Evaluating the Influence of Processing Conditions on Colloidal Stability and Particle Size in Fibrillated Nanocellulose

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Cellulose nanofibers (CNF) are nanostructures derived from cellulose's crystalline and amorphous regions through mechanical, chemical-mechanical, or enzymatic processes. Due to their high aspect ratio, extensive surface area, remarkable modulus of elasticity, and superior mechanical strength, CNFs have emerged as promising reinforcement materials in composite applications. Key properties such as colloidal stability, assessed via zeta potential, and nanofibril particle size provide critical insights into the dispersion and interaction of these fibers within a polymer matrix. These parameters are essential for optimizing composite performance and ensuring uniform fiber distribution. This study aimed to evaluate the influence of different preparation conditions on the zeta potential and particle size of CNFs, providing a better understanding of how processing parameters affect their characteristics.
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Cellulose is the most abundant biopolymer on Earth, predominantly sourced from lignocellulosic materials such as agro-industrial waste [1]. Brazil is strategically positioned in this field due to its rich diversity of lignocellulosic resources and status as one of the world's largest agricultural producers. This ensures a significant contribution to the global availability of lignocellulosic biomass [2].

Among the many applications of cellulose, the production of nanostructures, such as cellulose nanofibers (CNFs), stands out. CNFs are nanostructures characterized by crystalline and amorphous domains obtained through mechanical, chemical-mechanical, or enzymatic processing methods [3]. These nanofibers exhibit exceptional properties, including a high aspect ratio, extensive surface area, high crystallinity, and a superior modulus of elasticity. Moreover, their ability to form interconnected networks enhances their mechanical properties, such as tensile strength, making them ideal as reinforcing materials in composites [4,5].

For CNFs to function effectively as reinforcement materials, they must maintain stability and avoid agglomeration, as aggregation negatively impacts the composite's mechanical performance. Analyzing the zeta potential is one of the most reliable methods to evaluate this stability. This parameter provides insight into the electrical charge on the surface of suspended particles, which is crucial for determining the stability of colloidal dispersions. A high zeta potential (positive or negative) indicates strong electrostatic repulsion between particles, preventing aggregation and ensuring a stable suspension. Conversely, a low zeta potential suggests a tendency for particle aggregation, which can compromise the material's dispersion and, consequently, its mechanical and barrier properties [6].

Particle size analysis is another critical aspect of characterizing CNFs, as it directly influences their surface area, mechanical strength, and interaction with other composite components. Accurate particle size control ensures optimal nanofiber dispersion within matrices and tailors the material's performance in specific applications such as films, coatings, or biocomposites.This analysis allows researchers to assess the fibrillation process's efficiency, detect agglomerates, and make necessary adjustments to achieve desired material characteristics.

The duration of defibrillation significantly impacts the width and length of nanofibrils. Extended defibrillation times result in smaller

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fibril dimensions, which are crucial for enhancing specific properties. For example, De Carvalho and colleagues (2019) [7] demonstrated that longer fibrillation times improve the mechanical properties of nanopapers by reducing fibril size. Similarly, Eriksen and colleagues (2008) [8] explored the production of microfibrillated cellulose (MFC) and found that prolonged processing times decreased fibril diameter, thereby enhancing the strength of MFC-reinforced paper. This study aims to evaluate the influence of different preparation conditions on cellulose nanofibers' zeta potential and particle size. These findings will contribute to developing CNFs as effective reinforcing materials for various applications.

Materials and Methods

Obtaining Cellulose Nanofibrils

The detailed procedure for obtaining cellulose nanofibrils (CNFs), including the specific agricultural residue source, is currently under patent filing by TRL9 and cannot be disclosed in this work. However, the CNFs were produced through a mechanical defibrillation process using Ultra-Turrax equipment. The process parameters—homogenization speed and residence time—were varied, resulting in four distinct samples.

Zeta Potential and Particle Size Analysis

Zeta Potential Analysis

The zeta potential of the samples was analyzed using a Malvern Zetasizer Nano ZS. A 1 mL aliquot of the filtered CNF suspension was loaded into a DST1070 cuvette and placed into the equipment for measurement. For each sample, three measurement rounds were performed. The results were processed using the Zetasizer software, and the output data (intensity and power) were exported to Excel for compilation. The compiled data were further analyzed in Origin 2023b software, where the "Average Multiples Curves" function generated a single averaged graph for each sample's three readings.

