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BALANCING FLEXIBILITY AND STRENGTH OF HYDROXYPROPYLATED STARCH/CELLULOSE NANOFIBRILS BIOCOMPOSITES

EQUILIBRANDO A FLEXIBILIDADE E A RESISTÊNCIA DE BIOCOMPÓSITOS DE AMIDO HIDROXIPROPILADO/NANOFIBRILAS DE CELULOSE

EQUILIBRIO ENTRE FLEXIBILIDAD Y RESISTENCIA DE LOS BIOCOMPOSITOS DE NANOFIBRILLAS DE ALMIDÓN HIDROXIPROPILADO/CELULOSA

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Fernanda Andrade Tigre da Costa[1], Henrique Solowej Medeiros Lopes[2], Lucas Repecka Alves[3], Daniel Komatsu[4], Aparecido Junior de Menezes[5] and Duclerc Fernandes Parra[6]

ABSTRACT

This study investigates the thermal-mechanical properties of hydroxypropylated starch (HPS) as a plasticizer for conventional thermoplastic starch (TPS) films, reinforced with cellulose nanofibrils (CNF). A previous study showed that hydroxypropylation of starch led to in-situ poly(propylene oxide) (PPO) formation, inducing gelatinization and yielding TPS with significant plasticizing effect. To address this, blending native cassava starch with HPS and incorporating CNF, as well as hydroxypropylated CNF (mCNF), was explored as a sustainable reinforcement strategy. Films were prepared by casting, and their properties were evaluated using tensile strength tests, Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TG). Results indicate that the incorporation of unmodified CNF significantly increased the tensile strength of HPS/TPS films, demonstrating its effective reinforcing capability. Conversely, adding mCNF led to a reduction in tensile strength, suggesting that the chemical modification of CNF may hinder its reinforcing efficiency due to altered interactions with the starch matrix. FTIR confirmed molecular interactions, while DSC and TG provided insights into thermal transitions and stability. This research emphasizes the potential of combining HPS, native starch, and CNF to create sustainable, high-performance starch-based biocomposites with reduced synthetic plasticizer content, offering a promising approach for diverse applications.

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[1] Dr. in Nuclear Engineering. Nuclear and Energy Research Institute (IPEN-CNEN/SP).
E-mail: fernanda.tigre@outlook.com ORCID https://orcid.org/0000-0001-8046-6924

[2] Dr. in Materials Science. Faculdade de Tecnologia de Sorocaba (FATEC).
E-mail henrique.lopes01@fatec.sp.gov.br ORCID https://orcid.org/0000-0002-8222-0888

[3] Doctorate student in Materials Science. Universidade Federal de São Carlos (UFSCar).
E-mail: lucasrepecka@estudante.ufscar.br ORCID: https://orcid.org/0000-0001-5458-2403

[4] Researcher/Professor. Pontifícia Universidade Católica do Paraná (PUC). Faculdade de Tecnologia de Sorocaba (FATEC). E-mail: danielkomatsu23@gmail.com ORCID https://orcid.org/0000-0002-2441-8650

[5] Full Professor. Universidade Federal de São Carlos (UFSCar). E-mail: jrmenezes@ufscar.br
ORCID https://orcid.org/0000-0001-5638-489X

[6] Senior Researcher. Nuclear and Energy Research Institute (IPEN-CNEN/SP).
E-mail: parduclerc@yahoo.com.br ORCID https://orcid.org/0000-0002-6481-0155

Keywords: Hydroxypropylation. Starch. CNF. Plasticization. Biocomposites.

RESUMO

Este estudo investiga as propriedades termomecânicas do amido hidroxipropilado (HPS) como plastificante para filmes convencionais de amido termoplástico (TPS), reforçados com nanofibrilas de celulose (CNF). Um estudo anterior demonstrou que a hidroxipropilação do amido levou à formação in situ de poli(óxido de propileno) (PPO), induzindo a gelatinização e produzindo TPS com efeito plastificante significativo. Para abordar esse problema, a mistura de amido de mandioca nativo com HPS e a incorporação de CNF, bem como CNF hidroxipropilado (mCNF), foi explorada como uma estratégia de reforço sustentável. Os filmes foram preparados por fundição e suas propriedades foram avaliadas por meio de ensaios de resistência à tração, espectroscopia no infravermelho com transformada de Fourier (FTIR), calorimetria exploratória diferencial (DSC) e análise termogravimétrica (TG). Os resultados indicam que a incorporação de CNF não modificado aumentou significativamente a resistência à tração dos filmes de HPS/TPS, demonstrando sua eficaz capacidade de reforço. Por outro lado, a adição de mCNF levou a uma redução na resistência à tração, sugerindo que a modificação química do CNF pode prejudicar sua eficiência de reforço devido a interações alteradas com a matriz de amido. FTIR confirmou interações moleculares, enquanto DSC e TG forneceram insights sobre transições térmicas e estabilidade. Esta pesquisa enfatiza o potencial da combinação de HPS, amido nativo e CNF para criar biocompósitos sustentáveis e de alto desempenho à base de amido com teor reduzido de plastificante sintético, oferecendo uma abordagem promissora para diversas aplicações.

Palavras-chave: Hidroxipropilação. Amido. CNF. Plastificação. Biocompósitos.

