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REGENERATION AND PLASTICIZATION OF CELLULOSE FILMS THROUGH IMMERSION IN AQUEOUS GLYCEROL BATHS

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Abstract – Cellulose, the most abundant natural polymer, is traditionally used in fibrous form, but its insolubility limits broader applications. Regeneration into cellulose II offers a way to expand its use. However, conventional methods often result in brittle materials. This work aimed to plasticize regenerated cellulose (RC) by incorporating glycerol during regeneration, preventing strong hydrogen bonding. Cellulose xanthate solution was prepared and then its film form immersed in glycerol/water baths concentration (0-100% v/v), for regeneration and *in-situ* plasticization. Characterization included visual inspection, dimensional analysis, SEM, TGA, XRD and tensile testing. Higher glycerol bath concentrations improved flexibility and transparency, while lower concentration (<20%) led to significantly shrinkage (~50%). SEM confirmed homogeneous and free-porous structures; XRD confirmed cellulose I to II transition; and TGA showed progressive glycerol incorporation. Tensile test revealed a window between 2.5%-10% glycerol in the immersed bath to obtain a plasticized RC films, with elongation at break reaching up to 300% and a balanced strength and modulus. These flexible films show potential for uses in polymer blends, expanding the application of cellulose in its dissolved and regenerated form.

Keywords: *Plasticized cellulose; Regenerated cellulose films; Cellulose Dissolution; Regeneration by immersion; Regenerated cellulose properties.*

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Introduction

Cellulose-based materials are considered promising alternatives to non-biodegradable synthetic polymers due to their biodegradability, abundance, and renewable characteristics. Cellulose primary application has been widely used from nano- to macroscale forms, and commonly used as fibers and extends to the production of paper, cardboard and composite materials [1]. To expand its use, the derivatization of cellulose, its dissolution and subsequent regeneration to another polymorph type of cellulose offers innovative pathways to enhance utility of regenerated cellulose, showcasing potential applications beyond its traditional roles as fiber raw material [2]. However, its inherent insolubility, resulting from extensive hydrogen bonding, limits its direct use in broader cellulose applications. One strategy to overcome this challenge involved derivatizing cellulose, followed by dissolution and regeneration into a new polymorphic form know as cellulose type II [3]. Regenerated cellulose has been often produced through the viscose process, where cellulose is derivatized into cellulose xanthate and extruded into an acid bath for regeneration. This method is well-established, economically viable, and produces homogeneous, spinnable cellulose, especially suitable for the textile industry. However, the acidic regeneration environment results in materials that are fragile, porous, and prone to breakage, due to the formation of strong hydrogen cellulose-cellulose bonds during regeneration [4]. Although the final product is biodegradable, its low mechanical strength restricts their application in areas that demand mechanical performance, especially in flexible packaging and devices. To overcome these limitations, additional steps, such as plasticizer incorporation, are required to improve flexibility and make regenerated cellulose more suitable for uses where deformability is essential. Several strategies have been explored to enhance the mechanical properties of regenerated cellulose [5]. In many approaches, the addition of plasticizers is performed in a separate step after regeneration, requiring additional processing stages [6], [7]. Plasticizers such as glycerol reduce the intensity of hydrogen bonding between cellulose

chains, making the films less brittle and more flexible. These results point to a viable route for producing biodegradable, flexible films with improved handling and performance [8].
In this work, we proposed a methodology to obtain flexible and continuous regenerated cellulose films by incorporating a plasticizer agent during the regeneration process, through immersion of coagulated xanthate cellulose films in aqueous glycerol baths or systems. This strategy aimed to improve flexibility and mechanical behavior of regenerate cellulose materials. An aqueous regeneration system, such as glycerol/water, low-cost and easy to handle, offers advantages over acidic regeneration systems currently employed and has good potential for the preparation of regenerated cellulose-based materials. Different immersion bath concentration was used to regenerated and plasticized cellulose, to obtain homogeneous and flexible films by casting.

