Biohydrogel 3D printing: a feasible circular economy strategy for eco-friendly cellulose obtention from olive waste and its application in various fields

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Abstract

Cellulose extracted from olive tree pruning waste was used as a sustainable reinforcement in synthetic hydrogels based on acrylamide and epichlorohydrin. The cellulose-rich fraction was obtained through conditioning and chemical treatment of olive pruning biomass, contributing to the valorization of agricultural residues. Hydrogels containing commercial cellulose and cellulose extracted from olive tree pruning waste were synthesized to investigate the influence of cellulose source on swelling behavior and structural properties. Swelling tests over 24 h showed that all samples exhibited significant water absorption and dimensional expansion compared to the dry state. Cellulose content affected swelling capacity and dimensional stability, indicating changes in polymer network organization and water diffusion. The interaction between cellulose and the polymer matrix promoted porous structures favorable for water retention. These results demonstrate the potential of olive pruning waste as a renewable source for hydrogel production, with promising applications in sustainable materials. Further structural, thermal, and morphological analyses will be performed to better understand their properties and application potential.

Introduction

Agriculture plays a central role in the socio-economic development of Mediterranean countries, with the olive sector representing one of its most important pillars. Olive groves cover approximately 11.5 million hectares worldwide, accounting for nearly 1% of the planet's arable land, with Spain standing as the largest producer, contributing around 42% of global olive oil production [1]. This significant agricultural activity, however, generates substantial quantities of biomass residues, including pruning waste (branches, leaves, and wood) and processing by-products such as olive pomace and olive mill wastewater. It is estimated that nearly 70% of olive-derived residues are not efficiently valorized, highlighting a considerable opportunity for developing innovative routes for waste conversion into high-value products [2].

In the context of environmental sustainability, the agricultural sector is increasingly required to transition from linear resource consumption to regenerative systems based on circular economy principles. Within this framework, agricultural residues can serve as renewable feedstocks for advanced biomaterials, contributing to waste reduction while creating new industrial applications. Among the available biopolymers, cellulose is the most abundant renewable material in the biosphere, representing approximately 50% of plant biomass. It can be extracted from agro-industrial residues through chemical and mechanical treatments, enabling the transformation of low-value waste streams into functional bio-based materials [3].

The extensive intra- and intermolecular hydrogen bonding in cellulose, derived from hydroxyl groups, gives rise to a highly crystalline structure and low solubility in water. Nevertheless, these characteristics also make cellulose an attractive reinforcing biopolymer for hydrogel systems, where its abundance, biodegradability, non-toxicity, and structural versatility offer advantages over conventional petroleum-based materials. In recent years, cellulose-based biohydrogels (BHGs) have attracted considerable attention due to their potential applications in agriculture, water management, bioplastics, refrigeration systems, and environmental remediation [4].

BHGs are three-dimensional networks of hydrophilic polymers capable of absorbing and retaining large quantities of water while maintaining their structural integrity. Their final properties strongly depend on the type and concentration of monomers, crosslinkers, and biopolymers incorporated during synthesis. The incorporation of selected compounds into the polymeric network can significantly improve thermal stability, water retention capacity, swelling degree, and mechanical resistance. In particular, materials containing ionic groups tend to exhibit enhanced water absorption due to stronger interactions with water molecules. These characteristics are especially relevant for applications involving moisture control or liquid separation processes, where hydrophilicity and monomer polarity directly influence performance.

Among synthetic monomers, acrylamide (AAm) is one of the most extensively used in hydrogel production due to its hydrophilic nature, high water retention capacity, favorable mechanical properties, and ease of polymerization. Graft polymerization involving cellulose can be initiated through radical formation on the

cellulose surface, enabling the propagation of acrylamide chains and the formation of hybrid hydrogel networks [5]. While most cellulose hydrogel studies employ epichlorohydrin as a crosslinking agent, this route generally requires thermal induction and often relies on conventional cellulose sources, rather than biomass residues [4]. Consequently, sustainable alternatives based on waste-derived cellulose remain underexplored.