RESUMEN

Este estudio investiga las propiedades termomecánicas del almidón hidroxipropilado (HPS) como plastificante para películas convencionales de almidón termoplástico (TPS), reforzadas con nanofibrillas de celulosa (CNF). Un estudio previo demostró que la hidroxipropilación del almidón condujo a la formación in situ de poli(óxido de propileno) (PPO), lo que induce la gelatinización y produce TPS con un significativo efecto plastificante. Para abordar este problema, se exploró la mezcla de almidón de yuca nativo con HPS e incorporación de CNF, así como CNF hidroxipropilado (mCNF), como una estrategia de refuerzo sostenible. Las películas se prepararon mediante colada y sus propiedades se evaluaron mediante ensayos de resistencia a la tracción, espectroscopia infrarroja por transformada de Fourier (FTIR), calorimetría diferencial de barrido (DSC) y análisis termogravimétrico (TG). Los resultados indican que la incorporación de CNF sin modificar aumentó significativamente la resistencia a la tracción de las películas de HPS/TPS, demostrando su eficaz capacidad de refuerzo. Por el contrario, la adición de mCNF redujo la resistencia a la tracción, lo que sugiere que la modificación química del CNF podría afectar su eficacia de refuerzo debido a interacciones alteradas con la matriz de almidón. La FTIR confirmó las interacciones moleculares, mientras que la DSC y la TG proporcionaron información sobre las transiciones térmicas y la estabilidad. Esta investigación destaca el potencial de combinar HPS, almidón nativo y CNF para crear biocompositos sostenibles y de alto rendimiento a base de almidón con un contenido reducido de plastificantes sintéticos, lo que ofrece un enfoque prometedor para diversas aplicaciones.

Palabras clave: Hidroxipropilación. Almidón. CNF. Plastificación. Biocompositos.

1 INTRODUCTION

The escalating environmental concerns associated with conventional petroleum-based plastics have driven extensive research into sustainable and biodegradable alternatives. Starch, an abundant natural polymer, renewable, and low-cost polysaccharide, is a promising candidate for bioplastics. However, native starch's inherent brittleness, poor processability, and high moisture susceptibility limit its direct application, necessitating chemical or physical modifications [1–4]. The development of biodegradable polymers from renewable resources is crucial for mitigating environmental degradation and fostering a circular economy [5].

Thermoplastic starch (TPS) is produced by disrupting starch's granular structure through heat and shear with plasticizers, making it melt-processable [6]. This process involves the destruction of the native crystalline structure of starch, leading to amorphous material that can be produced using conventional polymer processing techniques like extrusion and injection molding. Common plasticizers like glycerol, water, and sorbitol reduce intermolecular hydrogen bonding within the starch matrix, thereby increasing chain mobility and flexibility [7]. Despite these advancements, TPS often suffers from several drawbacks, including low tensile strength, high water sensitivity, and a tendency for retrogradation, which collectively hinder its widespread adoption in various applications [8–11]. Retrogradation, a phenomenon where amorphous starch chains re-associate into more ordered structures, leads to increased brittleness and reduced flexibility over time [4]. Furthermore, the hydrophilic nature of starch results in high water absorption, leading to dimensional instability and a significant reduction in mechanical properties in humid environments [7]. Therefore, ongoing research efforts are intensely focused on improving TPS performance through various strategies, including chemical modification and the incorporation of reinforcing agents.

Hydroxypropylation involves the introduction of hydroxypropyl groups into the starch molecule, replacing the native hydroxyls present. This modification is known to improve starch's solubility, reduce its tendency for retrogradation, and enhance its film-forming capabilities, making it a more versatile material for various applications [12, 13]. On a previous study, the hydroxypropylation of starch resulted in a gelatinized material due to the in-situ formation of poly(propylene oxide) (PPO) during the reaction [1]. This unique process directly yielded thermoplastic starch (TPS) without the need for external plasticizers in the conventional sense.

To address the mechanical limitations of hydroxypropylated starch (HPS) and simultaneously reduce the reliance on synthetic plasticizers, blending native cassava starch with HPS in varying proportions emerges as a sustainable and promising alternative. This approach aims to enhance the inherent properties of native starch to provide structural integrity while benefiting from the plasticizing effect of HPS. In addition to blending, the incorporation of cellulose nanofibrils (CNF) is being extensively explored to further enhance the mechanical performance of these starch-based biocomposites and other materials [14–17]. CNF are bio-based nanomaterials derived from lignocellulosic biomass, renowned for their exceptional properties, including a high aspect ratio, excellent mechanical strength, and a large surface area [18, 19]. These characteristics make CNF ideal reinforcing agents for biocomposites, capable of forming a strong network within the polymer matrix through hydrogen bonding and mechanical interlocking, thereby effectively transferring stress and improving the overall composite integrity [20, 21]. The synergistic combination of HPS, native starch, and CNF is anticipated to yield novel biocomposites with significantly improved mechanical properties, offering sustainable solutions for a wide range of applications.