Experimental

Material and Preparation

Bleached eucalyptus pulp (Suzano S.A, Brazil), NaOH solution (6% and 18%), and glycerol were used. A viscose solution was prepared by reaction 4g of cellulose pulp in 125 ml of 18% NaOH at 40°C for 20 minutes, followed by CS_2 addition (1.5 ml) and standing at room temperature for 3 hours. Then, 75 ml of 6% NaOH was added and stirred for 48 hours to complete dissolution. Coagulation occurred in Teflon plates (76 mm diameter) over 24 hours in air-drying. The coagulated films were regenerated by immersion in glycerol/water baths with concentration ranging from 0% to 100% glycerol (v/v). The regenerated cellulose (RC) films were named RC-RS0G to RC-RS100G, according to glycerol content in regenerated system (RS). Fresh samples were air-dried and then conditioned by storing at 21°C and 53% RH until equilibrium.

Material characterization

The regenerated cellulose films were characterized thought visual inspection, and were reported mass, diameter and thickness. Morphology was also analyzed via SEM at 5000x magnification after gold coating. Compositional analysis was evaluated by TGA (20-600°C, under nitrogen atmosphere, ASTM E1131). XRD was used to verify cellulose regeneration into type II, with scans from 5° to 60° (2θ). Mechanical behavior was assessed by tensile test (ASTM D882), for samples regenerated in 0-100% glycerol immersion bath system.

Results and Discussion

Different immersion bath concentrations were used to regenerate, and in-situ plasticize cellulose, aiming to produce homogeneous and flexible films by casting. The effect of glycerol concentration in the immersion baths was evaluated for conditioned regenerated cellulose (RC) films (53%RH and 21°C), as presented in Fig 1. All films were prepared using 10g of cellulose xanthate viscous solution in 76 mm diameter Teflon dish, with a cellulose content of approximately 4.5%.

Visual and Morphological Observations:

Visual differences were immediately observed, as seen in Fig 1a, where RC-RS0G (Without glycerol) showed an opaque and rigid appearance, while RC-RS100G (100% glycerol bath) presented a transparent and flexible structure. This visual transformation suggests that glycerol content plays a key role in improving film flexibility and visual homogeneity. The flexibility was further confirmed through manual deformation test, indicating increased of ductility with higher glycerol concentrations. Qualitatively, at concentration above 7.5% glycerol in bath, films become progressively more transparent. In terms of dimensions, as is showed in Fig 1b, an increasing trend in mass and diameter was recorded with higher glycerol content in the immersion baths, suggesting that glycerol uptake significantly contributed to the film's composition and dimensional expansion. Thickness, however, remained relatively constant, around 0.50 mm. Related to dimensional variation, samples regenerated with low glycerol levels suffered a 50% reduction in size. When regenerated in bath containing more than 40% glycerol, the materials were dimensionally more stable, with only 25% shrinkage. As glycerol concentration increases, free volume and chain mobility improve while maintaining overall structural integrity.