As an initial proof-of-concept, this work evaluates the feasibility and quality of hydrogels prepared using extracted cellulose from olive pruning. Two hydrogel formulations were synthesized, differing according to the cellulose source, and their performance was preliminarily assessed through swelling behavior, which is a key parameter for determining water uptake capacity and network formation. The comparison between these materials provides a first understanding of how waste-derived cellulose influences hydrogel properties and supports future developments toward sustainable 3D-printable biomaterials. This strategy contributes not only to the valorization of olive agricultural residues but also to the establishment of a regenerative circular pathway capable of supplying bio-based materials for diverse technological applications.

Therefore, this study aims to evaluate the feasibility of using cellulose extracted from olive pruning waste as a reinforcing and structuring component in synthetic hydrogels, comparing its performance with commercial cellulose through swelling behavior analysis.

Methodology

Extraction of cellulose from pruning (olive waste)

The olive tree pruning used as raw material for cellulose production was previously pretreated according to the procedure described in our earlier study [6]. In summary, the biomass was initially subjected to mechanical conditioning, including grinding and sieving, followed by a two-step chemical treatment to obtain a cellulose-rich pulp. The first step consisted of acid hydrolysis using nitric acid at 8% (v/v), conducted at 90 °C for 240 min. This treatment promoted the partial removal of hemicellulose and lignin. The resulting material was subsequently submitted to alkaline hydrolysis with sodium hydroxide at 6% (w/v), carried out at 75 °C for 105 min, aiming to further purify the cellulose fraction. To increase cellulose purity, the treated biomass was then submitted to a bleaching step using a 2% (v/v) aqueous hydrogen peroxide solution at a solid-to-liquid ratio of 1:20, under heating at 70 °C for 1 h. Prior to bleaching, the pH was adjusted to 11–12 by the addition of sodium hydroxide. After bleaching, the sample was washed with water until neutral pH was reached and dried at room temperature. The cellulose obtained from this process, used in the subsequent hydrogel synthesis steps, presented a composition of approximately 95% cellulose [6].

Production of the cellulose hydrogels

Two types of hydrogels were prepared in this study: polyacrylamide hydrogels grafted onto cellulose and cellulose-based hydrogels crosslinked with epichlorohydrin. For both systems, the synthesis was carried out by varying the cellulose source, using either commercial cellulose or cellulose extracted from olive pruning residues. This approach enabled the assessment of the influence of cellulose origin on the synthesis process and on the physicochemical properties of the resulting hydrogels. The experimental procedures adopted for the preparation of each material are described in the following sections and were carried out following the methodologies previously reported [3-4].

1.Polyacrylamide hydrogels grafted onto cellulose

The hydrogel was synthesized with 4.8 g of acrylamide (AAm), 0.2 g of cellulose, 1 mL of TEMED (0.57 mol.L^{-1}, used as a catalyst) and MBAAm (0.015 mol per mol of monomers, used as a crosslinker). A total of 0.02 g of initiator ($Na_2S_2O_8$) was added to the mixture alongside 45 mL of distilled water. Then, the mixture was stirred until complete solubilization. Nitrogen (N_2) was bubbled into the solution until gel formation. After completion of the reaction, approximately 24 h, the hydrogels were cut and washed with distilled water to remove excess monomers. Samples were oven-dried at 60 °C until constant mass. At the end of the synthesis, two distinct hydrogels were obtained. These materials were designated as polyacrylamide hydrogel grafted onto commercial cellulose (**polyAAm-g-CC**) and polyacrylamide hydrogel grafted onto cellulose extracted from olive pruning residues (**polyAAm-g-CO**).

2.Cellulose hydrogels using epichlorohydrin as a crosslinker agent

To prepare the cellulose solution, a solvent system containing sodium hydroxide, urea, and water was formulated in a weight proportion of 7.5:11.5:81. Cellulose was then incorporated at a concentration of 4 wt%, and the suspension was stirred continuously for 2 h at 5 ± 2 °C to promote dissolution. Once a homogeneous mixture was obtained, it was kept at −18 ± 2 °C for 30 min and subsequently stored at 2.5 ± 0.8 °C for a maximum period of 24 h. For hydrogel formation, the cellulose solution was warmed to 30 °C and combined with 10 vol% epichlorohydrin. The mixture was maintained under stirring at 750 rpm for 1 h to ensure proper interaction between the components. Crosslinking was then induced by placing the material in a conventional oven at 60 °C for 4 h. After gelation, the obtained hydrogels were shaped into disks of approximately 1.0 cm in diameter. The samples

were immersed in distilled water for 24 h to remove residual reagents and impurities, followed by drying in a conventional oven at 60 °C. At the end of the synthesis, two distinct cellulose-based hydrogels crosslinked with epichlorohydrin were obtained. These materials were designated as commercial cellulose hydrogel crosslinked with epichlorohydrin (**CC-epi**) and olive pruning-derived cellulose hydrogel crosslinked with epichlorohydrin (**CO-epi**), according to the cellulose source used in their preparation.

