber mat inside composed of a metallic bottom plate and a transparent acrylic top plate in order to enable the flow front visibility. The fluid was injected at the mold inlet, and the mat impregnated. As the coconut fiber mat was impregnated, the flow front advanced forward up to the mold outlet. The flow front location as a function of time was video recorded with a camcorder equipped above the transparent top plate. From the recorded images analyzed in Image J software, the distance travelled from the inlet to the flow front was calculated and the processing time determined. Then, a straight line was found for the square of flow front position and corresponding time by curve fit of experimental data. Permeability process scheme is shown in figure 1.

A nonreactive glycerin, water and colorant solution with similar viscosity to an unsaturated polyester resin, equivalent value of $85 \text{ mPa}\cdot\text{s}$, was used for the experiment. The viscosity of the solution was measured by a Brookfield viscometer (same as previously used), reached at 85% glycerin and 15% distillate water v/v proportion.

In this study, Darcy's Law (DL) for unidirectional flow estimated UCM and TCM permeability values, which establishes that the velocity of the fluid through the reinforcement is proportional to the pressure gradient and inversely proportional to the fluid viscosity. Permeability (K), also known as coefficient of proportionality, is considered an important property that determine how easily the fluid flows through the reinforcement and can be obtained using equation (1), according to previous works from literature [18, 22, 39],

$$K = K_{DL} = \frac{\phi \cdot \mu}{2 \cdot P_{inj}} \cdot \frac{x^2}{t} \quad (1)$$



where K is the permeability value, ϕ the porosity ($\phi = 1 - vf$), vf the fiber volume fraction, μ the fluid viscosity, P_{inj} the injection pressure, x the distance between the inlet and the center of flow front until the outlet, and t the time. The injection pressure and the fluid viscosity were kept constant during the process. Kozeny-Carman (KC), an empirical model shown in equation (2), was chosen as a second method to estimate the reinforcement permeability according to previous works from literature [19, 40, 41],

$$K = \frac{d^2}{k} \frac{\phi^3}{(1 - \phi)^2} \quad (2)$$

where K is the KC permeability value, ϕ the porosity ($\phi = 1 - vf$), d the fiber diameter, k the the Kozeny constant. However, because of its complexity and the large number of related parameters, KC model presents some limitations, principally for natural fiber mats. Then, this method has frequently been modified and has different versions in order to improve permeability estimation [42]. Based on literature [18, 40], permeability estimation can be improved by modifying KC model in order to predict the experimental permeability-porosity relationships for glass and natural fiber mats as follows in equation (3),

$$K = K_{KC} = C \frac{\phi^{n+1}}{(1 - \phi)^n} \quad (3)$$

where C and n are empirical parameters for natural fibers [40].

3. Results and discussion

3.1. Coconut fiber characterization

3.1.1. SEM analysis

Morphological characteristics of UCM and TCM specimen were shown in figure 2. A variety in fiber diameter, ranging from 62 mm to 363 mm, can be observed for both cases, as shown in figures 2(a) and (d). From figures 2(a)–(c) is possible to observe a smooth surface covered by a layer of residual substances such as waxes, extractives and impurities, characteristics of lignocellulosic fibers, as observed by Muenstri *et al* Brahmakumar *et al* and Calado *et al* [43–45]. Globular particles, known as tyloses, which cover surface circular cavities and are spaced by regular intervals are also observed on the surface of these fibers (figure 2(c)). These globular particles are characteristics of coconut fibers also observed in the works of Benini, Carvalho and Wang [26, 46, 47].

From TCM micrographs, figures 2(d)–(f), partial removal of the superficial layer was observed, exposing the internal part of the fiber and increasing the contact area due to exposure of the fibrils through recesses appearance. It could be considered as consequence of the phenomenon known as etching during the plasma treatment, which allows an increase of the fiber surface roughness promoting the mechanical anchoring and contributing to a more adequate interfacial adhesion of the composite [13].

3.1.2. Contact angle analysis

Enhance surface interactions provides an adequate reinforcement-matrix interfacial adhesion, also known as surface energy [48]. Surface energy of a solid depends on the surface interaction between the molecules and functional groups present on its surface [49], and is measured based on the contact angle between liquids and solid surface. Table 1 presents results of the contact angle measurements for coconut fibers taken from UCM and TCM.