This study specifically investigates the thermal and mechanical properties of HPS/TPS films, with a particular focus on understanding the intricate interplay between the internal plasticization provided by PPO and the reinforcing capabilities of CNF. The overarching goal is to elucidate how the combination of hydroxypropylated starch, native starch, and CNF can lead to the creation of sustainable materials with a balanced and enhanced mechanical performance. By systematically evaluating the material's properties through tensile strength tests, Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TG), this research aims to optimize the formulations for improved mechanical performance. The ultimate objective is to formulate films with reduced synthetic plasticizer content, leveraging the synergistic effects of HPS, native starch, and CNF to create advanced, sustainable, and high-performance starch-based biocomposites suitable for diverse applications in packaging, agriculture, and biomedical fields.

2 MATERIALS AND METHODS

2.1 MATERIALS

Cassava starch of food grade (Pinduca, Brazil), potassium hydroxide (KOH) P.A. A.C.S. (Synth, Brazil), lithium hydroxide (LiOH) P.A. A.C.S. (Synth, Brazil), distilled water, propylene oxide (PO) P.A. A.C.S. (Sigma-Aldrich, USA), glycerol P.A. A.C.S. (Sigma-Aldrich, USA), bleached cellulose fibers from eucalyptus (kindly donated by Suzano, Brazil).

2.2 METHODS

Hydroxypropylation reaction of starch

Primarily, 20 g of cassava starch was activated with 20.21 g of KOH and 50 mL of ethanol/water solution (5/1 v/v) during 1h under vacuum. Then, 15 mL of PO was added, and the mixture was placed in an autoclave reactor. The reactor was sealed and heated to 125 °C ± 10 for 1h. Samples were removed from the reactor after cooling to room temperature and pressure. Prior to film casting, samples were kept immersed in a solution of distilled water/ethanol (1/5) per 180 min, followed by 50 mL of 1% acetic acid/ethanol solution and dried overnight at 60 °C, to remove potassium compounds identified earlier [1] and formed homopolymer [22].

2.2.1 Hydroxypropylation reaction of cellulose

Initially, 5 g of bleached cellulose fibers were pre-treated for 1 hour with 40 mL of ethanolic solution containing 2.21g of LiOH in equal volumes (50/50, v/v). After removing the ethanol by vacuum, 3.75 mL of PO was added, and the mixture was placed in an autoclave reactor. The temperature was raised and monitored until 125 °C ± 10 °C and maintained for 1 hour. Afterward, the reactor was cooled and the samples were collected. These were then subjected to Soxhlet extraction with n-hexane for 15 hours and subsequently dried to remove the homopolymer, a byproduct formed during the reaction [22].

2.2.2 CNF obtention

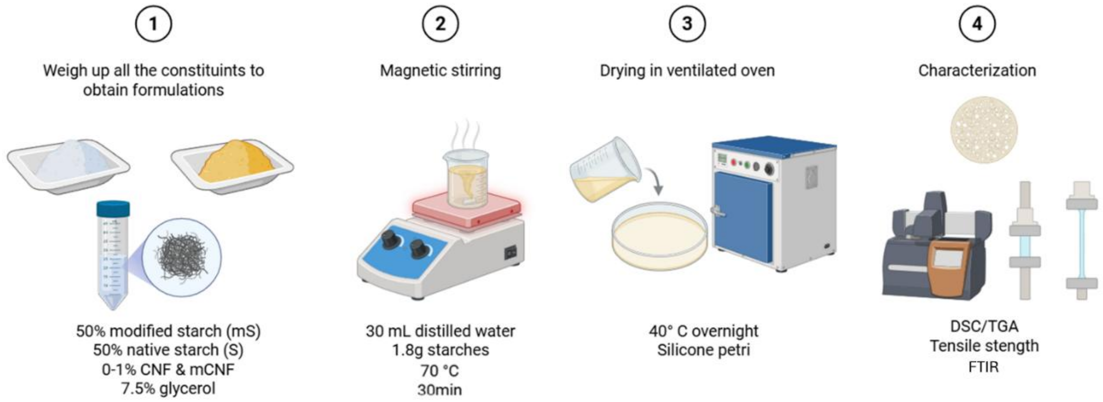
The modified cellulose fibers were homogenized using an Ultra-Turrax disperser in aqueous suspensions containing 1.5% of concentration. Subsequently, the samples were fibrillated using a Super Masscolloider ultra-disc refiner. The fibrillation process was carried out in cycles, with an aliquot being withdrawn at each cycle for particle size measurement, until reached the desired value.

2.2.3 Film preparation (casting)

Native starch was mixed with hydroxypropylated starch in 1:1 proportion and 7.5 wt% of glycerol was added to the mixture, based on starch weight content. 30 mL of distilled water was added as solvent until solution reaches concentration of 6% and stirred at 70 °C during 30 min. For the control sample of starch and modified starch (S/mS), no CNF was added to the mixture. For samples containing CNF (S/mS/CNF) and modified CNF (S/mS/mCNF), CNF suspension was added to the mixture prior to the stirring, representing 1 wt% in the final formulation. After mixing, samples were deposited in silicon plates and kept overnight for drying at 40 °C. The general representation of the films production via casting is illustrated in Figure 1.

Figure 1

Protocol to produce films via casting solution



Source: Authors.

2.2.4 Fourier-transform infrared spectroscopy (FTIR)

Obtained films were analyzed in a Perkin Elmer Frontier coupled with an attenuated total reflectance (ATR) apparatus in a spectral range of 600 to 4000 cm^{-1}, with resolution of 4 cm^{-1} and 16 scans.

