CELLULOSE AND NATURAL RUBBER NANOCOMPOSITES AEROGELS MORPHOLOGY AND THERMAL PROPERTIES

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Abstract: This study focuses on producing aerogels formed by cotton microfibrillated cellulose (MC), natural rubber latex (NR), and their nanocomposites. MC was produced through high-speed mechanical shear processes, enabling its dispersion in an aqueous medium. The nanocomposite's production occurred by blending the aqueous dispersions of microfibrillated cellulose (0.26 wt %) and the natural rubber latex (1 wt%), followed by freeze-drying. The morphology and thermal properties of aerogels were evaluated using scanning electron microscopy (SEM), thermogravimetry analyses (TGA), and differential scanning calorimetry (DSC). Aerogels with different proportions were prepared to comprehend each component's effects in the nanocomposite. Microscopy revealed the effectiveness in obtaining cellulose micro- and nanostructures using shear. All samples presented a very porous structure. The preparation of the nanocomposites allowed the uniform incorporation of cellulose into rubber despite the intrinsic differences between their composition and chemical properties. The increase in rubber the proportion promotes greater interconnectivity of macropores, rendering them denser and losing the laminar and microporous characteristics observed in aerogels with higher cellulose ratios. The aerogels exhibited satisfactory thermal stability at around 300 °C, underscores the effectiveness of the aerogel synthesis process in obtaining cellulose micro- and nanostructures through mechanical processes and in nanocomposite formation through aqueous medium followed by freeze-drying.

1. INTRODUCTION

In the pursuit of new technologies, the concern for the entire lifecycle of a material, from raw material to disposal, has become an inevitable point to consider during the development of new materials. Increasingly, efforts are directed toward more efficient solutions, sustainability, and less environmental harm, drawing inspiration from what already exists in nature.

In this context, a material that has garnered considerable attention is the aerogel. Its excellent properties, such as high porosity, high surface area, and low density, allow it to be applied in various technology fields [1,2]. It can be used for storing and transporting substances, as structuring agents, filter materials, absorbers, etc. Like a fruit, watermelon has a porous structure of fibers responsible for absorbing and encapsulating large amounts of liquid. A bone is also a porous structure designed to provide minimal density support. This illustrates the importance of correlating the functionality of a material with its microstructural characteristics when designing a new composite.

Cellulose is the most abundant naturally occurring biopolymer, being nontoxic, biocompatible, and biodegradable [3]. Cellulose nanostructures can be used as reinforcing fillers in composites and nanocomposites [4]. Various methods are used to obtain these nanostructures, including chemical, enzymatic, and mechanical processes. In some cases, acids are used, which can be highly aggressive to the user or harmful to the environment upon disposal, or they may not yield a favourable outcome for the process.

Similarly, natural rubber is a biopolymer with various intrinsic properties derived from the latex of different types of rubber trees. It is commercially highly valuable, used to manufacture industrial and medical products, and essential for the tire and anti-vibration industries [4]. Natural rubber's key characteristics include resilience, elasticity, and abrasion resistance. Moreover, its hydrophobic and oleophilic nature offers the rubber a range of possibilities in terms of compatibility with different materials [5]. These properties can be further enhanced through manufacturing and structuring processes, thus expanding its field of application, such as in the production of aerogels.

The synthesis of rubber composites containing cellulose as reinforcing fillers, or rubber with small rubber additions, is increasingly being studied. This trend is directly related to the different properties among them. Regarding the adhesion of these materials, it isn’t just the dispersion and orientation of the cellulose fibers but also the bonding forces between the polymers that influence the enhancement of mechanical properties [6,7]. Thus, the dimensions of the structures, such as fibers, and the medium in which the composites are synthesized are crucial in achieving effective matrix-fiber interaction in composites.

This study evaluated aerogels of cellulose derived from cotton and natural rubber latex, along with composites of the two materials in different proportions. The nanostructures were obtained through a mechanical shear and dispersion process. The formation of composites and aerogels occurred in an aqueous medium using freeze-drying. Freeze-drying involves a simple dehydration process that removes the solvent through sublimation at low temperatures from a previously frozen material [2]. This study aimed to analyze the effectiveness and results of the processes for synthesizing bio-aerogels from cellulose and natural rubber, aiming to create a material with high engineering utility, sustainable in nature, without chemical modification, and produced with simpler, efficient, and sustainable method.

