

Enhancing The Properties of Cellulose-Based Polymers for Potential Use In Membrane Applications: A Literature Review

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Abstract: There is increasing attention towards materials that are environmental-friendly, low-cost, and accessible. Natural polymers such as cellulose are used as substitutes for petroleum-based polymers. Cellulose is the main constituent of all-natural fibers and is porous, inexpensive, and hydrophilic. Cellulose is also suitable for converting petroleum-based polymers into more eco-friendly materials. Several fields, such as aerospace, the automotive industry, and the military, have taken advantage of cellulose-based materials. One field where cellulose-based materials have proved their value is water treatment. Two approaches to boosting the cellulose's potential use in membrane applications for water treatment are the synthesis of cellulose-based composites and graft copolymerization of cellulose. Both approaches have successfully

enhanced cellulose's mechanical properties. This paper mayor contributions are a) The calculation of mechanical properties from the graphs to be used as a source of information for simulations. b) The summary of the methods and tests results to decide what sources of cellulose are available to emulate the trials and enhance polymers properties for different applications such as membranes for water.

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I. INTRODUCTION

Water scarcity will affect half of the world's population by 2025 [1]. Every year, the scientific community conducts vast amounts of research to find robust and affordable water treatment methods. Therefore, membrane technology emerged to be at the forefront of water treatment processes [2]. On average, 54% of the available water treatment processes use membrane technology. Polymeric membranes proved to be effective in the elimination of both organic and inorganic bodies present in the water. They have a lower cost and more ductility than the ceramic ones. Some constraints of polymeric membranes are high hydrophobicity, low mechanical strength, and biofouling [3]. Attempts to improve the suitability of polymeric membranes include the use of bio-based polymers [4]. Over the last decade, the interest in the use of natural polymers in membrane technology increased. Natural polymers are safe for the environment and human health, are inexpensive, and easy to access [3].

Cellulose seems to be the perfect material for membrane applications due to its availability, porosity, and hydrophilic characteristics [3]. Two approaches pursued to accomplish the improvement of cellulose's properties are the synthesis of cellulose-based composites and graft copolymerization of cellulose. Thakur et al. performed an extensive amount of

research on both procedures, using pine needles, *Hibiscus sabdariffa*, *Grewia optiva*, *Saccharum ciliare*, among other sources [5]–[20]. The studies performed to assess the new materials were mechanical testing, thermal analysis, microscopy and spectroscopy characterization, chemical resistance behavior, swelling, moisture, and water uptake [5]–[20]. This communication presents a brief review of the synthesis methods, testing, and results from the two approaches.

II. MATERIALS AND METHODS

This communication is a scoping literature review focused on the work performed by Thakur et al. to obtain eco-friendly polymers suitable for membranes used in water treatment processes. The first step was to generate the information, for which the articles that deal with the improvement of the properties of cellulose through the synthesis of copolymers and bio-composites were searched and reviewed.

III. SUMMARY OF THE REVIEW

A. Background.

Cellulose-based composites

Cellulose-based composites are made by embedding cellulose reinforcements in a polymeric matrix. Methods to synthesize resorcinol-formaldehyde (RF) [5]–[8], phenol-formaldehyde (PF) [9], [10], and urea-formaldehyde (UF) polymeric matrices were developed and optimized by Thakur and Singha [11]. Cellulose reinforcement is used as either fibers or particles [5]–[11], [19], [20].

The standardized methods used to synthesize RF, PF, and UF polymer matrices consist of two steps. First, the reaction between the matrix's components is carried out. Next, a polymeric structure is formed through a condensation reaction. The optimum ratio between reagents was determined through the assessment of the mechanical, physical-chemical, and thermal properties [5], [9], [11].

After the matrices are synthesized, four different reinforcement-matrix mixes are prepared using a mechanical stirrer (10%, 20%, 30% and, 40% weight percent of fiber loading). Composite sheets (150 mm X 150 mm X 50 mm) are formed using the compression molding technique, where a hot press at 50 °C conveys a pressure of 3 – 4 Mpa for 30 minutes. Finally, all the sheets are post-cured in an oven at 150 °C for 12 hours [6].