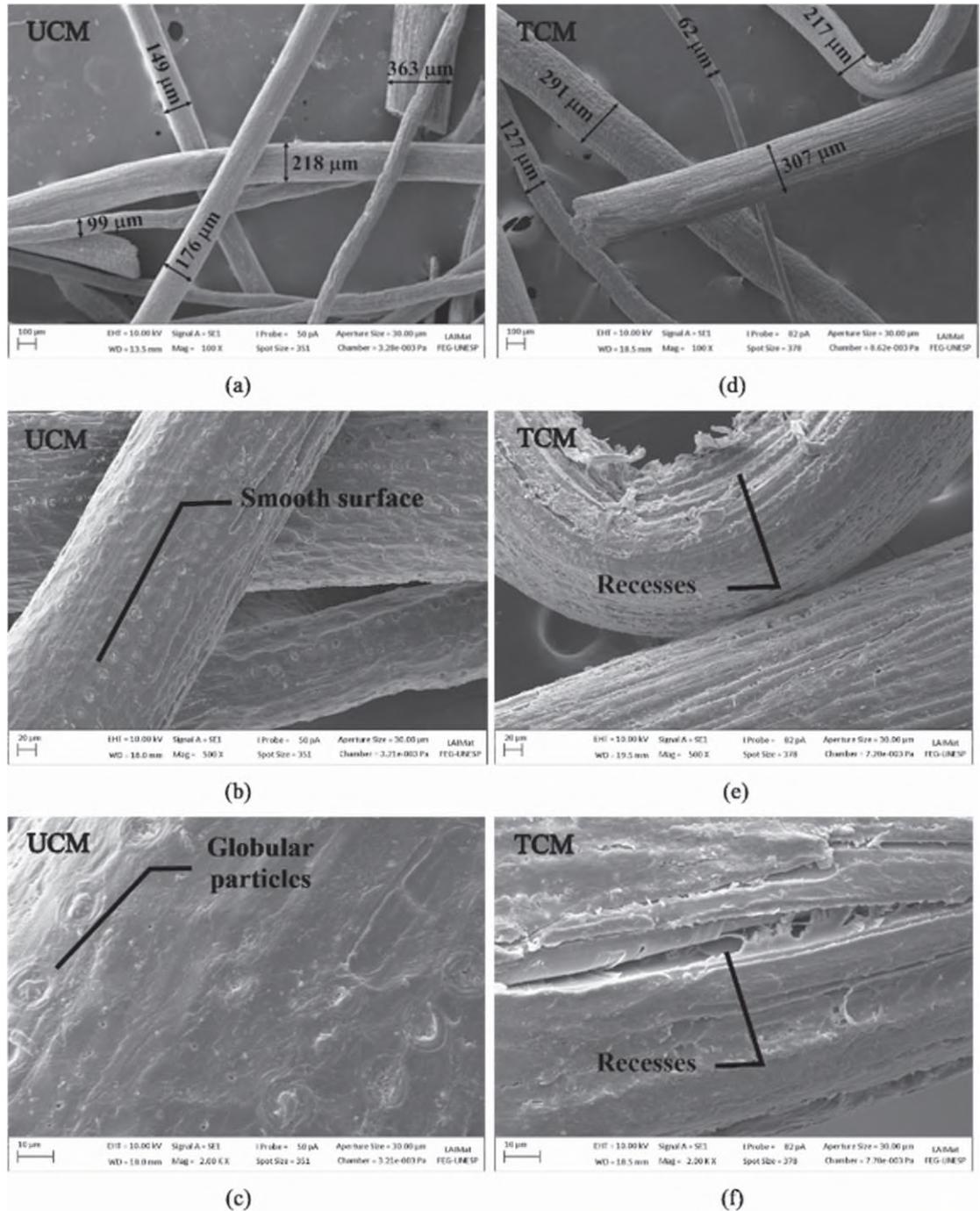


Figure 2. Micrographs of UCM 100X (a), 500X (b), 2000X (c) and TCM 100X (d), 500X (e), 2000X (f).

Table 1. Contact angle measurements of a single stretched coconut fiber taken from UCM and TCM.