2. METHODOLOGY

2.1. Materials

Micro and nanostructures were derived from commercial bulk cotton [Farol, Juiz de Fora MG] using the 500 W UltraTurrax disperser from IKA, using a top-down approach. The natural rubber latex was extracted from the rubber tree (*Hevea brasiliensis*) located at Fazenda Maira, in the city of Cidade Ocidental, Goiás, Brazil, and provided by Professor Dr. Floriano Pastore from the University of Brasília. The cotton dispersion and latex dilution were carried out using distilled water.

2.2. Production of cellulose aqueous dispersions

The cellulose aqueous dispersion was prepared using distilled water and commercial cotton at 0.25 wt%. The microfibrillation was adapted from the methodology used by Cheng [8]. The commercial cotton, previously dried, was untangled and cut into small pieces about 1 mm thick using scissors. Then, the cotton pieces were dispersed in water and processed in a commercial blender (Britannia, BLQ1280, 1150W) until an initial homogenization was achieved. The material was then subjected to high shear in a disperser (UltraTurrax T25 D S32, IKA) for 12 cycles of 5 minutes each, at a speed of 20,000 rpm. For the latex, the original solid content was determined and then diluted to create a colloid with 1% and 5% concentrations for producing two pure rubber aerogels and 10% for synthesizing the nanocomposites.

The preparation of the composites involved mixing the two dispersions in an aqueous medium with different ratios of solid content from each material. In addition to the pure dispersions of 100% cellulose (100/00 MC/NR) and 100% natural rubber (00/100 MC/NR), nanocomposites were created with 80% cellulose and 20% natural rubber (80/20 MC/NR), 50% cellulose and 50% rubber (50/50 MC/NR), and 20% cellulose and 80% rubber (20/80 MC/NR). The nanocomposites were then mixed and dispersed using the Ultra Turrax disperser.

2.3. Production of aerogels

The five dispersions were poured into molds and frozen at -24 °C for 24 hours, followed by -80 °C for another 4 hours. The frozen material was processed in a freeze-dryer (Liotop K 120) for 96 hours to produce the aerogel.

2.4. Material characterization

2.4.1. Density and porosity

The density (ρ_o) of each aerogel was determined using its mass (m) and its volume (v), which was calculated based on its external dimensions. The masses were determined using an analytical balance (Shimadzu, AY220), and the external dimensions were measured with a digital calliper (DIGIMESS). Three samples were considered for each dispersion, and each sample was measured three times. For each material, the mean of a triplicate was considered, and the density was calculated according to Eq. (1)

$$\rho_o = \frac{m}{v} \tag{1}$$

The calculated density ρ sub o and theoretical density ρ were considered to determine porosity, following the methodology used in [1]. The theoretical density of the biopolymers is obtained through the weighted average of the densities of the two components, according to their mass fractions, as shown in Eq. (2).

$$\rho = \frac{1}{\frac{w_1}{\rho_1} + \frac{w_2}{\rho_2}} \tag{2}$$

where w is the polymer's mass fraction and ρ is the theoretical density obtained from the literature in g/cm³. The densities used for the calculation were 1.50 g/cm³ for cellulose fibers, as referenced in [9], and 0.93 g/cm³ for natural rubber, according to reference [10]. Once the densities are determined, porosity, expressed as a percentage, can be calculated using Eq. (3).

$$porosity(\%) = \left(1 - \frac{\rho_o}{\rho}\right) 100 \tag{3}$$

2.4.2. Volume shrinkage

Volume shrinkage was defined by comparing the initial volume v_o of the molded and frozen dispersion with the external volume v_e of the material after freeze-drying, i.e., in its aerogel state.

$$VS(\%) = \frac{v_o - v_e}{v_o} 100 \tag{4}$$

2.5. Morphology

The aerogels' morphological analysis was carried out using a Scanning Electron Microscope (ZEISS FEG Sigma HV). The top surface of the samples was examined. Before analysis, the samples were coated with an approximately 20 nm layer of gold powder using a sputter coater (Q150T-ES Quorum Technologies).