Graft Copolymerization

Graft copolymerization is one of the best techniques to impart desirable attributes to cellulose without destroying its inherent properties. An initiator is used to create free radical sites on the surface of cellulose. Different monomers are grafted onto cellulose backbones [13], [15]–[18]. A purification treatment is carried out on the cellulose fibers before the graft copolymerization synthesis. Mercerization is always the first step in the chemical treatment of the fiber [11]. Once fibers are purified, 0.5 g of fibers are soaked in different amounts of distilled water for 24 hours. After continuous stirring for 5-10 minutes, the initiator and the monomer are introduced into the reaction flask and put in the microwave oven. Once the reaction is completed, the sample is filtered, washed with distilled water, and air-dried. The copolymer and the homopolymer are separated with Soxhlet extraction. Finally, the copolymer is dried [13]. This communication shows the results for Methyl Acrylate graft onto cellulose.

B. Materials Characterization

Mechanical Testing: The following table summarizes the mechanical testing methods using information from [5], [9], [16]

Table 1
Summary of Mechanical Testing Methods.

TEST	METHOD USED
TENSILE STRESS-STRAIN	ASTM D 3039
COMPRESSIVE STRESS-STRAIN	ASTM D 3410
3-POINT BEND FLEXURAL	ASTM D 790
WEAR	ASTM D 3702

Thermal Analysis: The differential thermal analysis (DTA) is a technique where a sample and a reference are heated identically. The temperature difference between a reference and a sample is analyzed. [5], [9], [16].

Thermal gravimetric analysis (TGA) is used to characterize the thermal stability and decomposition of materials in terms of weight loss percentage as a function of temperature. A thermal analyzer (Perkin Elmer) is used to conduct the TGA, and the DTA analysis of the samples at a heating rate of 10°C/min carried out in a nitrogen atmosphere [5], [9], [16].

Scanning Electron Microscopy (SEM): The analysis was performed using a LEO 435 VP scanning electron microscope [5], [9], [16].

Swelling Behavior: The cellulose-based composites and the graft copolymers swell in contact with different solvents. The composites were in contact with water (H_2O), methanol (CH_3OH), isobutyl alcohol (C_4H_9OH), and carbon tetrachloride (CCl_4). The graft copolymers were in contact with dimethyl formamide (DMF), water, methanol, and

isobutyl alcohol. This communication focused on the comparison between the same solvents.

The following formula allows to calculate the solubility percentage in different solvents, as seen in (1).

$$Ps = \frac{W_f - W_i}{W_i} * 100 \quad (1)$$

Where, W_f is the final weight, and W_i is the initial weight.

Moisture Absorbance: The moisture absorbance behavior study is performed in a humidity chamber. The following formula provides moisture absorbance behavior as seen in (2)

$$\%Moisture\ Absorbance = \frac{W_f - W_i}{W_i} * 100 \quad (2)$$

Where, W_f is the final weight, and W_i is the initial weight.

Chemical Resistance Behavior: The samples are placed in fixed volumes of 1N HCl (acid environment), and 1N NaOH (basic environment). The following formula provides the percentage of chemical resistance as seen in (3)

$$Percent\ of\ Chemical\ Resistance = \frac{T_w - W_{aci}}{T_w} * 100 \quad (3)$$

Where T_w is the known initial weight of the sample, and W_{aci} is the weight of the samples after certain intervals of time.

Further analysis of graft copolymers included grafting percentage, which is used to optimize the solvent amount, monomer amount, initiator ratio, temperature, and time of reaction was performed [13], [18].

C. Discussion of the Results

Mechanical Testing:

Cellulose-based composites. The composites' tensile, compressive, and flexural strength increased proportionally, with the fiber content reaching a maximum value when the fiber loading equals 30% of the weight of the composite. The rise in mechanical strength, according to the fiber content follows the trend: 30% > 40% > 20% > 10%.