Specimen	UCM	TCM
Contact angle (°)	94.8	60.6
	94.7	60.3
	94.9	60.9
	95.1	62.9
	97.4	62.7
	97.1	60.0
	95.9	59.2
	94.4	64.7
Average (°)	95.7 ± 1.1	61.4 ± 1.7

Data from contact angle measurements shown that TCM specimen presented a surface with hydrophilic nature due to the contact angle value lower than 90° resulting from a higher surface energy acquired from the atmospheric plasma treatment. [35] This lower value of contact angle is a consequence of a reduction on fibers hydrophobic character. This can be caused by a partial lignin removal resulting in the appearance of recesses exposing the internal layer, provided by the atmospheric plasma treatment, also observed by scanning electron microscopy [13, 14]. Hydrophobic nature is confirmed for UCM by the contact angle value higher than 90° , resulting from a lower surface energy caused principally by the presence of lignin on fibers surface observed by the smooth layer on the scanning electron microscopy analysis [14]. Lower value of contact angle, from 96° to 61° after the treatment, indicates the use of atmospheric plasma jet as a potential treatment alternative for natural fibers used as reinforcement in polymeric composite materials, once the surface energy is increased improving the interfacial adhesion between reinforcement and matrix.

Literature reports that it has been common to use contact angle measurement to investigate natural fiber properties. Brígida [28] in the wettability study of coconut fibers, observed by contact angle that the interaction between fiber/solvent depends on the chemical treatment used, and concluded that fibers treated with NaOCl or NaOCl/NaOH are more hydrophilic than the untreated one, due to the removal of lignin, having, as consequence, a reduction in hydrophobicity. Kocaman [14] measured contact angle values of untreated and NaOH treated coconut fibers and found 48.4° and 24.1° respectively. Treated coconut fibers had a hydrophilic nature compared to the untreated ones, concluding that the treatment reduced the contact angle of fibers, increasing their surface energy. According to Stepanova [50] plasma treatment decreases the C-H and C-C bonds (hydrophobic properties) and forms new bonds as O-C=O (hydrophilic properties) increasing the hydrophilic nature of treated fibers.

Traditional chemical methods have the disadvantage of using chemical reagents and generating polluting waste, requiring a proper disposal and presenting an environmental problem. Therefore, atmospheric plasma treatment appears as an environment friendly alternative considered a dry and clean process that changes fibers surface not using solvent or chemical reagents and not generating polluting waste.

3.2. Permeability

Figure 3 shows a sequence of recorded images of the flow front position at regular periods from which is possible to observe that both UCM and TCM have a positive impregnation profile. However, the TCM flow front behavior is laminar and presents a more regular concave shape and impregnation profile. During the experiment and from video analysis, it was observed the glycerin solution does not fully impregnate the UCM, which enables air entrapment, and consequently results in voids formation. It was also observed residual air present in the injection area (inlet) moving along the fluid flow and spreads in the area near the outlet, where the vacuum was applied, which also allows voids formation.

The square of distance travelled by the center of the flow front was plotted as function of time and the slope of the best fitting straight line calculated as shown in the graph of figure 4.

Table 2 presents experimental data and DL permeability values according to equation (1).

Considering data from table 2, it is possible to observe that DL permeability value of TCM is approximately three times lower than UCM DL permeability. This reduction in permeability after plasma treatment can be attributed to hydrophilicity increase provided by atmospheric plasma treatment, also observed by Kafi [51] who investigated jute atmospherically plasma treated using helium gas, concluding that plasma etching removed weakly bonded hydrophobic layer from the jute surface, increasing wettability. Kafi [52] also observed these results for atmospheric plasma treatment using different gas mixtures on the surface characteristics of jute fibers, verifying that the removal of the waxy or pectin layer from lignocellulosic fibers surface improves wetting properties. Brígida [28], for chemically treated coconut fibers, concluded that fibers treated with NaOCl are morphologically similar and a little more hydrophilic than the natural fiber.

Regarding UCM, the higher permeability value leads to a less regular flow front behavior as observed in figures 3(a)–(c). Contact angle results, as well as the formation of recesses observed from SEM analysis, indicates that the atmospheric plasma treatment on the coconut fibers surface allows more homogeneous impregnation and greater interfacial interaction between fluid and reinforcement, enhancing its permeability as was expected from DL permeability results. However, it is difficult to ensure, based on DL permeability data, that the difference in those permeability values are influenced only by the plasma treatment, being necessary to introduce a second analysis, as follows.