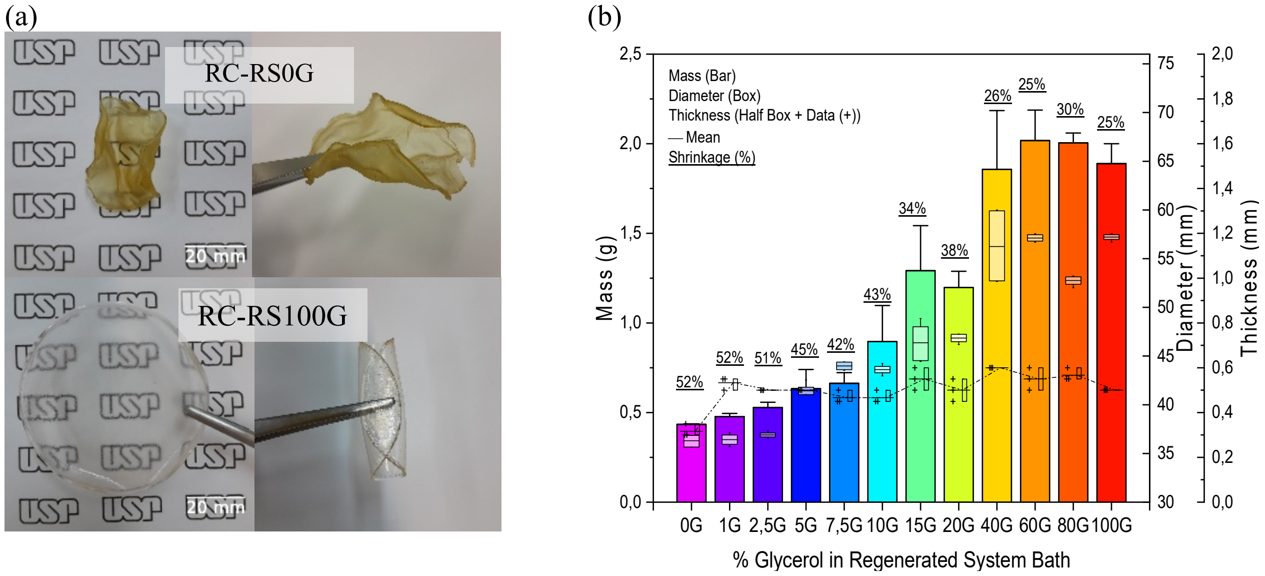

Figure 1 – (a) Visual appearance and shape behavior to manual deformation, and (b) Mass, diameter, thickness and shrinkage effect of conditioned plasticized RC films as a function of glycerol content in the immersion system bath (53% RH, 21°C). Casting technique. Diameter of Petri dishes used = 76 mm. Mass of Viscous Solution used = 10g.

SEM analysis:

To show the morphology of the cross section of the film, SEM analysis (Fig 2a) was performed for lower and higher glycerol content in baths. Samples exhibited homogeneous and dense structure with ductile fracture features, indicating of structural reorganization after regeneration [5]. Slightly variations in fracture surface roughness were observed on conditioned samples. At low glycerol concentrations in the regeneration baths (<5%), rougher and more irregular fracture surfaces were associated with the higher shrinkage values. In contrast, at higher glycerol concentration in the immersion bath (>20%), approaching glycerol saturation level, the fracture surfaces appeared smoother and more homogeneous consistent with lower shrinkages.

Compositional analysis by TGA:

Compositional analysis by TGA, as is shown in Fig 2b**,** illustrates the compositional profiles of regenerate cellulose samples obtained by TGA, to emphasize the influence of glycerol concentration in the immersion bath (0-100%) on glycerol and regenerated cellulose content. Based on glycerol and cellulose composition in samples, a transition was observed from a cellulose-rich to a glycerol-rich material. Samples regenerated in bath with > 5% glycerol showed a marked increase in glycerol composition content (from 31% to 58%) and a reduction in cellulose proportion (41% to 18%). Samples regenerated using low glycerol immersion bath concentration (RC-RS1G to RC-RS5G), glycerol incorporation remained in the range of 6%-18% of the total sample composition and regenerated cellulose remained the main component with more than 50% in mass. In this way, these samples resulted in a material still rich in regenerated cellulose and defined a plasticization window for plasticized regenerated cellulose. Samples regenerated in glycerol bath concentration >20% glycerol, were materials rich in glycerol and glycerol saturation level was reached.

*X-Ray Diffraction***:**

XRD tests were conducted to identify the presence of crystalline phases and ensure the regeneration of cellulose into cellulose type II. The XRD patterns are shown in Fig 3a. The XRD pattern of cellulosic pulp (type I) shows characteristic diffraction peaks at around 2θ =15.6°, 16.7° and 23.1°. These peaks are associated with the native cellulose I crystalline form, indicating the presence of the ordered structure of cellulose pulp before dissolution. After dissolution and regeneration, the RC samples exhibited notable changes in the diffraction patterns. The primary diffraction peaks appear at 2θ = 12.2°, 20.3° and 22°, which are characteristic of cellulose II [9].