2.2.5 Differential scanning calorimetry (DSC)

Up to 5 mg of films were placed in hermetic aluminum pan and analyzed in a TA Instruments DSC 25. The methodology used was heat-cool-heat, where samples were first heated from room temperature to 200 °C, followed by cooling to -90 °C and heated again to 200 °C. Heating and cooling rate were defined at 10 °C/min under inert atmosphere of nitrogen (50 mL/min).

2.2.6 Thermogravimetry (TG)

Samples decompositions were analyzed in a TA Instruments SDT Q600 from room temperature to 700 °C under inert atmosphere of nitrogen and heating rate of 10 °C/min. Derivative analysis was carried out in TRIOS software.

2.2.7 Tensile strength tests

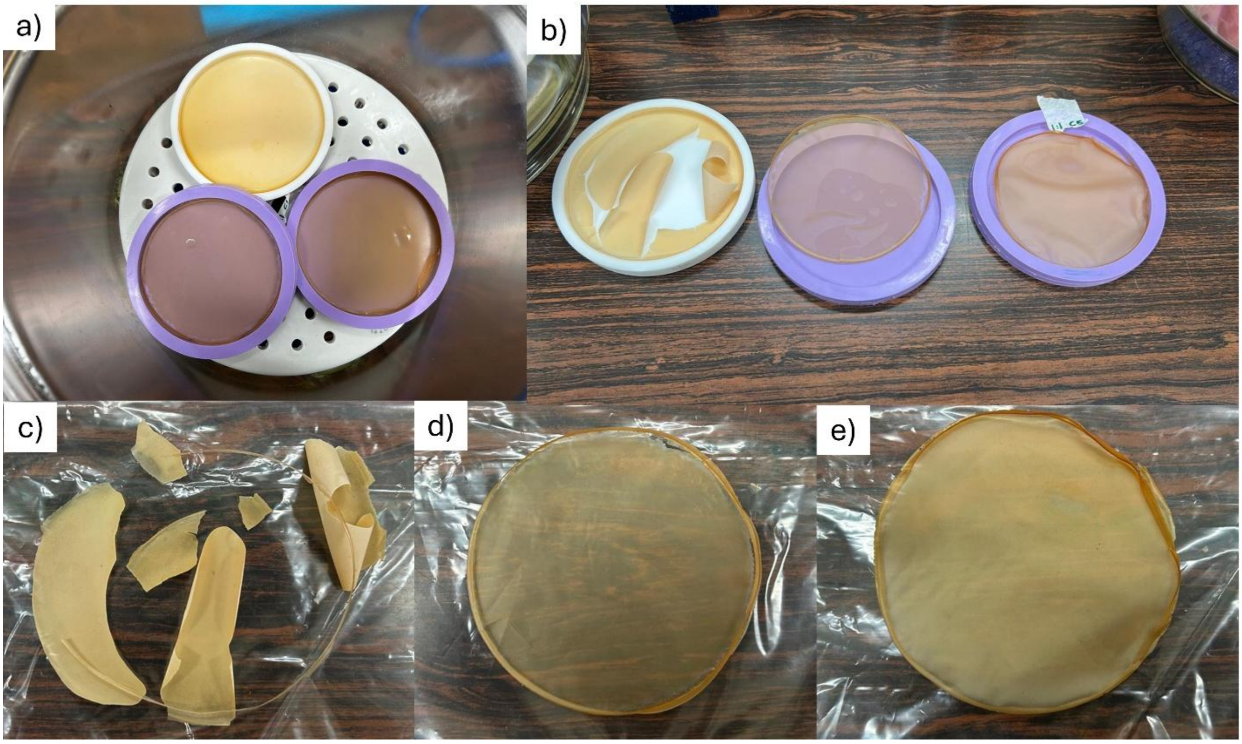
Tensile tests were conducted in film samples using an Instron Emic 23-30 universal testing machine. Grip separation rate was 5 mm/min and specimens were prepared according to ASTM D882 procedures [23]. All samples were tested in triplicate under room humidity and temperature (50 ± 5% and 25 ± 5 °C, respectively).

3 RESULTS AND DISCUSSION

The visual characteristics of the produced films are shown in Figure 2. The samples prepared by casting reveal distinct differences between formulations with and without CNF. For the films composed exclusively of native starch and modified starch (S/mS), a more brittle appearance is evident, suggesting limited flexibility and cohesion during the drying process. In contrast, the incorporation of CNF, as observed in the S/mS/CNF and S/mS/mCNF samples, results in visually continuous and cohesive films that are easily removable from the silicone plate. This observation emphasizes the reinforcing effect of CNF, which likely enhances intermolecular interactions within the matrix, thereby improving the structural integrity and handling properties of the films.

