Cellulose fiber network as reinforcement of thermoplastic paraffin films

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ORIGINAL ARTICLE

Abstract

The incorporation of natural fibers into polymer matrices poses challenges due to physicochemical incompatibility, which is typically addressed through precursor modification or the use of compatibilizers. Here, we introduce a novel type of composite that overcomes this challenge by utilizing a network of fine, porous cellulosic sheets inter-diffused with a commercial paraffin films. This approach physically adheres the fiber network to the matrix, preserving its structure. Microscopy images confirm the formation of the proposed microstructure, and mechanical testing reveals a gradual increase in modulus and strength with the incorporation of cellulose. The maximum incorporation achieved was 7.6% (w/w) of cellulosic fibers, resulting in a 167% increase (1.67 times improved) in composite stiffness. Moreover, these composites exhibit ductility, with an average deformation of $410 \pm 38\%$, corresponding to 20% reduction in relation to pure matrix. Our findings demonstrate the potential of this approach for developing sustainable materials with improved mechanical properties.

Keywords: *natural fibers, composites, network reinforcement, paper, polymer matrices.*

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1. Introduction

Natural fibers have been used as reinforcement in composite materials for over 2000 years[1]. The development of these materials has attracted attention for applications in several segments, mainly in the automotive and packaging industries[2]. In this scenario, cellulose fibers as a reinforcement material have advantages such as lower cost, lower density, abundance, availability and less abrasiveness of the processing equipment when compared to glass fibers[3,4].

Despite the potential of these composites, nonpolar matrices and cellulose fibers (polar) do not have good physical-chemical compatibility[5,6]. Due to this high fiber-matrix incompatibility, most of the works on these theme focuses on fiber modification, matrix functionalization or the addition of compatibilizing agents[7-9]. However, apart from these physical and chemical interactions, other adhesion mechanisms must be taken into account when designing new materials[10]. Thus, configurations that allow, for example, maintaining cellulose fibers in the form of a network mechanically connected to the matrix can be designed.

For reasons intrinsic to the method, the extrusion of polymeric matrices with cellulose (or lignocellulosic fibers) does not allow obtaining composites in which the reinforcement is presented as a fibrous network[11,12]. On a laboratory scale, one of the most used methods is solvent casting[11]. However, the method requires a high amount of solvent and is difficult to apply on an industrial scale[13]. In addition, for non-polar matrices it is necessary to use solvents that are harmful to men and the environment, such as toluene[14].

Another common processing method is compression molding. This stands out for its relatively low cost, simplicity and speed, and it is also very attractive for obtaining composites in the form of films[15]. Furthermore, with this method it is also possible to obtain composites in which the reinforcement is in the form of a fibrous network in the finished part. However, studies that describe the preparation of composite materials using this method reveal that the matrix is adhered to the fibers only on the surface[16,17]. Thus, the matrix does not represent a continuous phase throughout the reinforcement, serving basically as a covering layer.

In sheets of paper, cellulose fibers are connected by hydrogen bonds and form a tangled network of fibers[18]. In general, the fiber network is composed of cellulose fibers randomly distributed containing a set of cavity pore channels with a variety of capillary dimensions[19]. For the proposed application, the sheet of paper formed by the network of cellulosic fibers must be sufficiently thin to allow diffusion of the matrix.

In this work, we proposed the preparation and characterization of polymeric composites reinforced with cellulosic fibers in the form of a network. In this configuration, the polymeric matrix and the cellulose sheets will be arranged in layers so that after processing the matrix will be diffused, entangled and, thus, mechanically adhered to the cellulose

fibers (Figure 1). The aim was to obtain films in which the fiber network will be 'embedded' in the polymeric matrix, without the need for derivatization of the matrix and/or reinforcement and without the addition of compatibilizers.

2. Materials and Methods

2.1 Materials

Commercial bleached eucalyptus Kraft pulp with 60% humidity (supplied by *Suzano S.A.*) and Parafilm® (commercial paraffin films approximately 120 µm thick) produced by *Bemis Company*.

2.2 Production of cellulosic sheets

Since commercial sheets of paper do not have the desired cavity pore channels to allow the matrix diffusion through the cellulosic fibers (toilet paper has grammage of 15 g/m², for instance), we produced our own following the method described by Cordeiro et al.[20].