3.3. Kozeny-carman permeability

In order to ratify the influence of plasma treatment on the permeability of coconut fibers, it was also considered the modified Kozeny-Carman (KC) model that correlates permeability and porosity. Based on literature [40]

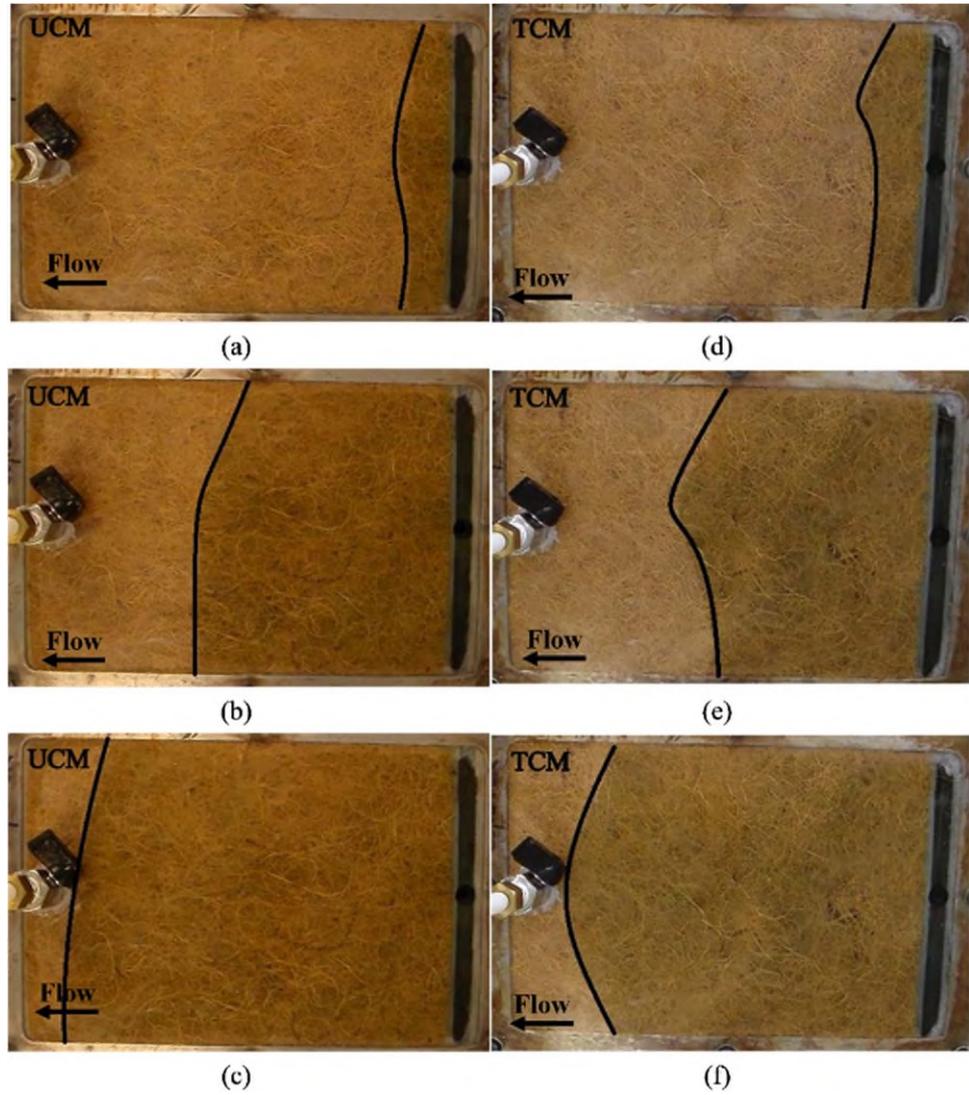


Figure 3. Detail of the flow front behavior for UCM at 1 s (a), 4 s (b) and 10 s (c) and for TCM at 2 s (d), 14 s (e) and 29 s (f).

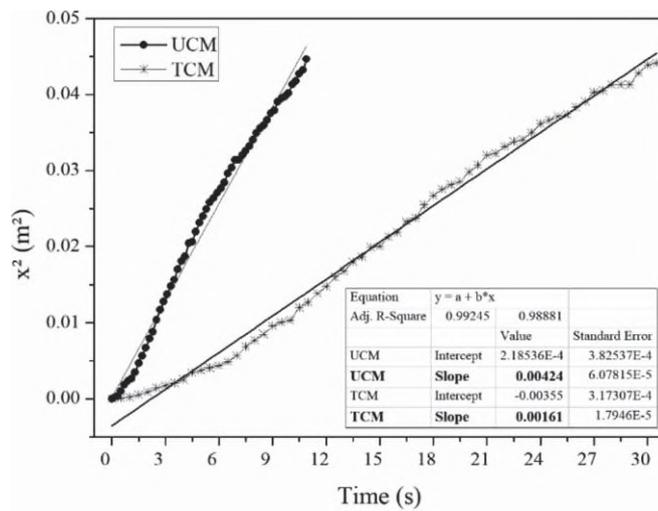


Figure 4. Relationship between the square of flow front position (x^2) and time for UCM and TCM.