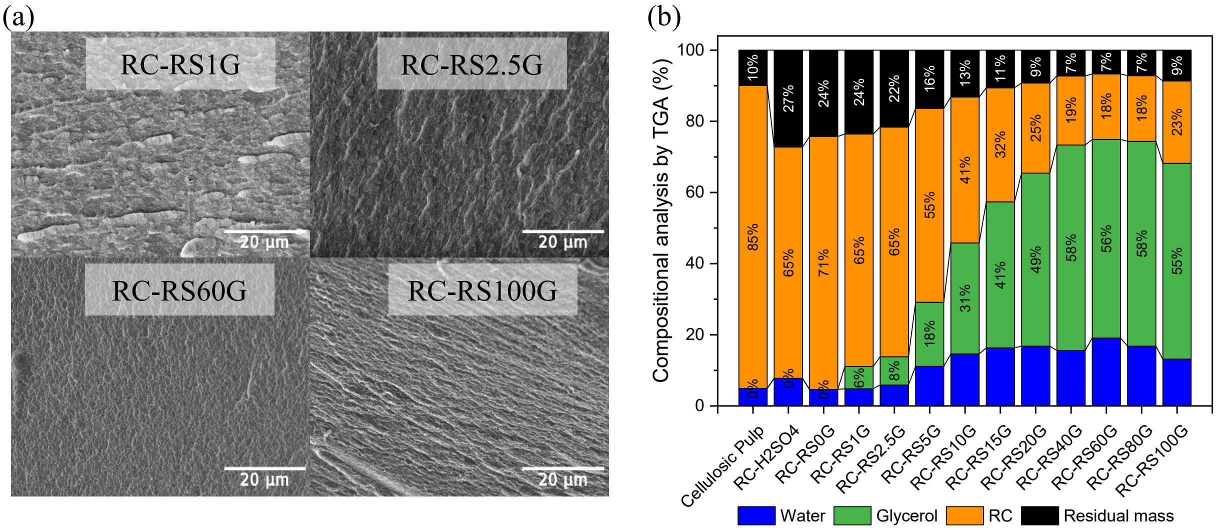

Figure 2 – (a) Cross-sectional SEM micrographs 5000x, samples in bath immersion with low and high Glycerol content, and (b) Compositional analysis by TGA of conditioned plasticized RC films as a function of glycerol content in the immersion system bath (53% RH, 21°C).

This transformation from cellulose I to cellulose II is typical in regenerated cellulose processes and well-document in the literature, where the dissolution and regeneration disrupt the native crystalline arrangement and allow for a new arrangement [5]. The XRD results demonstrated that glycerol concentration in bath plays a critical role in determining the crystalline structure of RC. A low glycerol concentration in baths (0-5%) favors higher crystallinity, while a higher glycerol concentration (≥40%) promotes amorphous structures, also due to samples reached the glycerol saturation stage.

Mechanical properties – Tensile Test:

While cellulosic pulp maintains its fiber network, the regenerated and in-situ plasticized cellulosic material showed a continuous and homogeneous network, as previously showed in SEM micrographs (Fig 2a). This change significantly altered the mechanical response of the regenerated cellulose-based materials obtained from aqueous glycerol regeneration baths. Tensile stress-deformation curves are shown in Fig 3b. The 0% glycerol-cellulosic material (RC-RS0G) revealed a stiffer and more brittle behavior, characterized by a sharp increase in stress and a sudden fracture at low strain (~48%). As glycerol content in the regeneration bath increased, a progressive change in the behavior of the curves were observed.