The effectiveness of obtaining nanometric cellulose structures through the applied mechanical process was evaluated by analyzing the dimensions of the fibers in the material from the microscopy images. Using the software ImageJ, the thickness of 100 cellulose fibers was measured, and the mean and standard deviation were calculated.

2.6. Thermal Analysis

Thermal analyses were performed using a simultaneous thermal analyser TGA/DSC (TA Instruments, SDT Q600) to investigate the thermal behavior of pure aerogels and composites. Samples of approximately 9 mg of each material were placed in alumina crucibles and subjected to controlled and monitored heating, ranging from 30 °C to 600 °C, under an inert nitrogen atmosphere at a flow rate of 100 mL/min and a heating rate of 20 °C/min. The analyses provided detailed information on the mass losses as a function of temperature increase associated with the thermal transitions of the studied materials.

3. RESULTS AND DISCUSSION

The results regarding density, porosity, and volumetric shrinkage are presented in Table 1. The table also includes the total solid content of the aqueous dispersions for each material produced before the freeze-drying process. We can relate the results of density and porosity to the solid content in each dispersion. As this content increases, density increases, while porosity decreases, as observed in [1]. Unlike the pure cellulose aerogels and composites, it was impossible to unmold the pure rubber aerogel with a 1% solid content. It remained bound to the mold used and experienced significant shrinkage when trying to remove it. Thus, a new attempt to obtain the pure rubber aerogel was made considering a 5% solid content. In this case, it was possible to get more structured material. Given this result, we see that the solid content of the rubber is an essential variable in obtaining pure rubber aerogels.

On the other hand, when comparing the pure rubber aerogel with the composite containing 80% rubber and 20% cellulose (20/80 MC/NR), despite having very similar solid contents, the latter showed the lowest volumetric shrinkage among all others developed, which indicates the influence of cellulose fibers in the material's structure.

Table 1. Physical properties of aerogels: 100/00 MC/NR, 80/20 MC/NR, 50/50 MC/NR, 20/80 MC/NR and 00/100 MC/NR

Sample	Solid/ dispersions (%w/w)	Density(g/cm³)	Porosity (%)	Volumetric Shrinkage (%)
MC pure	**0.25**	0.0039 ± 0.0002	99.73 ± 0.30	32 ± 4
80/20 MC/NR	0.31	0.0049 ± 0.0004	99.66 ± 0.03	38 ± 5
50/50 MC/NR	0.49	0.0067 ± 0.0008	99.43 ± 0.07	28 ± 8
20/80 MC	1.14	0.0119 ± 0.0004	98.82 ± 0.04	6 ± 3
NR pure	1.00	0.0114 ± 0.0001	98.77 ± 0.03	12 ± 2
NR pure*	5.00	0.0518 ± 0.0012	94.95 ± 0.16	2 ± 2

* Pure natural rubber aerogel is produced later with higher solid content.

Analyses of the structure and morphology of the aerogels were conducted using scanning electron microscopy, as shown in Fig. 1. Fig. 1a present cellulose fibers obtained through the mechanical shear and dispersion process. Visualizing a network structure with fiber thicknesses ranging from 26 to 147 nm is possible. This result demonstrates the process's effectiveness in obtaining dispersed nanostructures, according to the definition in [3]. Fig. 1b presents the aerogel with 80% cellulose and 20% rubber (80/20 MC/NR). We can observe the adhesion of small rubber particles along a cellulose fiber, indicating a good surface bonding between MC and NR.

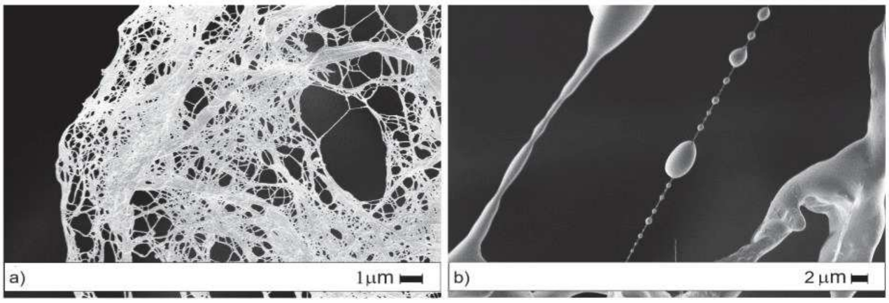

Figure 1. The SEM images of (a) cellulose pure aerogel and (b) 80/20 MC/NR nanocomposite aerogel.