Figure 2

Casting film preparation: (a) samples before drying; (b) samples after drying; (c) final S/mS sample; (d) final S/mS/CNF sample; (e) final S/mS/mCNF sample



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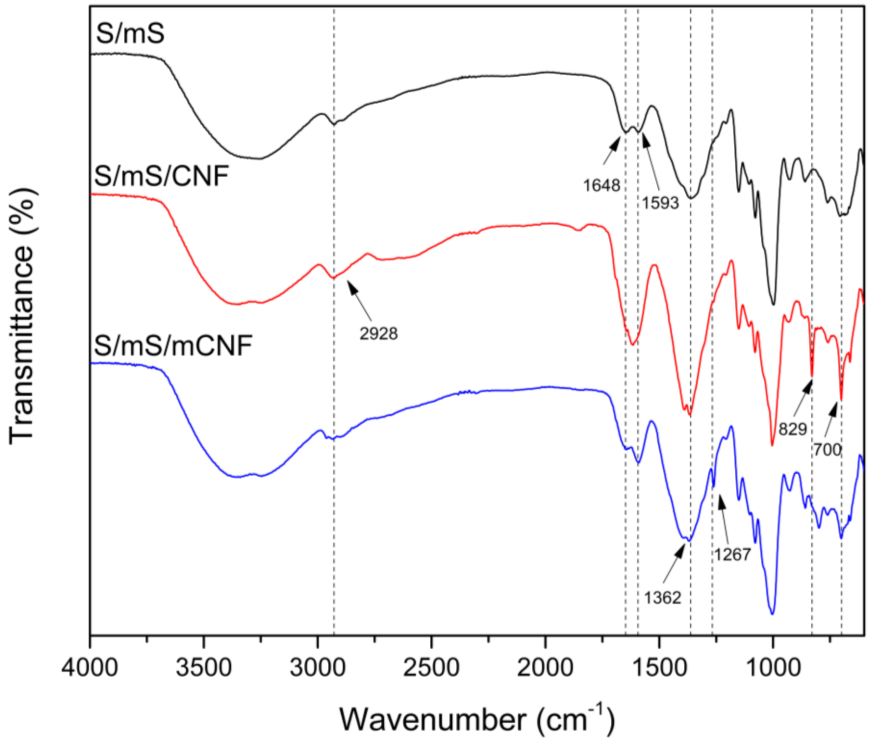
3.1 FOURIER-TRANSFORM INFRARED SPECTROSCOPY (FTIR)

The spectra of the three samples provide valuable insights into the molecular interactions and chemical modifications occurring within the composite films. The spectral features reveal changes in functional group environments, indicating differences in hydrogen bonding, polymer compatibility, and interfacial interactions (Figure 3).

Figure 3

FTIR spectra for all film samples



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All three samples exhibit a broad absorption band around 3400 cm^{-1}, corresponding to the O–H stretching vibrations of hydroxyl groups from starch, glycerol, and water. The intensity and shape of this band are influenced by hydrogen bonding. In S/mS/CNF and S/mS/mCNF, the peak appears slightly broader and shifted compared to S/mS, suggesting enhanced hydrogen bonding networks due to the presence of CNF. This indicates strong intermolecular interactions between the starch matrix and cellulose nanofibrils, which can improve mechanical and thermal properties. A distinct peak at 2928 cm^{-1} is attributed to the symmetric stretching of CH_2 groups from the cellulose backbone and is observed in all samples, with no observed differences by the addition of CNF or mCNF. The S/mS and S/mS/CNF samples show peaks near 1648 cm^{-1} and 1593 cm^{-1}, which could correspond respectively to O-H stretching vibrations from glycerol and moisture, and -C=C bondings, this latter, shifted to higher wavenumbers than the commonly found in the literature. These peaks are reduced in intensity in S/mS/mCNF, indicating that the hydroxypropylation of CNF may have weakened hydrogen bonding networks involving hydroxyls. Peaks at 1362 cm^{-1}, 1267 cm^{-1}, 829 cm^{-1}, and 700 cm^{-1} are characteristic of C–O–C and C–O stretching vibrations in polysaccharides. These bands are more pronounced in S/mS/mCNF, due to the etherification performed [1, 24, 25].

3.2 TENSILE STRENGTH TESTS

The incorporation of cellulose nanofibrils (CNF) into starch-based films significantly influenced their mechanical properties, as evidenced by variations in tensile strength and elongation at break showed in Table 1. The addition of 1% unmodified cellulose nanofibrils (CNF) to the blend of native starch and hydroxypropylated starch (S/mS) resulted in a notable increase in tensile strength, from 1.66 MPa to 2.13 MPa, compared to the control film without CNF, as shown in Figure 4 and Figure 5. This improvement can be attributed to the reinforcing effect of CNF, which acts as a physical crosslinker within the polymeric matrix. The high aspect ratio and strong hydrogen bonding capability of CNF enhance the interfacial adhesion between the starch chains, thereby improving the load-bearing capacity of the composite material.

Table 1

Mechanical properties of starch-based films and CNF

Sample	Tensile strength (MPa)	Elongation at break (%)
S/mS	1.66±0.85	3.80±0.53
S/mS/CNF	2.13±0.38	41.88±3.97
S/mS/mCNF	0.76±0.17	31.88±2.40

Source: Authors.