The interfacial bonding strength between the matrix and the fiber explains this behavior. The interface transfers the load successfully from the matrix to the reinforcement depending on the fiber's wetting level from the matrix. For these cellulose bio-composites, the optimum wetting happens at 30% weight of cellulose reinforcement. The following tables, summarize information as presented in in [5, Tabs. 1, 2 and 3], [9, Tabs. 1,2 and 3], [19, Tabs. 2,3 and 4] compile mechanical testings' results from Bio-composites with 30% weight of 200 μ m pine needle particle reinforcement in different matrices.

The mechanical properties of the bio-composites are enhanced when using cellulose-based graft copolymers as reinforcement, in comparison to raw cellulose reinforcement.

Table 2.
Parameters obtained from the tensile stress-strain curve at 30% weight of 200 μm pine needle particles loading in different matrices.

MATRIX USED	ULTIMATE TENSILE STRESS N/MM ²	YIELD STRENGTH N/MM ²	FRACTURE STRESS N/MM ²	TENSILE MODULUS N/MM ²
PF	32.38	25.16	29.3	712.55
UF	6.94	5.9	6.49	207.95
RF	16.5	13.37	14.87	467.57

Table 3.
Parameters obtained from the compressive stress-strain curve at 30% weight of 200 μm pine needle particles loading in different matrices.

MATRIX USED	ULTIMATE COMPRESSION STRESS N/MM ²	YIELD STRENGTH N/MM ²	FRACTURE STRESS N/MM ²	TENSILE MODULUS N/MM ²
PF	101.74	89.38	96.57	2417.38
UF	54.06	46.95	51.07	901
RF	90.44	76.4	83.1	2370

Table 4.
Parameters obtained from the flexural stress-strain curve at 30% weight of 200 μm pine needle particles loading in different matrices.

MATRIX USED	ULTIMATE FLEXURAL STRESS N/MM ²	YIELD STRENGTH N/MM ²	FRACTURE STRESS N/MM ²	TENSILE MODULUS N/MM ²
PF	386.1	375.2	381.36	13079.27
UF	37.5	25.98	34.36	3125
RF	35.1	23.09	32.27	2925

Table 5.
Comparison between Raw *Grewia optiva* reinforced, and *Grewia optiva* graft copolymer reinforced Bio-composites. 30% weight of reinforcement.

MATRIX	REINFORCEMENT SOURCE	REINFORCEMENT SIZE	ULTIMATE TENSILE STRESS N/MM ²	ULTIMATE COMPRESSIVE STRESS N/MM ²
PF	Raw <i>Grewia optiva</i>	200 μm particles P-Rnf	9	58
		3 mm (short-fiber) SF-Rnf	7.5	55
		6 mm (long-fiber) LF-Rnf	9	50
PF	<i>Grewia optiva</i> -g-poly (MA) (Methyl Acrylate graft onto <i>Grewia optiva</i>)	200 μm particles P-Rnf	33.6	90
		3 mm (short-fiber) SF-Rnf	31.6	80
		6 mm (long-fiber) LF-Rnf	29.6	70

Figure 1 shows the load elongation, deformation, deflection, and wear resistance curves of *Grewia optiva*-g-poly (MA) biofibers/bio-composites with particle, short and long fiber reinforcement.