In brief, the pulp was dispersed in 800 mL of water for 8 minutes using a Turrax Mixer. The resulting dispersion was poured over a specially adapted system consisting of a PVC tube with a nylon fabric attached to one end, positioned on top of a metal sieve, both of which were submerged in water during the process. After the sieve system was suspended to drain the water, it was taken to an oven at 40 °C to dry. The resulting cellulosic sheet was manually removed from the nylon fabric. The process is illustrated in Figure 2.

Different grammages of the cellulosic fibers sheets were produced, including 4 g/m², 6 g/m², and 8 g/m², to test their effectiveness as reinforcement materials in the composites. The produced sheets were porous and lightweight, thus

suitable for our purpose of matrix diffusion through the cellulosic fibers.

2.3 Preparation of composites

Composites were prepared through a continous process using a commercial Lassane laminator model A3-330C. In this method, cellulosic sheets were arranged in an interspersed manner between commercial films of Parafilm®, following the specifications described in Table 1. To ensure smooth surfaces and prevent adhesion to the rollers, the arrangement was placed between two sheets of PET. This set was also placed between two aluminum sheets to facilitate the manipulation (Figure 3). The procedure was performed at a temperature of 160 °C. The sets of sheets and parafilm were passed through the laminator rolls twice (5 seconds each turn).

2.4 Microstructural analysis

Images obtained by optical microscopy with a digital camera attached were used to evaluate the morphology, compaction, distribution and orientation of the fibers in both sheets and composite films.

Micrographs obtained by Scanning Electron Microscopy were used to evaluate the formation of the proposed composite (checking the presence of matrix between the fibers). The samples were fractured in liquid N_2. Then, they were placed in samples holder and submitted to a gold bath. Images of the fragile fracture of these materials were obtained in a ZEISS LEO 440 equipment.

2.5 Tensile properties

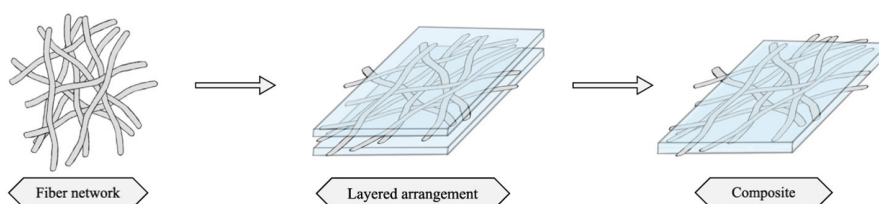Tensile tests were performed in triplicate to obtain information about the limit of tensile strength σ, the stiffness
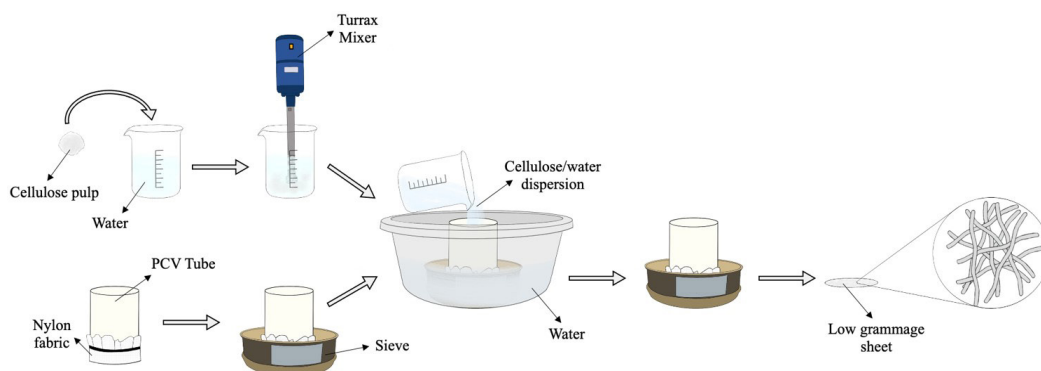

Figure 1. General steps to obtain the composites.