Particle Size Analysis

Particle size measurements were performed on the same equipment (Malvern Zetasizer Nano ZS) and followed the same three-round measurement protocol. The main differences were the type of analysis and the cuvette configuration, which were adjusted in the equipment's software for particle size evaluation.

Results and Discussion

Zeta Potential and Colloidal Stability

Zeta potential plays a pivotal role in characterizing cellulose nanofibrils (CNFs), influencing the colloidal stability of suspensions and the material's overall quality. During the production of CNFs, zeta potential monitoring is essential to optimize conditions such as pH or the addition of stabilizing agents, ensuring fibrils remain well-dispersed and prevent agglomeration. Table 2 summarizes each sample's zeta potential and particle size (Z-Ave) values. Values exceeding ±30 mV generally indicate high colloidal stability due to strong electrostatic repulsion between particles. None of the samples achieved this threshold, suggesting moderate to low stability.

Influence of Processing Conditions on Zeta Potential

The samples were differentiated based on homogenization speed and residence time. The following trends were observed:

Effect of Residence Time

Comparing A1 to A2 and A3 to A4, increased residence time reduced zeta potential. This indicates a greater tendency for particles to

agglomerate over time, potentially due to thermal agitation and heating during prolonged processing.

Effect of Homogenization Speed

A rise in homogenization speed (from 14,000 to 18,000 rpm) also reduced zeta potential. Increased speed intensifies thermal agitation and ion mobility in the surrounding medium, altering the electrical double layer and promoting agglomeration.

As particles' kinetic energy increases with temperature, ion redistribution in the electrical double layer diminishes the magnitude of the zeta potential, reducing suspension stability. CNFs with high zeta potential values are crucial for homogeneous composite production and maintaining mechanical and barrier properties [9,10].

Chemical surface modifications of CNFs may help improve their zeta potential, enhance stability, and ensure better interaction with polymer matrices [11].

Particle Size Analysis

Particle size is critical in determining the dispersion quality and mechanical properties of CNF-based composites. The results indicate the following:

Effect of Speed on Particle Size

Comparing A1 to A3 and A2 to A4, higher homogenization speeds significantly reduced particle size due to the intensified shear forces breaking down the fibers.

Effect of Time on Particle Size

Prolonged defibrillation time also reduced particle size, as observed when comparing A1 to A2 and A3 to A4.

Increased residence time enhances fiber fragmentation, promoting the production of smaller nanofibrils.

Table 1. Sample preparation conditions (speed and time).

Sample	Homogenization Speed (rpm)	Homogenization Residence Time (min)
A1	14,000	10'
A2	14,000	20'
A3	18,000	10'
A4	18,000	20'

Table 2. Zeta potential values and particle size distribution of the samples.

Sample	Homogenization Condition (rpm)/(min)	Zeta Potential (mV)	Z-Ave (d.nm)
A1	14,000 / 10'	-15.7	957.6
A2	14,000 / 20'	-10.8	499.4
A3	18,000 / 10'	-15.4	438.3
A4	18,000 / 20'	-2.94	338.6

These findings align with previous studies demonstrating that longer defibrillation times result in reduced fibril dimensions, crucial for applications requiring high mechanical strength and uniformity [12,13].

Key Observations

- Increasing homogenization speed and time during mechanical defibrillation reduces particle size but adversely affects zeta potential.
- Achieving optimal CNF stability and particle size balance may require chemical stabilization techniques or controlled processing parameters to minimize heat generation
- This analysis underscores the importance of carefully optimizing defibrillation conditions to produce CNFs with desirable characteristics for industrial and biomedical applications.

Conclusion

This study demonstrated that increasing mechanical defibrillation time and speed during Ultra-turrax processing effectively reduces cellulose nanofibril (CNF) particle size. The observed dimension reduction can be attributed to intensified shear forces and fiber fragmentation under prolonged and higher-speed defibrillation conditions.

Zeta potential was identified as a crucial parameter for assessing the colloidal stability of CNFs, which directly impacts their dispersion within polymer matrices and the resulting composite properties. A1 and A3 exhibited comparable zeta potential values among the samples, indicating moderate stability. However, these values can be further improved through surface modifications of the nanofibrils, which will be a key focus in future work. Optimizing zeta potential and particle size will pave the way for developing sustainable composites with enhanced mechanical and functional properties.

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