Fig. 2 presents SEM images of samples of each aerogel formed, with Fig.2a and Fig.2b representing the pure cellulose and pure rubber aerogels, respectively. Generally, we can see a high degree of porosity in the aerogels and a plate-like formation pattern. The formation of a porous structure and the development of plate-like formations can be associated with synthesizing aerogels in an aqueous medium, where the dispersions are frozen and then subjected to freeze-drying. During the freezing process, ice crystals form, causing the cellulose and rubber particles to assume a specific arrangement, which remains after the water sublimates [2]. When comparing the pure aerogels, the cellulose aerogel shows a rougher appearance with micropores, unlike the pure rubber aerogel, which has a denser and more interconnected reticular structure. These same characteristics are observed progressively in the composites. Increasing the rubber proportion promotes greater interconnectivity of the macropores, making them denser and losing the laminar and microporous characteristics observed in aerogels with higher cellulose proportions.

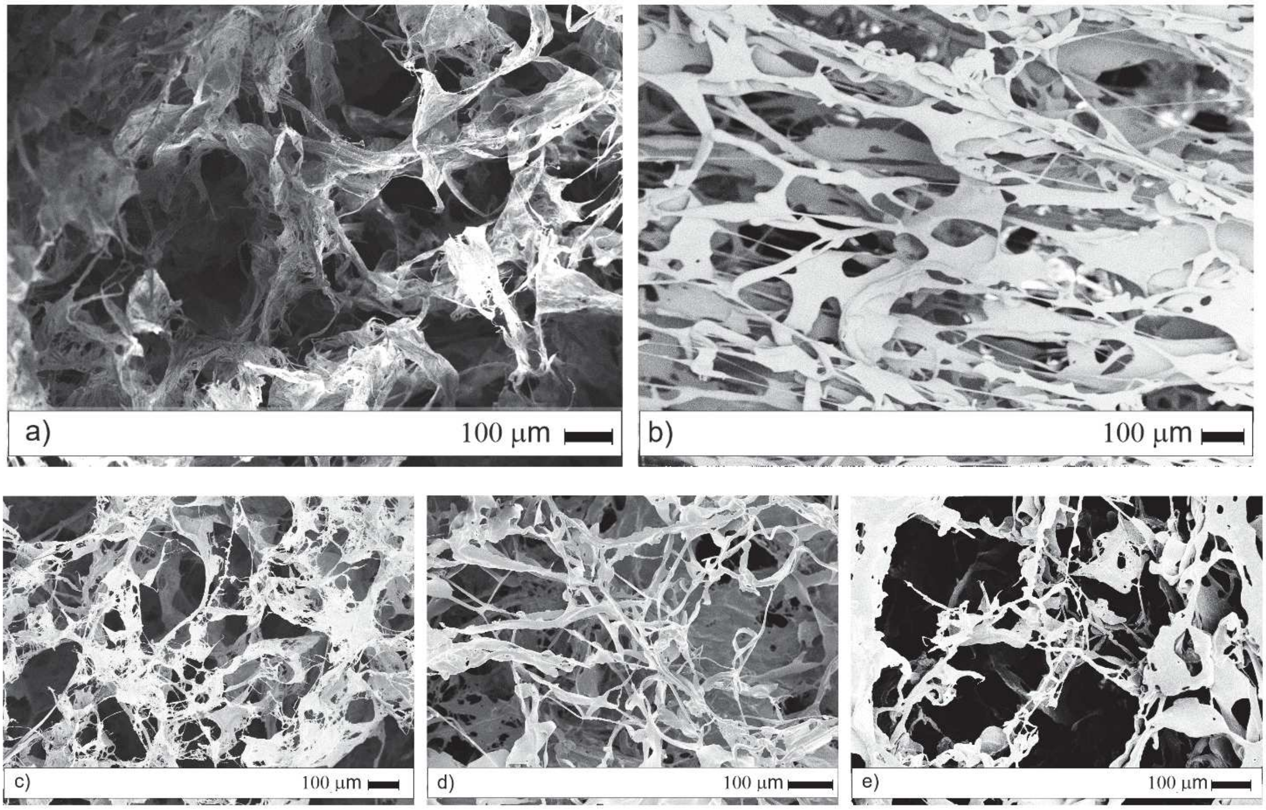

Figure 2. The SEM surface images of (a) pure cellulose 100/00 MC/NR, (b) pure natural rubber 00/100 MC/NR and (c) 80/20 MC/NR, (d) 50/50 MC/NR and (e) 20/80 MC/NR nanocomposites aerogels.

The curves thermogravimetric (TG), derivative thermogravimetric (DTG), and differential scanning calorimetry generated from the thermal analysis of the pure cellulose aerogel, the natural rubber aerogel, and their composites are presented in Figure 3. Initially, all samples exhibit a similar TG curve shape, indicating a similarity in thermal behaviour among them. In samples with higher cellulose content, most notably in pure cellulose, the first stage of degradation occurs at a temperature close to 50 °C. This weight loss can be related to the moisture content in the samples, accounting for about 6% of the total weight in pure sample 100/00 MC/NR, attributed to its hydrophilic nature. The residual weight at 600 °C was also proportional to the cellulose content, with zero residual weight for the pure rubber aerogel.

When analyzing the DSC curves in Fig. 3c, we observe that materials containing higher cellulose content have a greater enthalpy of degradation than those with higher rubber proportions. This significant difference, even with similar degradation curves, can be attributed to a better structural arrangement of cellulose molecules, resulting in increased bond energy between them. Since the analyses were conducted in an inert atmosphere, it was observed that the presence of oxygen in the cellulose molecules and its absence in the rubber molecules directly impacted the onset temperature of material degradation.