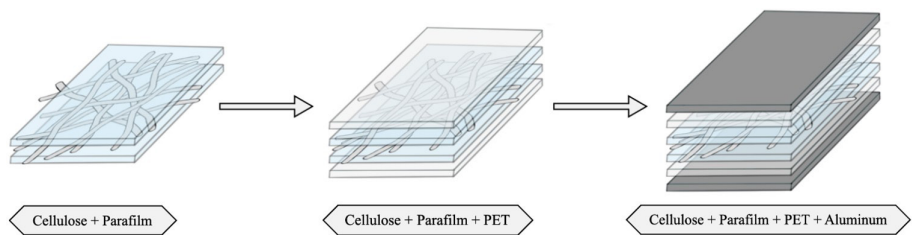**Figure 2.** Scheme for obtaining low weight cellulosic fiber sheets.

Figure 3. Arrangements in composite preparation.

Table 1. Specimen notation for fabricated composites.

Specimen	Description	
2P	Parafilm® films with two layers	
2P-Cel.G4	Two Parafilm® layers with a 4 g/m² grammage cellulosic sheet between them	
2P-Cel.G6	Two Parafilm® layers with a 6 g/m² grammage cellulosic sheet between them	
2P-Cel.G8	Two Parafilm® layers with a 8 g/m² grammage cellulosic sheet between them	
2P-3Cel.G6	Two Parafilm® layers interspersing three 6 g/m² grammage cellulosic sheet	
2P-4Cel.G6	Two Parafilm® layers interspersing four (two in the middle) 6 g/m² grammage cellulosic sheet	

(through the elasticity module, E), and the ductility (through the percentage elongation, ε (%)). The specimens, in the form of films (thicknesses varying between 250 μm and 400 μm), had dimensions of 20 x 50 mm and were analyzed with a useful length of 30 mm. The tensile versus strain tests were performed on an Instron 5969 Universal Material Testing Machine, equipped with a 5kN load cell, at a strain rate of 30 mm min⁻¹.

Table 2. Cellulosic mass concentration and material thickness.

Specimen	% (w/w)	Thickness (mm)
2P	-	0.25
2P-Cel.G4	1.7	0.26
2P-Cel.G6	2.7	0.26
2P-Cel.G8	3.4	0.27
2P-3Cel.G6	7.6	0.27
2P-4Cel.G6	9.9	0.28

3. Results and Discussions

Composites were obtained with different fibers percentages (w/w), varying between 1.1% and 9.9%. The low amount of reinforcement in the films obtained is due to the high mass and thickness of the matrix. The descriptions of the prepared materials and their cellulosic mass concentration and thickness data are shown in Table 1 and Table 2, respectively.

3.1 Optical transparency and homogeneity

Cellulose fibers are naturally opaque, while Parafilm® films are transparent (Figure 4a and 4b). However, by combining these materials in a composite, it is possible to create a transparent and homogeneous product (Figure 4c).

It can be explained by light refraction and scattering. When light passes through the composite, it travels through the transparent matrix before reaching the interface between the Parafilm® and cellulose layers. In this case, the material tends to have low reflection and high transmittance, as the refractive indices of the materials at the interface are similar ($n_{CELLULOSE} = 1.54$; $n_{PARAFILM} \sim n_{POLYETHYLENE} = 1.51$)

When the composite is stretched (Figure 4d), it becomes whitish due to light scattering caused by a Stress Whitening effect[21]. This occurs because the voids formed by detachament of the fibers from the matrix. This new interface (parafilm/void/cellulose) generates significant light scattering and the whitening effect.

3.2 The composite microstructure

The optical microscopy images of the cellulosic sheets reveal a good fiber distribution and random orientation with empty spaces between the fibers, which can facilitate the diffusion of the polymeric matrix (Figures 5a, 5b).

Similarly, the composites prepared using the continuous laminating process show a maintained good fiber distribution with a cellulose network that is not destroyed during the process (Figures 5c, 5d). The stretching of the composite films leads to the orientation of the cellulose fibers in the direction of the applied load (Figures 5e, 5f).

SEM images of the cryogenic fracture confirm the formation of the composite with the planned microstructure. The cellulosic fibers are surrounded by the Parafilm® matrix (Figures 6a, 6b). No large voids are observed amid the fibers, except for cases where fibers are pulled out. Although the fibers are surrounded by matrix, there is a detachment of the fiber from the matrix due to the low interaction between cellulose and Parafilm® (Figure 6b).