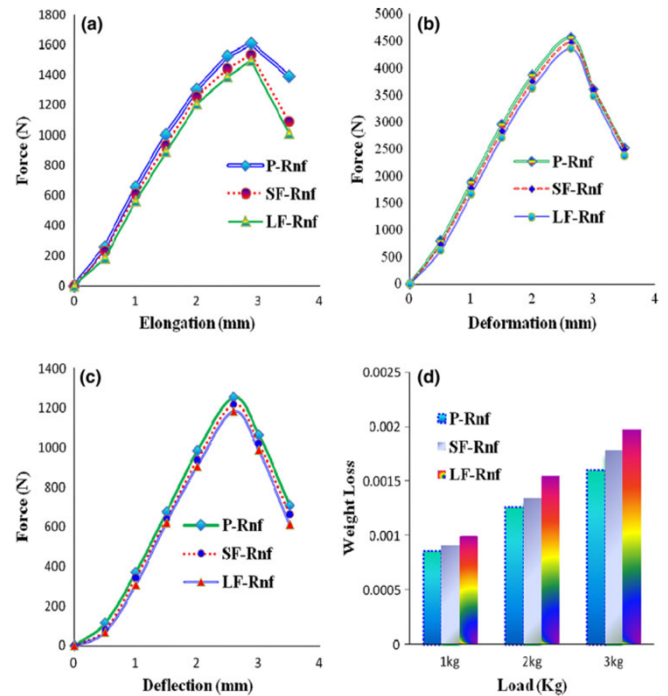


Fig. 1. Load elongation/ deformation/deflection and wear resistance curves of *Grewia optiva*-g-poly (MA) biofibers/bio-composites with particle, short and long fiber reinforcement (a, b, c, d) [16].

Figure 2-4 show the load elongation, deformation, and wear resistance curves for *Grewia optiva* fiber reinforced polymer composites with particle, short fiber, and long fiber.

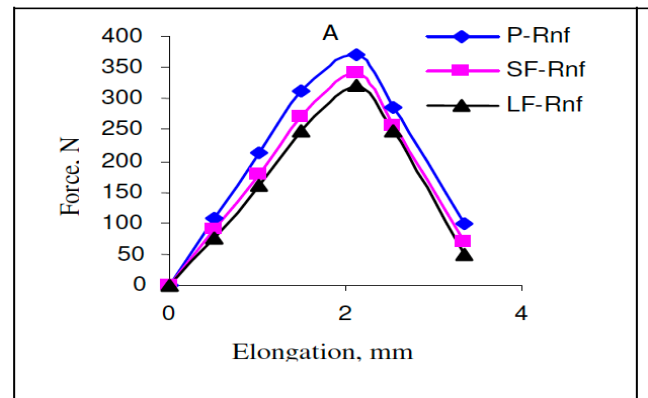


Fig. 2. Tensile Curve of *Grewia optiva* fiber reinforced polymer composites with particle, short fiber, and long fiber [20].

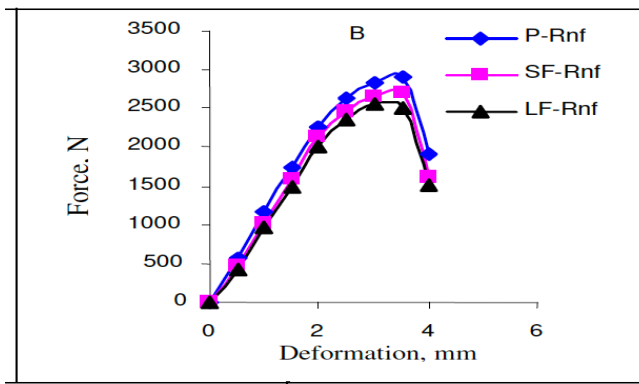


Fig. 3. Compressive Curve of *Grewia optiva* fiber reinforced polymer composites with particle, short fiber, and long fiber [20].

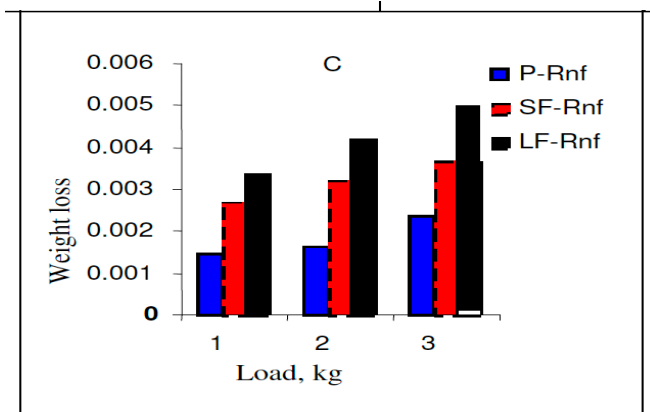


Fig. 4. Wear Resistance Curve of *Grewia optiva* fiber reinforced polymer composites with particle, short fiber, and long fiber [20].