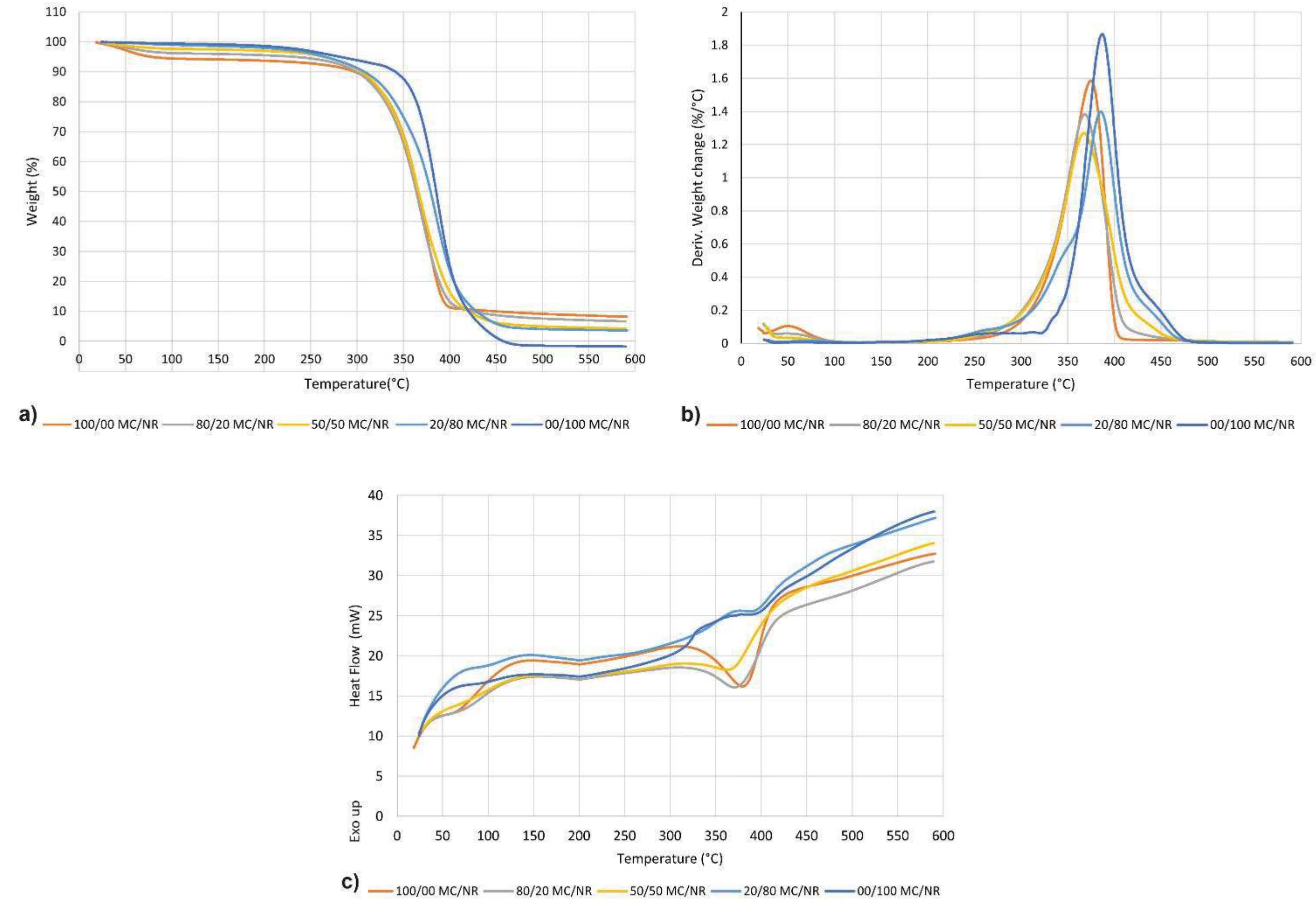

Figure 4. Thermal properties of 100/00 MC/NR, 80/20 MC/NR, 50/50 MC/NR, 20/80 MC/NR, and 00/100 MC/NR aerogels. (a) TGA, (b) DTG, and (c) DSC curves.

The main degradation temperatures of the material are presented in Table 2. The materials exhibited thermal stability up to 250 °C, with no notable differences. Regarding the pure materials, natural rubber has a higher onset temperature of degradation than cellulose. For the composites with 80% and 50% cellulose (80/20 MC/NR and 50/50 MC/NR), the T_{onset} values are lower than those of pure cellulose, indicating that degradation begins earlier in these composites than in pure cellulose. This relationship also extends to the recorded peak temperature. However, the end temperature of the event, T_{endset}, for the two composites is higher than the cellulose, indicating a broader degradation range. On the other hand, the composite with 80% rubber (20/80 MC/NR) has a higher onset temperature of degradation than cellulose and a higher peak temperature, with its end event temperature closer to the rubber. Additionally, the composites showed less intense and broader degradation peaks than pure materials, suggesting greater thermal stability [11].

The presence of a single stage of degradation in the composites indicates good dispersion and adhesion of cellulose fibers with rubber particles [12], supporting the effectiveness of the composite synthesis process in the aqueous medium.