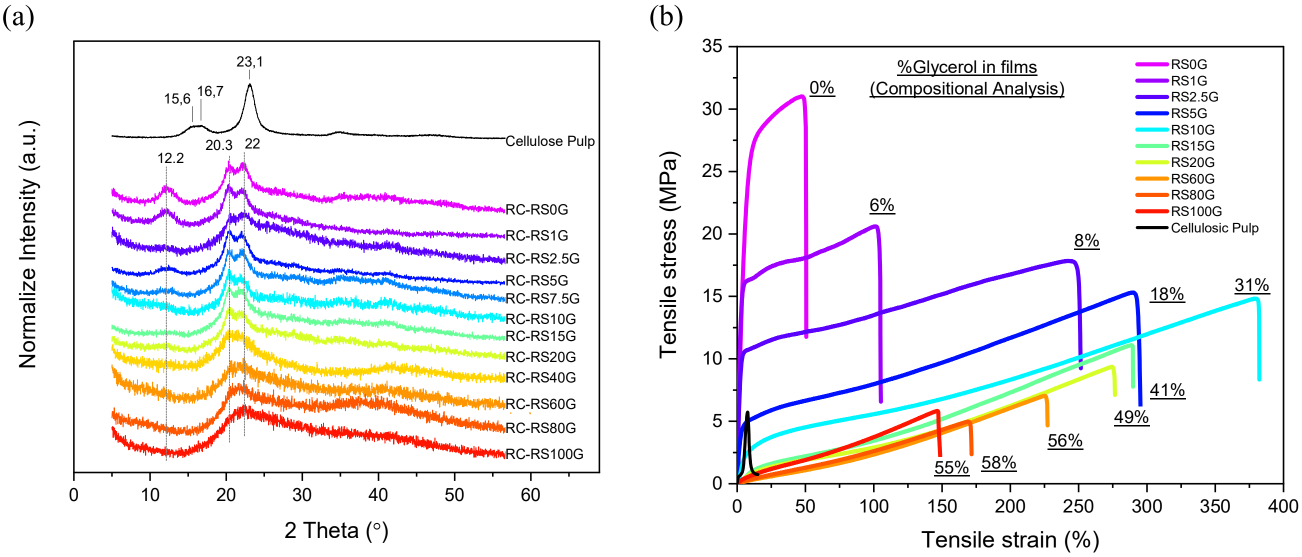

Figure 3 – (a) X-Ray Diffraction patterns and (b) Tensile strain-stress curves of conditioned plasticized RC films as a function of glycerol content in the immersion system bath (53% RH, 21°C).

The materials became less rigid and show more pronounce elongation (~50-350%), particularly in the 2.5%-10% glycerol bath content, indicating the onset of plasticization during the regeneration-in situ plasticization process. At higher glycerol concentrations in baths (≥ 15%), the films exhibited also a markedly ductile profile, with lower stress values and relatively higher deformation at break (300-150%), consistent with flexible material behavior.

Conclusions

This study demonstrated that regenerated cellulose films could be effectively plasticized by incorporation glycerol during the regeneration step. The approach resulted in continuous, transparent and flexible films, with improved ductility as glycerol content increased. At low glycerol concentration (<5% in bath), materials were rich in regenerated cellulose, showing significant shrinkage and higher stiffness. In contrast, higher glycerol contents (>20% in bath) led to glycerol-rich films, with reduced shrinkage and improved flexibility, though with lower mechanical strength. A defined plasticization window was identified between 2.5% and 10% glycerol in the immersion bath, corresponding to ~8% - 18% glycerol in films. Within this range, films exhibited balanced mechanical properties, maintaining integrity while gaining ductility.

The reduction in modulus and tensile strength, alongside increased elongation at breaks, confirmed that glycerol effectively reduced intermolecular interactions and enhanced chain mobility during regeneration. These finding support the proposed methodology as a viable strategy for producing flexible and homogeneous regenerated cellulose materials. As the plasticization window was defined and flexible regenerated cellulose films were successfully obtained, future works will explore the use of this plasticized regenerated cellulose as a matrix to be blended with other polymers. This approach aims to expand the use of cellulose to develop new cellulose-based materials from its dissolved and regenerated state rather than from its fibrous form.

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