Figure 4

Typical Stress x Strain curves for all films samples

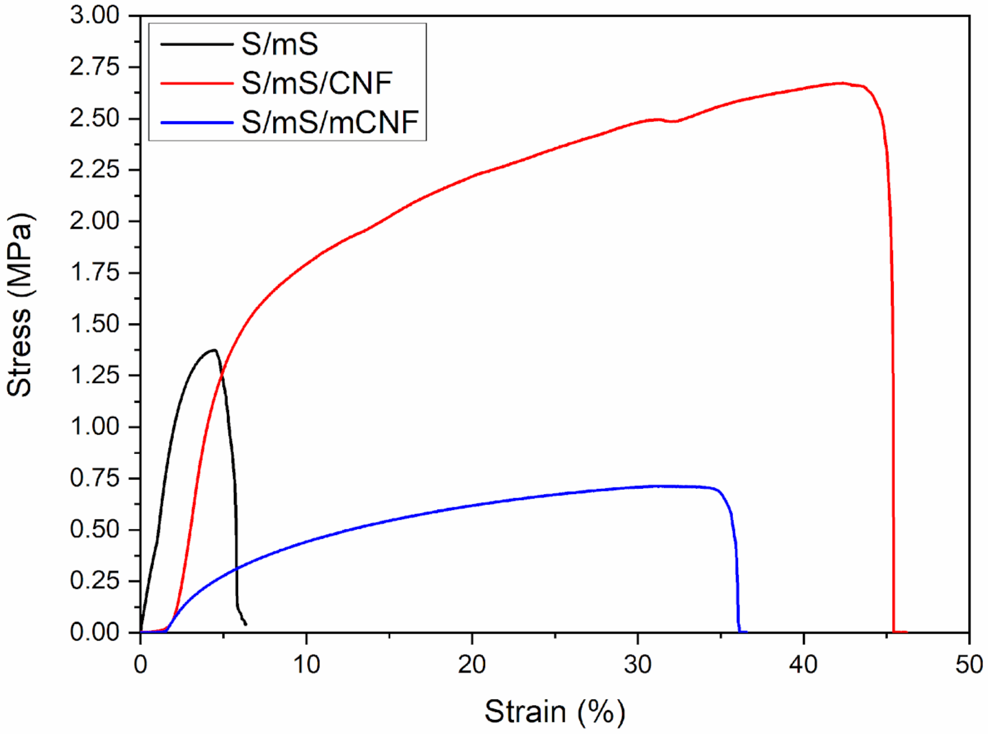

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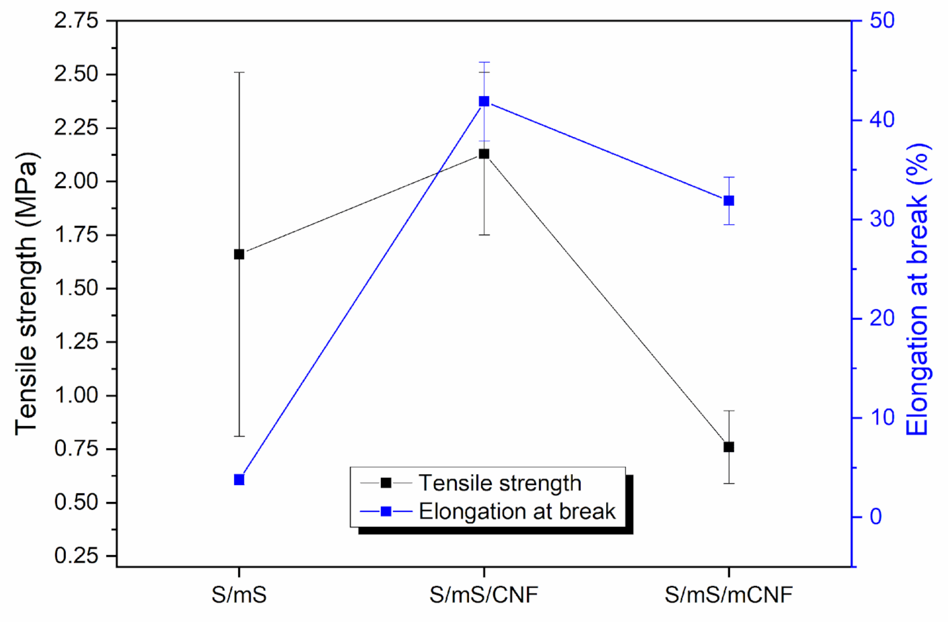
Figure 5

Tensile properties for all films samples



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In contrast, the incorporation of 1% hydroxypropylated CNF (mCNF) led to a significant reduction in tensile strength, dropping to 0.76 MPa. This decrease may be associated with the chemical modification of CNF, which introduces bulky hydroxypropyl groups that disrupt the hydrogen bonding network between CNF and the starch matrix [22]. As a result, the compatibility and interaction between the modified CNF and the starch components are weakened, leading to poor stress transfer and reduced mechanical performance. Probably, the presence of mCNF may have increased the moisture quantity within starch chains, when compared to CNF, decreasing its strength [25].

Interestingly, the tensile strength of the CNF-reinforced films (2.13 MPa) is comparable to that of thermoplastic starch/poly(butylene adipate-co-terephthalate) (TPS/PBAT) blends at an 80/20 ratio and three times higher than pure hydroxypropylated starch (HPS) films [26]. This suggests that the combination of native starch, hydroxypropylated starch, and unmodified CNF creates a synergistic interaction that enhances the mechanical robustness of the material, making it suitable for applications requiring moderate strength and flexibility.