Table 2. Thermal degradation events of aerogels.

Samples	**Degradation Temperature (°C)**		**Residue at 600°C (%)**	**Maximum Degradation Temperature (T_{max}, °C)**	**ΔH (J/g)**
	T_{onset}	T_{endset}			
Pure cotton MC	**340**	**390**	**8**	**375**	**195**
Pure NR	**360**	**415**	**0**	**387**	**14**
80/20 MC/NR	323	395	7	368	128
50/50 MC/NR	325	400	4	368	71
20/80 MC	345	410	4	385	15

4. CONCLUSIONS

Cellulose aerogels from cotton, rubber, and their composites were synthesized from an aqueous formulation followed by freeze-drying. Through a mechanical process, nanostructured particles were obtained from commercial cotton, allowing for the formation of a uniformly dispersed colloid. This resulted in a homogeneous dispersion of the composites with natural rubber latex. The morphology of the nanostructures from both materials and the aqueous medium in which they were dispersed influenced the adhesion quality, improving the material's thermal stability and conformation. Cellulose proved an important structuring agent, while rubber contributed to increased thermal stability in the composites. Water was an effective medium for obtaining composites and formulating the aerogels through freeze-drying. The method demonstrated significant effectiveness in obtaining nanostructures and synthesizing aerogels through processes that do not rely on chemical or enzymatic products, making them more accessible regarding material requirements.

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