Swelling in the presence of water

In this experiment, approximately 0.1 g of dried hydrogel was immersed in 200 mL of distilled water and kept in a thermostatic bath at 22 °C for 24 hours. The swelling was assessed by gravimetry and calculated using Eq. 1, where W_t represents the swelling degree ($g.g^{-1}$) at time "t" and m_0 and m_t are the masses (g) of the hydrogels at the beginning and after time "t" of swelling. All experiments were performed in triplicate.

$$W_t = \frac{m_t - m_0}{m_0} \quad (1)$$

Results

The swelling degree is a key parameter for evaluating hydrogel performance, as it reflects the balance between water diffusion into the polymeric matrix and the elastic resistance imposed by the crosslinked structure. During the swelling process, water initially interacts with hydrophilic groups in the polymer chains, promoting expansion of the network until equilibrium is reached between osmotic forces and the restoring elastic forces. Thus, water absorption depends not only on chemical composition but also on crosslinking density, polymer flexibility, and the structural characteristics of the raw materials [3-4].

The hydrogels containing acrylamide exhibited the highest swelling degrees, with polyAAm-g-CC and polyAAm-g-CO reaching 9.80 and 10.07 $g.g^{-1}$, respectively (Table 1). This behavior is consistent with the highly hydrophilic nature of acrylamide-based networks, which contain amide groups capable of establishing strong interactions with water molecules. In addition, the flexible polyacrylamide chains facilitate water diffusion and retention throughout the three-dimensional structure [7-8]. Since these formulations were composed predominantly of acrylamide and contained only a small amount of cellulose, the swelling behavior was mainly governed by the synthetic polymer matrix. The small difference between polyAAm-g-CC and polyAAm-g-CO indicates that cellulose origin has a secondary influence in these formulations. It is possible to visualize the dimensional expansion observed after 24 h, where polyAAm-g-CO increased from 0.82 cm to 1.76 cm, while polyAAm-g-CC increased from 0.75 cm to 1.35 cm (Figure 1).

A different behavior was observed for the hydrogels prepared exclusively from cellulose crosslinked with epichlorohydrin. The CC-epi and CO-epi samples exhibited lower swelling degrees, reaching 3.74 and 6.36 $g.g^{-1}$, respectively (Table 1). In these systems, the cellulose source played a more relevant role because the hydrogel network was formed entirely by cellulose, making the intrinsic characteristics of the biopolymer determinant for the final structure. Epichlorohydrin promotes the formation of ether bridges between cellulose chains, generating a crosslinked network that is generally denser and more rigid than acrylamide-based hydrogels. This compact structure limits chain mobility and restricts water diffusion, leading to lower swelling capacity. The higher swelling observed for CO-epi indicates that the extracted cellulose contributes to a less compact and more accessible structure, probably due to modifications introduced during the extraction process. Structural factors such as reduced crystallinity and greater porosity may increase the accessibility of hydroxyl groups, facilitating water penetration. Previous studies report that these cellulose characteristics directly affect the porosity and swelling of epichlorohydrin-crosslinked hydrogels, which supports the superior performance of the extracted cellulose in this formulation [9-10]. The visual analysis after 24 h swelling further complements the gravimetric results by revealing that dimensional expansion does not always directly correlate with mass gain. CC-epi increased from 1.12 cm to 2.08 cm, whereas CO-epi expanded from 1.38 cm to 1.61 cm (Figure 1). Although CO-epi presented higher gravimetric swelling, CC-epi showed greater dimensional expansion. This suggests that water distribution within the hydrogel matrix differs according to the internal structure. In some cases, the material may undergo significant external expansion while retaining less water overall, depending on how the polymer chains reorganize and how water is distributed between external and internal regions.