Thermal Analysis: The results from the TGA Analysis shows that the degradation process of the cellulose fiber is improved by both the synthesis of cellulose-based bio-composites as presented in [9, Tab. 4], and the graft copolymerization of cellulose [13, Tab. 1]. The following table summarizes the results.

Table 6.

TGA Results: Improvement of raw cellulose Initial Decomposition Temperature and Final Decomposition Temperature.

MATERIAL	IDT (°C)	%WEIGHT LOSS	FDT (°C)	%WEIGHT LOSS	FINAL RESIDUE %
CELLULOSIC PINE NEEDLES	214	20.5	503	81	19
GRAFTED CELLULOSIC PINE NEEDLES	221	22.25	511	77	33
30% WEIGHT PINE NEEDLE PARTICLE REINFORCED PF MATRIX	332	25.57	983	56.25	43.74

Scanning Electron Microscopy Characterization:

The SEM analysis of the composites shows suitable mixing of the reinforcement and the matrices, as illustrated in Fig. 5.

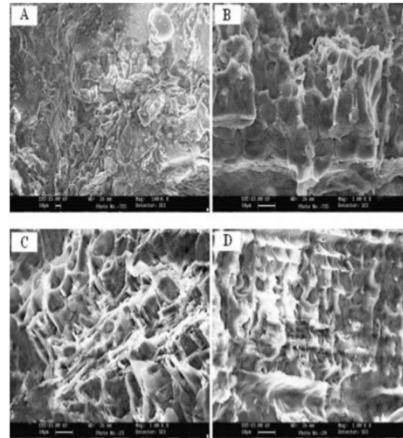


Fig. 5. Scanning electron micrographs of bio composites with (A) 10%, (B) 20%, (C) 30%, and (D) 40% loading. [10]

The SEM analysis of raw cellulose and cellulose-based graft copolymers provides evidence for the change in surface morphology of the bio-fibers surface on grafting, showing suitable grafting as illustrated in Fig. 6

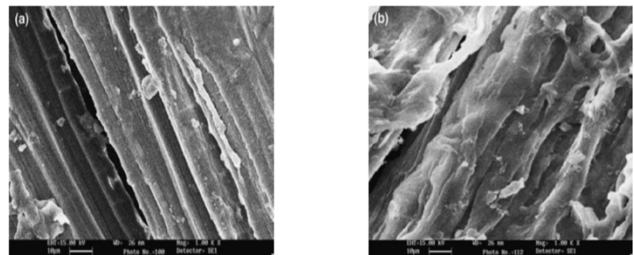


Fig. 6. Scanning electron micrographs of a *Grewia optiva* biofibers, b *Grewia optiva*-g-poly (MA) biofibers [16].

Swelling Behavior

The swelling behavior in different solvents varies depending on the percentage of cellulose in both the cellulose-based composites [6] and the graft copolymers [13].

For the cellulose-based composites, the trend found by Thakur et al. is $H_2O > CH_3OH > C_4H_9OH > CCl_4$. The swelling Behavior of the composites is related to the loading percentage. As expected, the higher the loading percentage the higher the swelling behavior of solvents that contain an OH groups, as illustrated in Fig. 7.

IV EXAMPLES OF APPLICATIONS

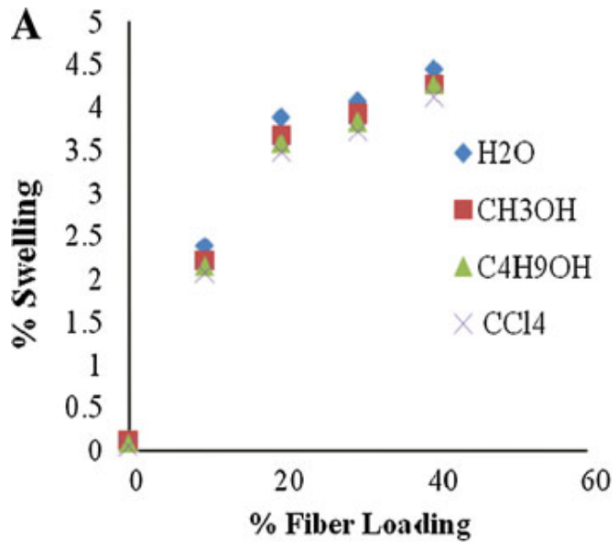


Fig. 7. Swelling Behavior of cellulose-based composites as a function of % of Fiber Loading [6].