In composites where the cellulosic sheets were positioned as the outermost layer, the matrix completely passed through the sheet towards the outside of the composite after processing (Figure 6c). However, there is a limit to the matrix diffusion between the fiber network. The increase in the fiber concentration obstructs the channels through which the matrix would pass, resulting in discontinuities between the fiber and matrix. The use of two cellulosic sheets with $6~g/m^2$ grammage between two Parafilm® layers resulted in composites in which the fibers are not completely enveloped by the polymeric matrix (Figure 6d). Such discontinuities can cause premature material failure.

In addition, the relatively high thickness of Parafilm® films compared to the cellulosic sheets is the reason for the low reinforcement/matrix ratio observed in the SEM images. The use of thinner thermoplastic films would allow for the production of composites with a greater amount of reinforcement.

3.3 Tensile tests

Table 3 summarizes the results for the Elastic Modulus, Tensile Strength, and Elongation at Break of the investigated compounds. Figure 7 shows the stress x strain curves for composites with the same amount of Parafilm® and variable numbers of cellulosic sheets. Compared to the double layer
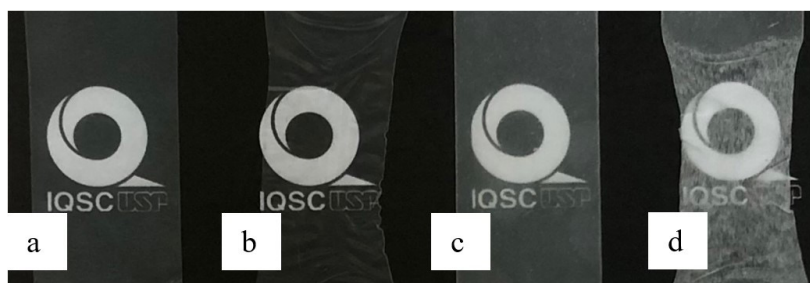

Figure 4. Photos of the materials: (a) and (b) Parafilm® before and after tensile stress, respectively; (c) and (d) 2P-Cel.G6 composites before and after tensile stress, respectively.
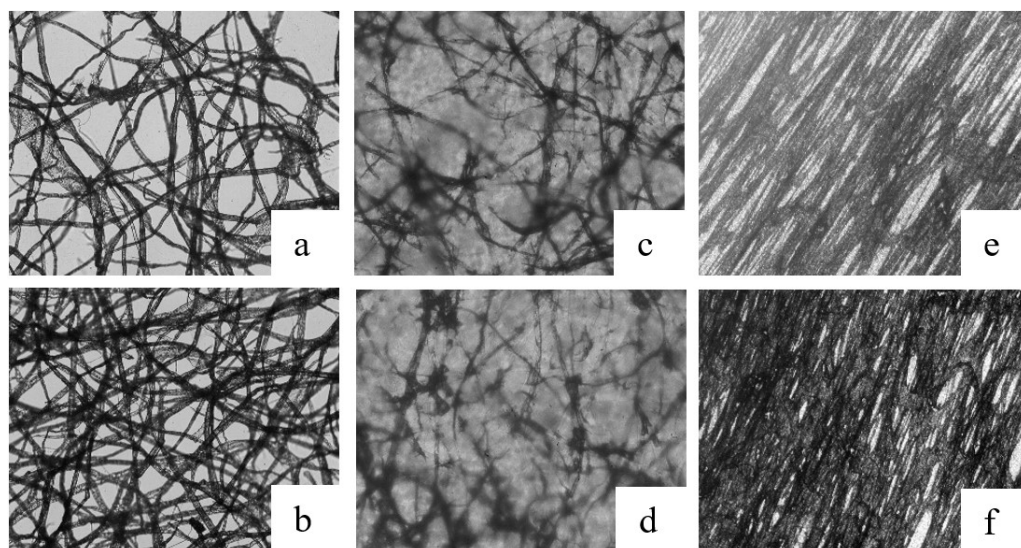