These observations demonstrate that gravimetric swelling and dimensional expansion provide complementary information about hydrogel behavior. While the swelling degree reflects the total amount of absorbed water, dimensional measurements indicate how the network responds structurally during hydration. The results show that hydrogel composition is the main factor controlling water uptake, with acrylamide-based systems displaying superior absorption due to their highly hydrophilic matrix. However, the cellulose origin becomes more significant when cellulose constitutes the main structural component. In both synthesis routes, the cellulose extracted from olive pruning showed favorable performance, confirming its potential as a renewable precursor for the development of sustainable hydrogels and supporting its future application in advanced bio-based materials.

Table 1. Swelling degree of the hydrogels after 24 hours.

W ($g.g^{-1}$) after 24 h	polyAAm-g-CC	polyAAM-g-CO	CC-epi	CO-epi
	9.80 ± 0.08	10.07 ± 1.09	3.74 ± 0.13	6.36 ± 0.42

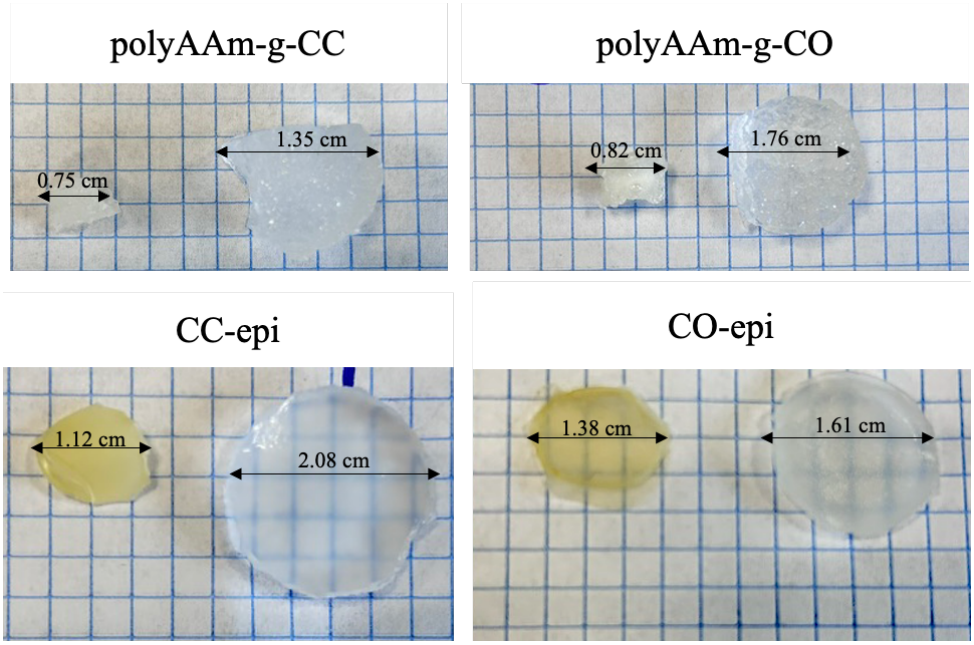

Figure 1. Comparison of cellulose-based hydrogels in the dried state and after 24 h of swelling.

Conclusion

In summary, the results demonstrate that both hydrogel composition and cellulose origin influence swelling behavior, although their effects vary according to the synthesis route. The acrylamide-based hydrogels showed higher swelling due to the predominance of the hydrophilic polyacrylamide matrix, while the cellulose-based hydrogels crosslinked with epichlorohydrin presented lower water absorption as a result of their denser and more rigid structure. In both systems, the cellulose extracted from olive pruning exhibited promising performance, particularly in terms of gravimetric swelling, indicating that this agricultural residue can be successfully valorized as a renewable precursor for hydrogel production. These preliminary findings highlight the potential of olive pruning-derived cellulose for sustainable biomaterial development and reinforce its applicability within a circular economy framework. Further analyses, including structural, thermal, morphological, and mechanical characterisation, will be carried out to provide a deeper understanding of the hydrogel networks, clarify the observed swelling behavior, and better assess the properties and potential applications of the produced materials.

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