Table 2. Values of porosity (ϕ), injection pressure (P_{inj}), injection time (t), slope and permeability for UCM and TCM.

Specimen	UCM	TCM
ϕ (%)	82.6	80.7
P_{inj} (Pa)	1.4×10^5	1.4×10^5
t (s)	10.9	30.5
Slope ($x^2.t-1$)	4.2×10^{-3}	1.6×10^{-3}
DL permeability (m^2)	10.1×10^{-10}	3.7×10^{-10}

Table 3. KC permeability for different fiber volume fraction.

Specimen	ϕ (%)	V_f (%)	KC permeability (m^2)
UCM	82.6	17.4	1.6×10^{-6}
TCM	80.7	19.3	1.3×10^{-6}

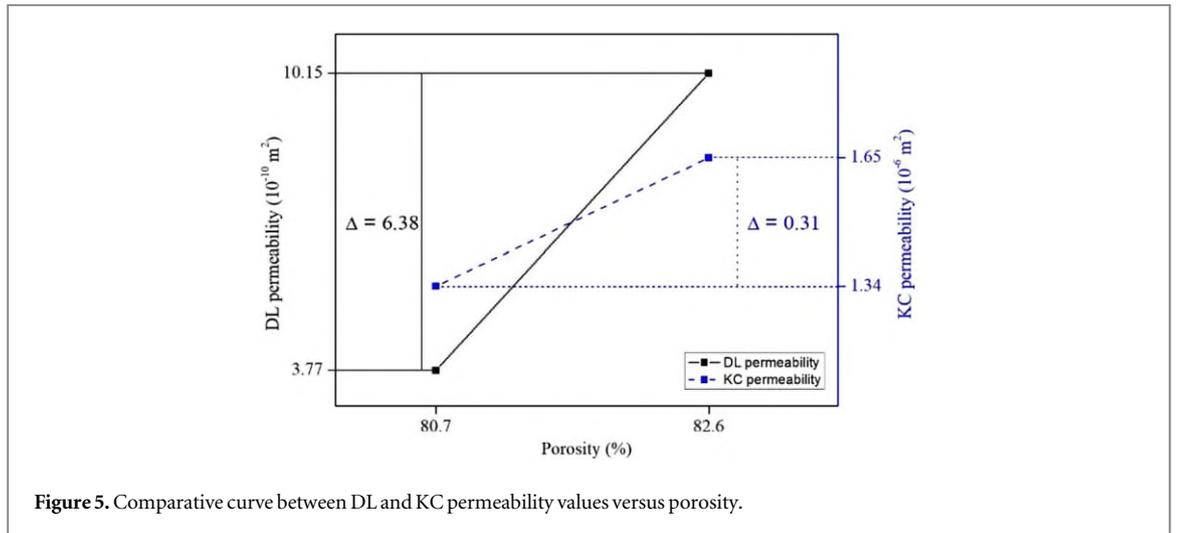


Figure 5. Comparative curve between DL and KC permeability values versus porosity.

and from equation (3), it was possible to predict KC permeability for UCM and TCM, as shown in table 3, considering $C = 2.09 \times 10^{-7} m^2$ and $n = 1.45$ as empirical parameters.

KC permeability takes into account only reinforcement properties, without considering processing parameters, so it is possible to notice the small variation of the fiber volume fraction between UCM and TCM is not the factor that most influences KC permeability value. Therefore, it was plotted a comparative curve between DL and KC permeability values versus porosity in order to understand the porosity influence as observed in figure 5.

It is possible to observe that KC permeability, calculated based only on the fiber porosity, presents $0.31 m^2$ delta. On the other hand, experimental results from DL permeability presents $6.38 m^2$ delta. Considering that processing parameters were kept constants, it is possible to conclude that plasma treatment was the main factor for delta difference and then the decrease in DL permeability, ratifying results found by the difference in contact angle analysis and from SEM analysis by the morphology of fibers caused by the plasma treatment. Therefore, it is possible to infer that great difference between DL permeability and modified KC permeability values are not prevented from the small variation of volume fraction or from the processing parameters, but from the atmospheric plasma treatment influence on fibers surface.