The elongation at break values further elucidates the influence of CNF addition on the ductility of the films. The control film (without CNF) exhibited an elongation at break of 3.80%, indicative of its brittle nature. However, the incorporation of 1% unmodified CNF dramatically increased the elongation at break to 41.88%, demonstrating a substantial improvement in film ductility. This enhancement is likely due to the good interactions between CNF and starch chains [25], and the ability of CNF to form a percolated network within the matrix, which effectively dissipates stress and delays crack propagation under deformation.

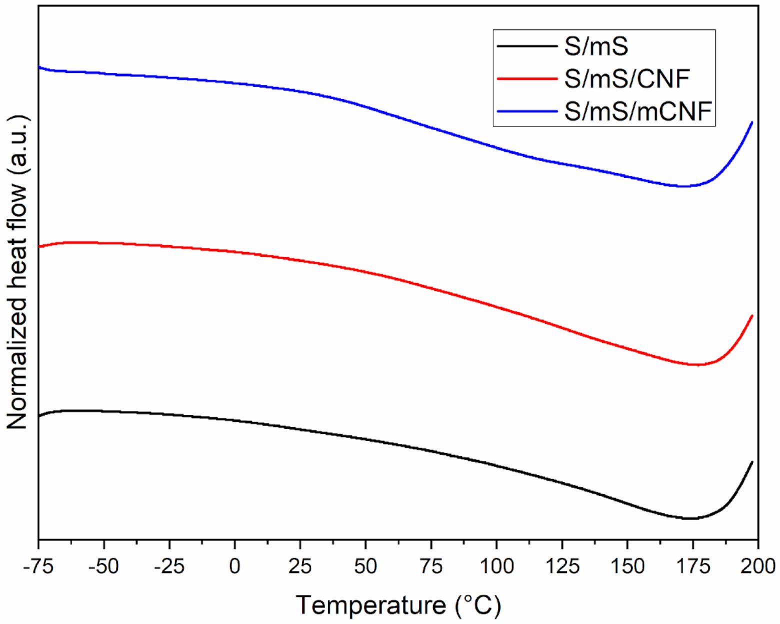
On the other hand, the film containing 1% hydroxypropylated CNF showed a lower elongation at break (31.88%) compared to the unmodified CNF-reinforced film. This reduction can again be linked to the disrupted interactions caused by the chemical modification of CNF, which compromises the structural integrity of the composite and limits its deformation capacity. Notably, the elongation at break of the unmodified CNF-reinforced film (41.88%) is approximately 30% higher than that of TPS/PBAT 80/20 blends and similar to pure HPS films [26]. This indicates that the hybrid system achieves a balance between ductility and strength, surpassing the performance of conventional biopolymer blends.

3.3 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The Differential Scanning Calorimetry (DSC) analysis of the starch-based films revealed no observable endothermic peaks corresponding to gelatinization or melting events during either the first or second heating scans (Figure 6). Additionally, no glass transition temperature (Tg) was detected. These findings can be interpreted considering the amorphous nature of the material and the effects of processing conditions, as well as the presence of plasticizers and hydroxypropylated starch (HPS) [1].

Figure 6

Second heating scan of DSC analysis for all films samples



Source: Authors.

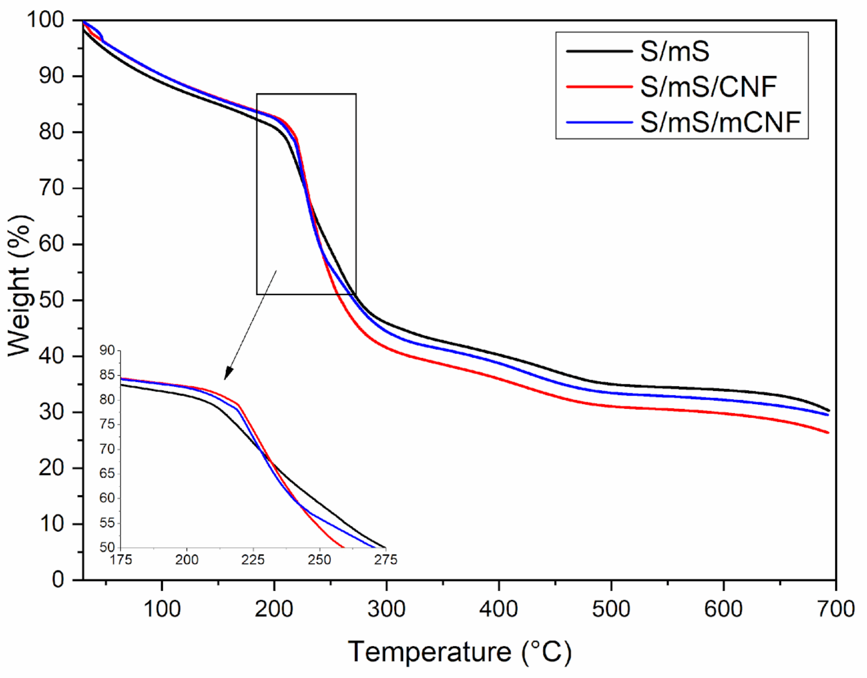
The lack of endothermic peaks associated with gelatinization or melting during all cycles suggests that the starch within the films is fully amorphous and is not retrograding. This outcome is positive, which the presence of hydroxypropyl groups and CNF likely prevented the reorganization of starch chains into crystalline structures [22, 26]. Furthermore, the presence of glycerol, water, and hydroxypropylated starch (HPS) likely contributed to the stabilization of the amorphous phase. Glycerol acts as a strong plasticizer, disrupting hydrogen bonding between starch chains and preventing recrystallization. Similarly, HPS, with its bulky hydroxypropyl groups, further inhibits the formation of ordered structures, reinforcing the amorphous nature of the material.