Figure 5. Micrographs at 125x (a, b, c, d) and 32x (e, f) magnification. (a) and (b) $4~g/m^2$ and $8~g/m^2$ grammage cellulosic sheets, respectively; (c) 2P-Cel.G4; (d) 2P-Cel.G8; (e) and (f) composite films with unidirectional applied load.
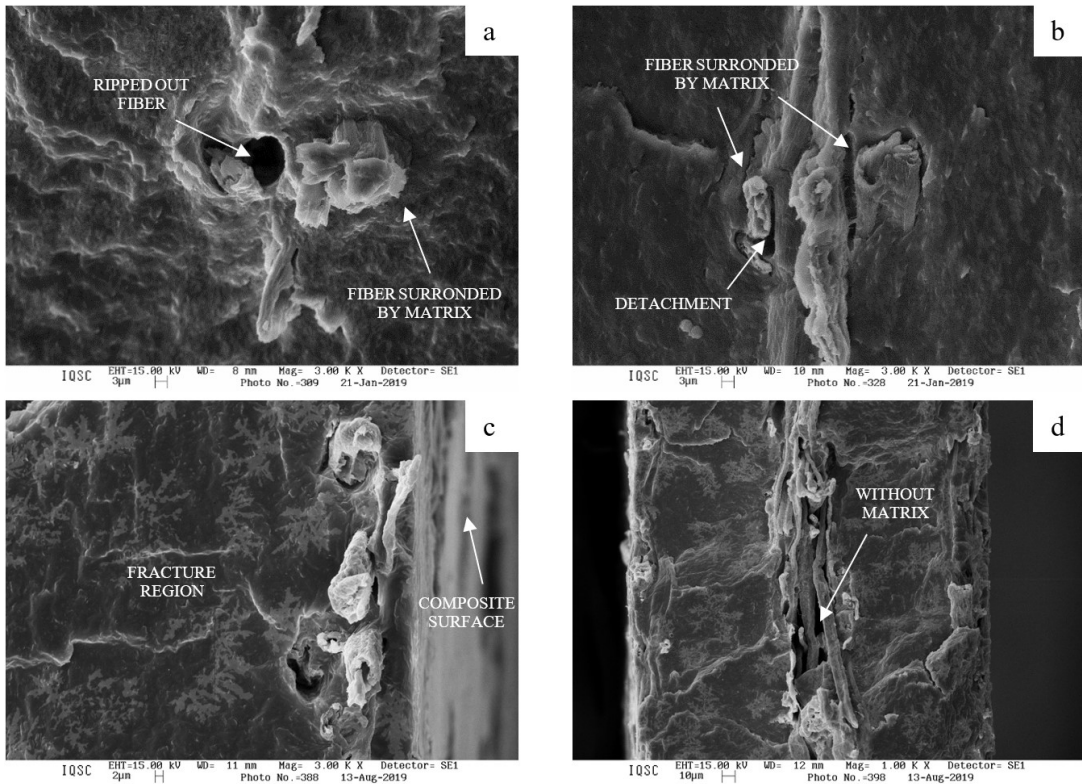
Figure 6. SEM images for: (a) fragile fracture of 2P-Cel.G4; (b) fragile fracture of 2P-Cel.G8; (c) fragile fracture of 2P-3Cel.G6 – limit region of the fracture surface; (d) fragile fracture of 2P-4Cel.G6.
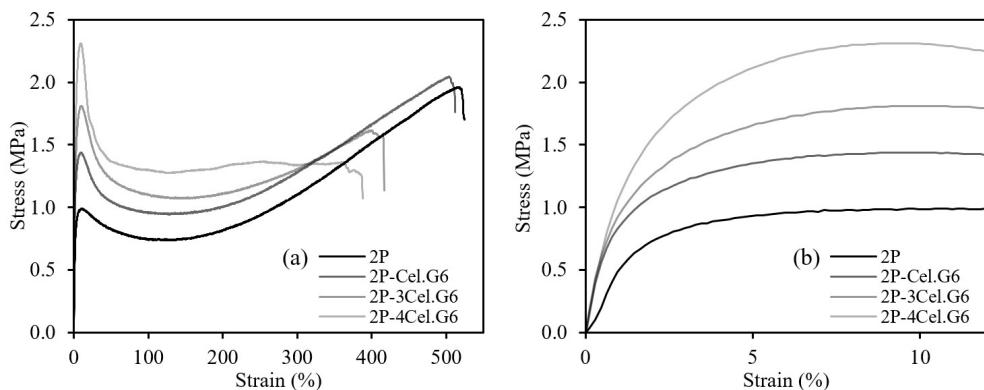

Figure 7. Stress x strain graph for (a) Parafilm® films and composite films containing one, three or four cellulosic sheets of 6 m/g² (average curve); (b) enlargement of a.

of Parafilm®, the incorporation of bleached cellulose fibers resulted in a significant increase in the modulus of elasticity, with a 118.7%, 166.8%, and 291.1% increase observed for 2.7% (w/w), 7.6% (w/w), and 9.9% (w/w) of fibers, respectively. However, the composite obtained with 9.9% (w/w) fibers did not have the desired configuration due to the inability of the plastic film to permeate the cellulosic fibers network.