4. Conclusion

Coconut fiber mats were atmospheric plasma treated in order to improve interfacial adhesion between fiber and matrix for natural fiber composite manufacturing. SEM analysis show that atmospheric plasma treatment modifies the morphological properties of coconut fibers due to etching effect resulting in the appearance of recesses, and possibly increasing their roughness. A decrease in contact angle value for TCM with a consequent increase of surface energy also confirmed this effect. These results suggest that changes in coconut fibers surface

could result in enhancing interfacial adhesion, mechanical interlocking and consequently better composite mechanical properties. From permeability studies, it was possible to conclude that the treatment is a suitable technique that allows better process control resulting in a more homogeneous impregnation of the reinforcement by the matrix, besides a more regular and laminar flow front, avoiding entrapped air formation. Darcy's law permeability results presented a decrease for TCM due to an adequate interfacial interaction between reinforcement and impregnation fluid as result of plasma treatment. Considering Kozeny-Carman permeability, it was found that reinforcement porosity do not influences permeability value once UCM and TCM KC permeability are similar.

In addition, this treatment technique presents advantages when compared to the most used chemical treatments, such as alkaline and bleaching, as an environmental friendly alternative considered as a clean, dry and high-efficient method and an environment less aggressive process that allows the surface modification of fibers not using chemical reagents and not generating polluting waste.

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References

- [1] Al-Oqla F M, Sapuan S M, Anwer T, Jawaid M and Hoque M E 2015 Natural fiber reinforced conductive polymer composites as functional materials: a review *Synth. Met.* **206** 42–54
- [2] Lau K T, Hung P Y, Zhu M-H H and Hui D 2018 Properties of natural fibre composites for structural engineering applications *Compos. Part B Eng.* **136** 222–33
- [3] Sanjay M R, Madhu P, Jawaid M, Sentharamkannan P, Senthil S and Pradeep S 2017 Characterization and properties of natural fiber polymer composites: a comprehensive review *J. Clean. Prod.* **172** 566–81
- [4] United Nations 2018 Transforming our world: the 2030 agenda for sustainable development *A/RES/70/1* https://www.un.org/ga/search/view_doc.asp?symbol=A/RES/70/1&Lang=E
- [5] Adhikari R K and Gowda B S K 2017 Exploration of mechanical properties of banana/jute hybrid polyester composite *Mater. Today Proc.* **4** 7171–6
- [6] Dicker M P M, Duckworth P F, Baker A B, Francois G, Hazzard M K and Weaver P M 2014 Green composites: a review of material attributes and complementary applications *Compos. Part A Appl. Sci. Manuf.* **56** 280–9
- [7] Westman M P, Fifield L S, Simmons K L, Laddha S G and Kafentzis T A 2010 *Natural Fiber Composites: A Review PNNL-19220* Pacific Northwest National Laboratory Richland, WA (United States) https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-19220.pdf (<https://doi.org/10.2172/989448>)
- [8] Chen J and Chou N 2016 Compressive behaviour of flax FRP double tube confined coconut fibre reinforced concrete *Constr. Build. Mater.* **112** 666–73
- [9] Scalici T, Fiore V and Valenza A 2016 Effect of plasma treatment on the properties of Arundo Donax L. leaf fibres and its bio-based epoxy composites: a preliminary study *Compos. Part B Eng.* **94** 167–75
- [10] Monte M C, Fuente E, Blanco A and Negro C 2009 Waste management from pulp and paper production in the European Union *Waste Manag.* **29** 293–308
- [11] Väisänen T, Haapala A, Lappalainen R and Tomppo L 2016 Utilization of agricultural and forest industry waste and residues in natural fiber-polymer composites: a review *Waste Manag.* **54** 62–73
- [12] Divyashree A, Shoriya Aruni Bt A M, Yallappa S, Chaitra K, Kathyayini N and Gurumurthy H 2016 Low cost, high performance supercapacitor electrode using coconut wastes: eco-friendly approach *J. Energy Chem.* **25** 880–7
- [13] de Farias J G G, Cavalcante R C, Canabarro B R, Viana H M, Scholz S and Simão R A 2017 Surface lignin removal on coir fibers by plasma treatment for improved adhesion in thermoplastic starch composites *Carbohydr. Polym.* **165** 429–36
- [14] Kocaman S, Karaman M, Gursoy M and Ahmetli G 2017 Chemical and plasma surface modification of lignocellulose coconut waste for the preparation of advanced biobased composite materials *Carbohydr. Polym.* **159** 48–57
- [15] Monteiro S N, Terrones L A H and D'Almeida J R M 2008 Mechanical performance of coir fiber/polyester composites *Polym. Test.* **27** 591–5
- [16] Bodaghi M, Cristóvão C, Gomes R and Correia N C 2016 Experimental characterization of voids in high fibre volume fraction composites processed by high injection pressure RTM *Compos. Part A Appl. Sci. Manuf.* **82** 88–99
- [17] Nguyen V H, Deléglise-Lagardère M and Park C H 2015 Modeling of resin flow in natural fiber reinforcement for liquid composite molding processes *Compos. Sci. Technol.* **113** 38–45
- [18] Francucci G, Rodríguez E S and Vázquez A 2010 Study of saturated and unsaturated permeability in natural fiber fabrics *Compos. Part A Appl. Sci. Manuf.* **41** 16–21
- [19] Rodríguez E, Giacomelli F, Vázquez A and Vazquez A 2004 Permeability-porosity relationship in RTM for different fiberglass and natural reinforcements *J. Compos. Mater.* **38** 259–68