3.4 THERMOGRAVIMETRY (TG)

The initial weight loss observed at lower temperatures in Figure 7 is likely associated with the evaporation of volatile components, such as excess of plasticizer (e.g., glycerol), water, and any residual processing aids (e.g., polyols or PO). This step is typical for starch-based materials, where plasticizers like glycerol and absorbed water are present. The volatilization of these components occurs below 200 °C, consistent with their low thermal stability and high mobility within the amorphous matrix. The primary decomposition of the polysaccharide chains occurred near 225 °C, followed by carbonization at higher temperatures (Figure 8). This behavior is characteristic of starch-based systems [25], where the glycosidic bonds in the polysaccharide backbone begin to break down. The onset of decomposition at this temperature range indicates the thermal stability limit of the starch matrix under the experimental conditions.

Figure 7

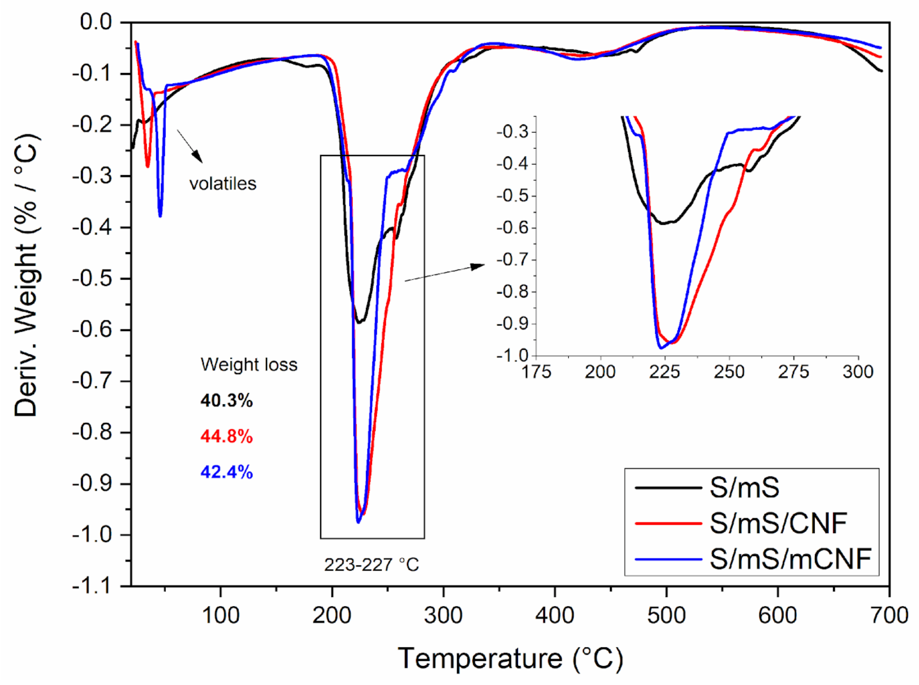
TG curves for all films samples



Source: Authors.

Figure 8

DTG curves for all films samples



Source: Authors.

Notably, the incorporation of 1% unmodified cellulose nanofibrils (CNF) enhanced the thermal stability of the films. Respectively, samples S/mS, S/mS/CNF and S/mS/mCNF presented T_{onset} values of 193.28, 198.89, 195.79 °C. This slight improvement can be attributed to the increased interactions between CNF and the starch matrix, more prominent for the unmodified CNF, which increases the overall cohesion and resistance to thermal degradation. Similar findings have been reported in previous studies, where the addition of CNF improved the thermal stability of biopolymer composites due to enhanced interfacial adhesion and reduced segmental mobility [25].

4 CONCLUSION

This study successfully investigated the structural, mechanical and thermal properties of native starch (S)/hydroxypropylated starch (mS) films, reinforced with cellulose nanofibrils (CNF) and modified cellulose nanofibrils (mCNF), aiming to develop sustainable biocomposites with balanced performance. The incorporation of CNF significantly enhanced the tensile strength of the films, demonstrating its effectiveness as a reinforcing agent by improving interfacial adhesion and stress transfer within the starch matrix. Conversely, the addition of mCNF led to a reduction in tensile strength, suggesting that the chemical modification performed may disrupt its reinforcing capabilities due to altered interactions with the starch matrix and the presence of moisture.

Thermal characterization through DSC and TG showed plasticizing effect of PPO and an increase of thermal stability of the biocomposites with CNF. FTIR analysis confirmed molecular interactions between the components, supporting the observed mechanical and thermal behaviors. The synergistic combination of modified starch, native starch, and CNF offers a promising pathway for developing advanced, sustainable, and high-performance starch-based biocomposites with reduced reliance on synthetic plasticizers. Future work should focus on optimizing the mCNF modification process to enhance its compatibility and reinforcing efficiency within the starch matrix, further advancing the development of fully bio-based and mechanically robust materials for diverse applications.

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