The cellulose-based composites exhibit a similar trend $H_2O > CH_3OH > C_4H_9OH$ and the swelling behavior depends on the grafting percentage, as illustrated in Fig. 8

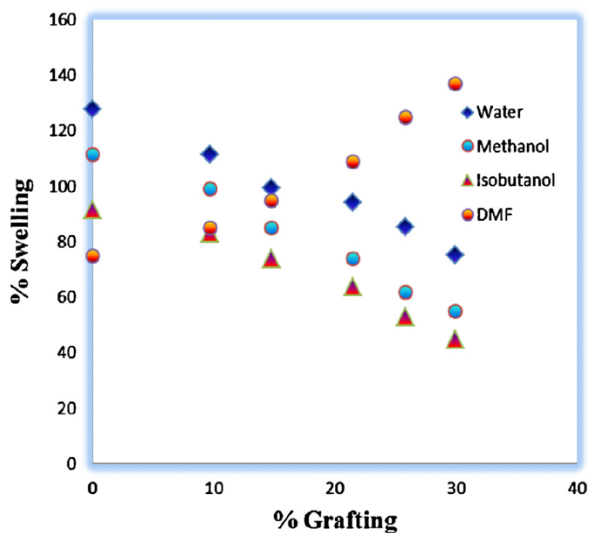


Fig. 8. Swelling Behavior of cellulose-based copolymers as a function of grafting percentage [2].

Moisture Absorbance

The hydrophilicity of the cellulose causes the increase in the moisture absorbance when raising the cellulose percentage of both the composites [6] and the graft copolymers [13].

Chemical Resistance

Cellulose is vulnerable to chemical attack. Therefore, the chemical resistance decreases when increasing the fiber percentage for the composites [6] and increases when raising the grafting percentage for the copolymers [13].

In the reviewed papers, the authors synthesized composites with different matrices and reinforcements combinations and Methyl Acrylate graft onto various cellulose sources. Therefore, it was necessary to choose a common material to compare the mechanical properties improvement with both enhancing techniques.

The material chosen to compare the different enhancing techniques was bio-composites with a 30% loading of 200 micrometers particles.

Table 7, 8, and 9 summarizes the mechanical properties of an PF (Phenol-Formaldehyde) matrix loaded with cellulose particles (pine needle & *Grewia optiva*) and cellulose-based copolymers (Methyl Acrylate graft onto *Grewia optiva*) respectively.

Table 7.
Summary: Biocomposite with PF Matrix and 30% loading of 200 micrometers Pine Needle particles.

PROPERTY	Value	Source
ELASTIC MODULUS (N/M ²)	7.1255E+08	Table 2
TENSILE STRENGTH (N/M ²)	3.2380E+07	Table 2
COMPRESSIVE STRENGTH (N/M ²)	1.1017E+08	Table 3
YIELD STRENGTH (N/M ²)	2.5160E+07	Table 2

Table 8.
Summary: Biocomposite with PF Matrix and 30% loading of 200 micrometers *Grewia optiva* particles.

PROPERTY	Value	Source
ELASTIC MODULUS (N/M ²)	3.20E+08	Table 5, and Figure 2
TENSILE STRENGTH (N/M ²)	9.00E+06	Table 5, and Figure 2
COMPRESSIVE STRENGTH (N/M ²)	5.80E+07	Table 5, and Figure 3
YIELD STRENGTH (N/M ²)	6.50E+06	Table 5, and Figure 2

Table 9.
Summary: Bio-composite with PF Matrix and 30% loading of 200 micrometers particles of *Grewia optiva*-g-poly (MA) (Methyl Acrylate graft onto *Grewia optiva*).