- [20] Rodrigues J, Souza J A and Fujiyama R 2015 Compósitos poliméricos reforçados com fibras naturais da Amazônia fabricados por infusão *Rev. Mater.* **20** 946–60
- [21] Umer R, Bickerton S and Fernyhough A 2011 The effect of yarn length and diameter on permeability and compaction response of flax fibre mats *Compos. Part A Appl. Sci. Manuf.* **42** 723–32
- [22] Li Y, Xie L and Ma H 2015 Permeability and mechanical properties of plant fiber reinforced hybrid composites *Mater. Des.* **86** 313–20
- [23] Asasutjarit C, Charoenvai S, Hirunlabh J and Khedari J 2009 Materials and mechanical properties of pretreated coir-based green composites *Compos. Part B Eng.* **40** 633–7
- [24] Albinante S R, Pacheco É B A V and Visconte L L Y 2013 Revisão dos tratamentos químicos da fibra natural para mistura com poliolefinas *Quim. Nova* **36** 114–22
- [25] Narendar R and Priya Dasan K 2014 Chemical treatments of coir pith: morphology, chemical composition, thermal and water retention behavior *Compos. Part B Eng.* **56** 770–9
- [26] Carvalho K C C, Mulinari D R, Voorwald H J C and Cioffi M O H 2010 Chemical modification effect on the mechanical properties of HIPS/coconut fiber composites *Bio. Resources* **5** 1143–55
- [27] dos Santos J C, Siqueira R L, Vieira L M G, Freire R T S, Mano V and Panzera T H 2018 Effects of sodium carbonate on the performance of epoxy and polyester coir-reinforced composites *Polym. Test.* **67** 533–44
- [28] Brígida A I S, Calado V M A, Gonçalves L R B and Coelho M A Z 2010 Effect of chemical treatments on properties of green coconut fiber *Carbohydr. Polym.* **79** 832–8
- [29] de Carvalho Benini K C C, Brocks T, Montoro S R, Cioffi M O H and Voorwald H J C 2015 Effect of fiber chemical treatment of nonwoven coconut fiber/epoxy composites adhesion obtained by RTM process *Polym. Compos.* **16** 101–13
- [30] D'Agostino R, Favia P, Oehr C and Wertheimer M R 2005 Low-temperature plasma processing of materials: past, present, and future *Plasma Process. Polym.* **2** 7–15
- [31] Björkman M 2012 *Improved Adhesion of Polyolefin Laminates to Textiles Using New Plasma Technology* Chalmers University of Technology Master of Science Thesis <http://publications.lib.chalmers.se/records/fulltext/161579.pdf>
- [32] Li Y, Manolache S, Qiu Y and Sarmadi M 2016 Effect of atmospheric pressure plasma treatment condition on adhesion of ramie fibers to polypropylene for composite *Appl. Surf. Sci.* **364** 294–301
- [33] Liu D, Chen P, Chen M and Liu Z 2012 Surface modification of high performance PBO fibers using radio frequency argon plasma *Surf. Coatings Technol.* **206** 3534–41
- [34] Morent R, De Geyter N, Verschuren J, De Clerck K, Kiekens P and Leys C 2008 Non-thermal plasma treatment of textiles *Surf. Coatings Technol.* **202** 3427–49
- [35] Kale K H and Desai A N 2011 Atmospheric pressure plasma treatment of textiles using non-polymerising gases *Indian J. Fibre Text. Res.* **36** 289–99
- [36] Rombaldoni F, Montarsolo A, Mossotti R, Innocenti R and Mazzuchetti G 2010 Oxygen plasma treatment to reduce the dyeing temperature of wool fabrics *J. Appl. Polym. Sci.* **118** 1173–83