The incorporation of fibers also resulted in increased mechanical strength at low deformations, with the largest tensile strength observed for the thermoplastic

Table 3. Mechanical properties – Elastic modulus (E); Ultimate tensile strength (σ); elongation at break, ε (%); and its respective standart desviation.

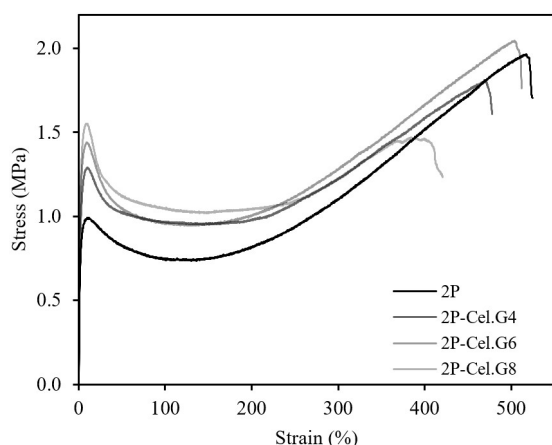| Specimen	E (MPa)	σ (MPa)	ε (%)
2P	24.7 ± 1.2	1.94 ± 0.05	513 ± 14
2P-Cel.G4	54.6 ± 7.8	1.89 ± 0.16	487 ± 61
2P-Cel.G6	56.5 ± 6.2	2.02 ± 0.02	502 ± 10
2P-Cel.G8	65.5 ± 11.7	1.44 ± 0.11	389 ± 46
2P-3Cel.G6	65.9 ± 4.8	1.83 ± 0.06	410 ± 38
2P-4Cel.G6	96.6 ± 9.2	2.27 ± 0.10	362 ± 68

Figure 8. Stress x strain graph for Parafilm® films and composite films containing a cellulosic sheets with 4 m/g^2, 6 m/g^2 or 8 m/g^2.

matrix due to the alignment of polymer chains in greater deformations.

The elongation at break for the composites with 7.6% (w/w) of bleached cellulosic fibers was around 410%, with an approximately 20% reduction in strain compared to 2P. Some specimens showed deformations of up to 452%, indicating that necking of the specimen was propagated by the sample. However, the spread of necking was often halted due to the presence of regions with a high concentration of fibers, which acted as stress concentrators, causing the fracture of the material earlier than expected[22,23].

Figure 8 shows the stress x strain curves for composites with the same amount of Parafilm® (constant) and a single cellulosic sheet but with different variable weights. The insertion of reinforcement caused an increase in the material module. However, when associated the modulus growth with the increase of the sheet grammage, it is noticed that there is not such a significant improvement.

The incorporation of bleached cellulose fibers resulted in an increase in the modulus of elasticity and mechanical strength of the composite. However, higher amounts of fibers led to a reduction in ductility and a lower elongation at break due to the presence of regions with high concentrations of fibers that acted as stress concentrators. Furthermore, the increase in sheet grammage did not result in a significant improvement in the composite's material properties.

4. Conclusions

Composites were obtained laminating thin cellulosic sheets with low grammage (4 g/m^2, 6 g/m^2 and 8 g/m^2) and commercial Parafilm® films. In these composites, no chemical modification of the constituents was carried out and no additives were used. Characteristics of the composites microstructure include: (1) cellulosic fibers network with a set of cavity pore channels; (2) fill and permeation of the spaces amid the cellulosic fibers by the matrix; (3) good matrix distribution throughout the cellulosic sheet.

Regarding the amount of reinforcement, the increase in the number of cellulosic sheets layers leads to a gradual increase in module and mechanical resistance (at low and medium deformations). However, the grammage of the sheets (between 4 g/m^2 and 8 g/m^2) did not have as much influence on the property of these composites. Properties of composites containing 7.6% (w/w) cellulosic fibers include greater tensile strength than Parafilm® in low and medium strain (less than 300%), greater rigidity than Parafilm® (increase in modulus up to 167%) and high deformations (average of 410%).