PROPERTY	Value	Source
ELASTIC MODULUS (N/M ²)	3.20E+08	Table 5, and Figure 1
TENSILE STRENGTH (N/M ²)	9.00E+06	Table 5, and Figure 1

COMPRESSIVE STRENGTH (N/M ²)	5.80E+07	Table 5, and Figure 1
YIELD STRENGTH (N/M ²)	6.50E+06	Table 5, and Figure 1

Ordoñez et al. proved efficacy of Solidworks to validate models and predictions of a system [21]. Based on the methodology presented by Ordoñez et al., and the summarized information in the tables shown in this communication, different simulations were performed in Solidworks. Using fluid simulations, it is possible to obtain the pressures and fluid behavior over different materials, as shown in Fig.9 and Fig. 10. Also stress test can be done using the mechanical properties of the bio-composite material.

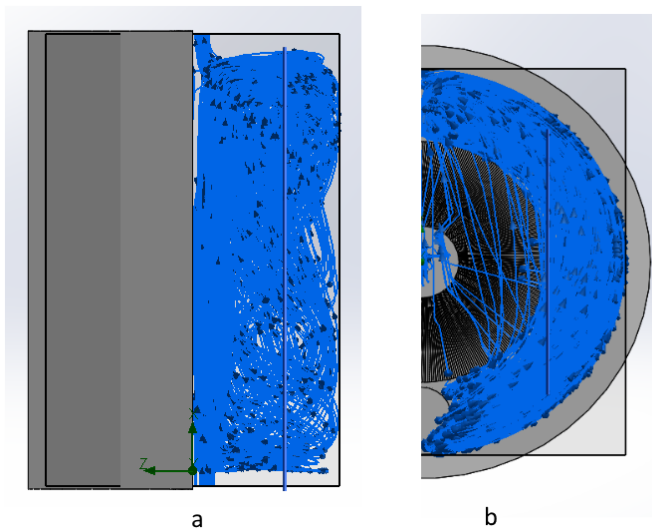


Fig. 9. Solidworks flow simulation for a membrane a) lateral view b) top view.

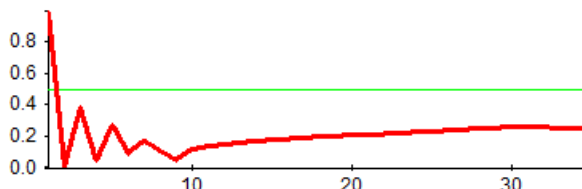


Fig. 10. Solidworks flow simulation surface results (red) pressure and (green) fluid velocity.

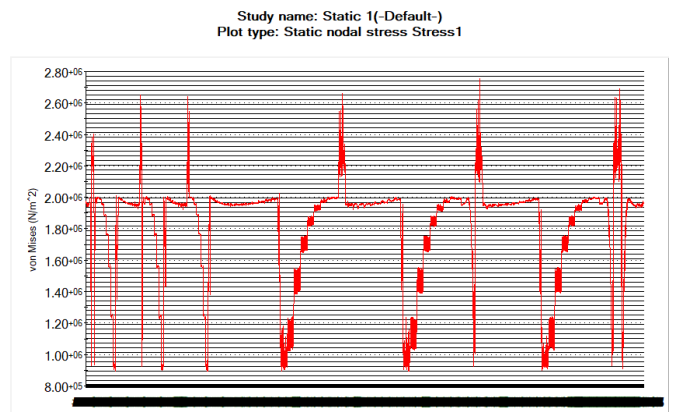


Fig. 11. Solidworks stress simulation

V CONCLUSIONS AND SUMMARY

The synthesis of cellulose-based composites and Graft copolymerization of cellulose were studied as potential approaches to enhance cellulose's properties. In both cases, the SEM, thermal, and chemical resistance analysis supported the results obtained in the mechanical behavior tests. The improvement of cellulose's properties was successfully achieved by both approaches, boosting the potential use of cellulose in membrane technologies. However, further investigation is needed to validate the suitability of the new materials for membrane formation techniques and to test the properties of the membranes to assess the behavior of these new materials in practical water treatment applications. Solidworks is a tool that shows great potential to further study these materials' suitability for different membrane applications.

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