- [37] Carneiro M R D, Thiré R M, da S M and Simão R A 2012 Uso de plasma para aumento da compatibilidade interfacial entre fibras de coco e matrizes poliméricas *Painel PEMM (Rio de Janeiro, RJ, 24, 25, 26 october)* (COPPE UFRJ) 25–26 <http://painelpemm.metalmat.ufrrj.br/trabalhos/2012/SF/SF-IC-7399.pdf>
- [38] Nguyen V H, Lagardère M, Park C H and Panier S 2014 Permeability of natural fiber reinforcement for liquid composite molding processes *J. Mater. Sci.* **49** 6449–58
- [39] Schmidt T M, Goss T M, Amico S C and Lekakou C 2009 Permeability of hybrid reinforcements and mechanical properties of their composites molded by resin transfer molding *J. Reinf. Plast. Compos.* **28** 2839–50
- [40] Costa A 2006 Permeability-porosity relationship: a reexamination of the Kozeny-Carman equation based on a fractal pore-space geometry assumption *Geophys. Res. Lett.* **33** L02318
- [41] Amico S and Lekakou C 2001 An experimental study of the permeability and capillary pressure in resin-transfer moulding *Compos. Sci. Technol.* **61** 1945–59
- [42] Xu P and Yu B 2008 Developing a new form of permeability and Kozeny-Carman constant for homogeneous porous media by means of fractal geometry *Adv. Water Resour.* **31** 74–81
- [43] Muensri P, Kunanopparat T, Menut P and Siriwanayotin S 2011 Effect of lignin removal on the properties of coconut coir fiber/wheat gluten biocomposite *Compos. Part A Appl. Sci. Manuf.* **42** 173–9
- [44] Brahmakumar M, Pavithran C and Pillai R M 2005 Coconut fibre reinforced polyethylene composites: effect of natural waxy surface layer of the fibre on fibre/matrix interfacial bonding and strength of composites *Compos. Sci. Technol.* **65** 563–9
- [45] Calado V, Barreto D W and D'Almeida J R M 2000 The effect of a chemical treatment on the structure and morphology of coir fibers *J. Mater. Sci. Lett.* **19** 2151–3
- [46] Benini K C C 2011 *Desenvolvimento e caracterização de compósitos poliméricos reforçados com fibras lignocelulósicas: HIPS/fibra da casca do coco verde e bagaço de cana de açúcar* Faculdade de Engenharia de Guaratinguetá, Universidade Estadual Paulista - UNESP Dissertação (Mestrado em Engenharia Mecânica - Materiais) https://repositorio.unesp.br/bitstream/handle/11449/99334/benini_kccc_me_guara.pdf?sequence=1&isAllowed=y
- [47] Wang W and Huang G 2009 Characterisation and utilization of natural coconut fibres composites *Mater. Des.* **30** 2741–4
- [48] Praveen K M, Thomas S, Grohens Y, Mozetič M, Junkar I, Primc G and Gorjanc M 2016 Investigations of plasma induced effects on the surface properties of lignocellulosic natural coir fibres *Appl. Surf. Sci.* **368** 146–56
- [49] Karger-Kocsis J, Mahmood H and Pegoretti A 2015 Recent advances in fiber/matrix interphase engineering for polymer composites *Prog. Mater. Sci.* **73** 1–43
- [50] Stepanova V, Slavicek P, Stupavská M, Jurmanová J and Cernak M 2015 Surface chemical changes of atmospheric pressure plasma treated rabbit fibres important for felting process *Appl. Surf. Sci.* **355** 1037–43
- [51] Kafi A A, Hurren C J, Huson M G and Fox B L 2009 Analysis of the effects of atmospheric helium plasma treatment on the surface structure of jute fibres and resulting composite properties *J. Adhes. Sci. Technol.* **23** 2109–20
- [52] Kafi A A, Magniez K and Fox B L 2011 A surface-property relationship of atmospheric plasma treated jute composites *Compos. Sci. Technol.* **71** 1692–8