These results suggest that careful optimization of the amount and distribution of cellulosic fibers in the composite matrix is crucial for obtaining the desired mechanical properties.

5. Author's Contribution

- **Conceptualization** – Matheus Fernandes Flores; Luciano Cordeiro; Antonio Aprigio da Silva Curvelo.
- **Data curation** – Matheus Fernandes Flores.
- **Formal analysis** – Matheus Fernandes Flores; Luciano Cordeiro.
- **Funding acquisition** – Antonio Aprigio da Silva Curvelo.
- **Investigation** – Matheus Fernandes Flores; Luciano Cordeiro.
- **Methodology** – Matheus Fernandes Flores; Luciano Cordeiro; Antonio Aprigio da Silva Curvelo.
- **Project administration** – Matheus Fernandes Flores; Luciano Cordeiro; Antonio Aprigio da Silva Curvelo.
- **Resources** – Matheus Fernandes Flores; Luciano Cordeiro; Antonio Aprigio da Silva Curvelo.
- **Software** – NA.
- **Supervision** – Antonio Aprigio da Silva Curvelo.
- **Validation** – Matheus Fernandes Flores.
- **Visualization** – Matheus Fernandes Flores.
- **Writing – original draft** – Matheus Fernandes Flores.
- **Writing – review & editing** –Antonio Aprigio da Silva Curvelo.

6. Acknowledgements

7. References

1. Kumar, K. P., & Sekaran, A. S. J. (2014). Some natural fibers used in polymer composites and their extraction processes: a review. *Journal of Reinforced Plastics and Composites*, *33*(20), 1879-1892. http://dx.doi.org/10.1177/0731684414548612.

2. Kalia, S., Kaith, B. S., & Kaur, I. (2009). Pretreatments of natural fibers and their application as reinforcing material in polymer composites - a review. *Polymer Engineering and Science*, *49*(7), 1253-1272. http://dx.doi.org/10.1002/pen.21328.

3. Kalia, S., Kaith, B. S., & Kaur, I. (Eds.) (2011). *Cellulose fibers: bio-and nano-polymer composites: green chemistry and technology*. Germany: Springer-Verlag Berlin Heidelberg. http://dx.doi.org/10.1007/978-3-642-17370-7.

4. Joshi, S. V., Drzal, L. T., Mohanty, A. K., & Arora, S. (2004). Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites. Part A, Applied Science and Manufacturing*, *35*(3), 371-376. http://dx.doi.org/10.1016/j.compositesa.2003.09.016.

5. Arrakhiz, F. Z., Malha, M., Bouhfid, R., Benmoussa, K., & Qaiss, A. (2013). Tensile, flexural and torsional properties of chemically treated alfa, coir and bagasse reinforced polypropylene. *Composites. Part B, Engineering*, *47*, 35-41. http://dx.doi.org/10.1016/j.compositesb.2012.10.046.

6. Portella, E. H., Romanzini, D., Angrizani, C. C., Amico, S. C., & Zattera, A. J. (2016). Influence of stacking sequence on the mechanical and dynamic mechanical properties of cotton/glass fiber reinforced polyester composites. *Materials Research*, *19*(3), 542-547. http://dx.doi.org/10.1590/1980-5373-MR-2016-0058.

7. Pracella, M., Haque, M.-U., & Alvarez, V. (2010). Functionalization, compatibilization and properties of polyolefin composites with natural fibers. *Polymers*, *2*(4), 554-574. http://dx.doi.org/10.3390/polym2040554.

8. Cipriano, J. P., Zanini, N. C., Dantas, I. R., & Mulinari, D. R. (2019). Mechanical properties of polypropylene composites reinforced with Macadamia Nutshell Fibers. *Journal of Renewable Materials*, *7*(10), 1047-1053. http://dx.doi.org/10.32604/jrm.2019.00001.

9. Lima, L. P. F. C., Santana, R. M. C., & Rodríguez, C. D. C. (2020). Influence of Coupling Agent in Mechanical, Physical and Thermal Properties of Polypropylene/Bamboo Fiber Composites: Under Natural Outdoor Aging. *Polymers*, *12*(4), 929. http://dx.doi.org/10.3390/polym12040929. PMid:32316512.

10. Kinloch, A. J. (2012). *Adhesion and adhesives: science and technology*. UK: Springer Science & Business Media.

11. Oksman, K., Aitomäki, Y., Mathew, A. P., Siqueira, G., Zhou, Q., Butylina, S., Tanpichai, S., Zhou, X., & Hooshmand, S. (2016). Review of the recent developments in cellulose nanocomposite processing. *Composites. Part A, Applied Science and Manufacturing*, *83*, 2-18. http://dx.doi.org/10.1016/j.compositesa.2015.10.041.

12. Oksman, K., Mathew, A. P., & Sain, M. (2009). Novel bionanocomposites: processing, properties and potential applications. *Plastics, Rubber and Composites*, *38*(9-10), 396-405. http://dx.doi.org/10.1179/146580109X12540995045723.

13. Kong, I., Tshai, K. Y., & Hoque, M. E. (2015). *Manufacturing of natural fibre-reinforced polymer composites by solvent casting method.* In M. S. Salit, M. Jawaid, N. K., Yusoff, & M. E., Hoque (Eds.), *Manufacturing of natural fibre reinforced polymer composites* (pp. 331-349). Switzerland: Springer International Publishing. http://dx.doi.org/10.1007/978-3-319-07944-8_16.

14. Ljungberg, N., Cavaillé, J.-Y., & Heux, L. (2006). Nanocomposites of isotactic polypropylene reinforced with rod-like cellulose whiskers. *Polymer*, *47*(18), 6285-6292. http://dx.doi.org/10.1016/j.polymer.2006.07.013.

15. Shamsuri, A. A. (2015). Compression moulding technique for manufacturing biocomposite products. *International Journal of Applied Science and Technology*, *5*(3), 23-26. Retrieved in 2023, April 17, from https://www.ijastnet.com/journals/Vol_5_No_3_June_2015/3.pdf

16. Zampaloni, M., Pourboghrat, F., Yankovich, S. A., Rodgers, B. N., Moore, J., Drzal, L. T., Mohanty, A. K., & Misra, M. (2007). Kenaf natural fiber reinforced polypropylene composites: A discussion on manufacturing problems and solutions. *Composites. Part A, Applied Science and Manufacturing*, *38*(6), 1569-1580. http://dx.doi.org/10.1016/j.compositesa.2007.01.001.

17. Wu, Y., Xia, C., Cai, L., Shi, S. Q., & Cheng, J. (2018). Water-resistant hemp fiber-reinforced composites: in-situ surface protection by polyethylene film. *Industrial Crops and Products*, *112*, 210-216. http://dx.doi.org/10.1016/j.indcrop.2017.12.014.

18. Fengel, D., & Wegener, G. (Eds.) (2011). *Wood: chemistry, ultrastructure, reactions*. Germany: Walter de Gruyter.

19. Sahin, H. T., & Arslan, M. B. (2008). A study on physical and chemical properties of cellulose paper immersed in various solvent mixtures. *International Journal of Molecular Sciences*, *9*(1), 78-88. http://dx.doi.org/10.3390/ijms9010078. PMid:19325721.

20. Cordeiro, L., Prado, A. P. G. A., & Curvelo, A. A. S. (2022). Ductile composite films of polyethylene and low grammage paper. *Industrial Crops and Products*, *184*, 115039. http://dx.doi.org/10.1016/j.indcrop.2022.115039.

21. Singleton, A. C. N., Baillie, C. A., Beaumont, P. W. R., & Peijs, T. (2003). On the mechanical properties, deformation and fracture of a natural fibre/recycled polyemer composites. *Composites. Part B, Engineering*, *34*(6), 519-526. http://dx.doi.org/10.1016/S1359-8368(03)00042-8.

22. Fotouh, A., Wolodko, J. D., & Lipsett, M. G. (2014). Fatigue of natural fiber thermoplastic composites. *Composites. Part B, Engineering*, *62*, 175-182. http://dx.doi.org/10.1016/j.compositesb.2014.02.023.

23. Beaumont, P. W. R. (2003). *Fatigue*. In B. Harris (Ed.), *Composites: science and technology of the fatigue response of fiber-reinforced plastics* (pp. 365-412). UK: Woodhead Publishing.