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Research Article

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Cellulose-Based Superabsorbent Hydrogels for Hygiene Applications: A Study of Absorbency Properties

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Abstract

Superabsorbent polymers (SAPs) are widely used in hygiene products, but commercial polyacrylate SAPs raise environmental concerns due to their lack of biodegradability. Research on bio-based SAP alternatives has focused on maximizing water absorption and related parameters, rather than considering scenarios that reflect application conditions. In this research, we explored fully bio-based SAPs made from cellulose derivatives and starch crosslinked with citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA). The parameters for hygiene applications in saline solutions, including absorption under load (AUL), centrifuge retention capacity (CRC), and swelling kinetics, and their relationships with crosslinker type, concentration, network properties, and morphology, were studied. The optimized performance resulted in an AUL of 9 g/g and a CRC of 22 g/g. The network parameters for this performance achieved a storage modulus (G') of 150–200 Pa and a mesh size of 2.8×10^{-8} m. A CA–BTCA blend showed improved fluid uptake compared to single crosslinkers, indicating a synergy between network density and carboxylic groups.

Morphology was further adjusted through solvent exchange, which introduced macro porous and accelerated swelling but reduced mechanical strength, decreasing AUL to 3 g/g. These findings reveal a fundamental trade-off between swelling rate and retention in natural SAPs.

1.Introduction

Superabsorbent polymers (SAPs) are cross-linked hydrophilic materials that can absorb and retain large amounts of aqueous fluid relative to their own mass. Cross-linked polyacrylic acid (and its sodium salt) has been the dominant type of commercial SAPs due to its high absorbency (often more than 100 times its weight in water) and its ability to maintain mechanical integrity under load. (Mondal 2019). These properties have made polyacrylate SAPs indispensable in hygiene products such as baby diapers, sanitary pads, napkins, and adult incontinence products. However, the non-biodegradable nature of polyacrylic SAPs has raised environmental concerns. After disposal, these polymers persist in landfills and can contribute to microplastic pollution (Chen et al. 2025). With increasing legislative and consumer pressure to reduce persistent plastics, there is a growing need to develop sustainable, bio-based SAP alternatives.

One promising approach is to derive SAP hydrogels from natural polymers, e.g., polysaccharides such as cellulose and starch (Prasad et al. 2023), which are renewable and biodegradable. Researchers have focused on grafting vinyl monomers (such as acrylic acid) onto polysaccharide backbones to create “semi-synthetic” SAPs (Batara et al. 2025). These grafted hybrids still exhibit high absorbency and some biodegradability thanks to the natural component (Klinpituksa and Kosaiyakanon 2017). However, such systems still contain a fraction of non-degradable poly(acrylate) chains (Chen et al. 2025). To develop sustainable SAPs, recent efforts have focused on fully bio-based hydrogels made from natural polymers

and non-toxic crosslinkers. For example, researchers have developed SAPs using only renewable materials such as citric acid and other polycarboxylic acids as cross-linkers, resulting in products with moderate water absorbency but improved biodegradability (Shen et al. 2015).

Polyfunctional organic acids such as citric acid (CA), 1,2,3,4-butanetetracarboxylic acid (BTCA), and even dicarboxylic acids such as malic acid (Seidel et al. 2001) have gained attention as crosslinkers for natural-polymer hydrogels, since they can form a cross-linked network via ester or acetal linkages without the toxicity of conventional reagents (e.g., aldehydes or epichlorohydrin) (Zhang and Qiao 2021). Cellulose or starch-based hydrogels crosslinked with citric acid, for instance, have been reported to exhibit good swelling capacity. (Demitri et al. 2008; Prasad et al. 2023), making them a promising alternative for the synthetic version. However, previous studies have primarily focused on maximizing SAPs' water absorption capacity by optimizing the swelling ratio. (Chung et al. 2025). For instance, absorption under load (AUL), the ability of a swollen gel to retain fluid against pressure, and centrifuge retention capacity (CRC), the amount of fluid retained after centrifugation, are critical for hygiene applications. However, few reports detail these results for fully bio-based SAPs.

On the other hand, natural polymer hydrogels have shown limitations when compared to synthetic polyacrylates. The swelling of an ideal SAP involves four main mechanisms: osmotic pressure from ionized groups, elastic network expansion, polymer–water affinity, and porosity filling (Zhang et al. 2023). In cellulose-rich systems, each of these mechanisms is less efficient than in polyacrylates. Polysaccharides such as cellulose have a lower charge density (fewer dissociated ionic groups per gram) than neutralized poly(acrylic acid), thereby

limiting osmotic swelling. The cellulose backbone (even when modified, such as with carboxymethyl cellulose or other derivatives) is relatively rigid. It can form crystalline or hydrogen-bonded domains, reducing chain mobility and entropy-driven swelling. Moreover, unmodified polysaccharides are only moderately hydrophilic; they bind a thin layer of water but do not naturally absorb large quantities of fluid beyond that without osmotic drive from ionic groups. Introducing porosity (e.g., via freeze-drying to produce aerogels) can enhance initial water uptake, but such highly porous gels often collapse under load, resulting in poor retention when compressed. Thus, cellulose- and starch-based hydrogels tend to have lower, slower absorbency and especially struggle with retention under pressure compared to state-of-the-art polyacrylate SAPs.

To overcome these challenges, researchers have explored various chemical and structural modifications to natural polymers. Generally, the choice and amount of crosslinker are crucial for balancing absorbency. (Kabiri et al. 2003) and mechanical strength (Ramazani-Harandi et al. 2009; Seidel et al. 2001). A low crosslink density may yield a very high initial swelling, but the gel can become soft and prone to dissolution if it is too loosely cross-linked. Conversely, excessive crosslinking produces a rigid network that prevents polymer expansion, thereby reducing swelling capacity. In synthetic SAPs, this principle is well established: for example, lightly surface-crosslinked polyacrylates achieve high AUL by reinforcing only the gel surface, preventing deformation, while preserving a loosely cross-linked interior for absorption.

In natural SAPs, finding this optimum is equally important. Indeed, a recent review on cellulose-based hydrogels emphasized that using too little crosslinker yields water-soluble polymers, whereas using too much crosslinker reduces swelling capacity (Nasution et al.

2022). The chemistry of the polymer backbone and crosslinker also plays a significant role. Polysaccharides differ in flexibility and hydrophilicity (e.g., starch is generally more amorphous and hydrophilic than native cellulose). Crosslinkers such as CA and BTCA differ in functionality and steric size, which can influence how efficiently they form crosslinks within a given polymer matrix (Omidian et al. 2024). Despite numerous studies on individual biopolymers and crosslinkers, the understanding of how base polymer type and crosslinker type/concentration affect absorption capacity, rate, and retention under load in bio-based SAPs is still emerging.

In this research, we address this gap by evaluating a series of bio-based superabsorbent hydrogels prepared from sustainable polymers and non-toxic crosslinkers. Specifically, it is investigated how (1) the base polymer type, (2) the crosslinker type (and concentration), and (3) the overall hydrogel network and morphology influence the performance of the hydrogels. Carboxymethyl cellulose (CMC) and a corn starch are chosen as representative polysaccharide bases, and they are cross-linked using citric acid (a tri-carboxylic acid) or 1,2,3,4-butanetetracarboxylic acid (BTCA, a tetra-carboxylic acid) under controlled conditions. The resulting hydrogels are characterized by total absorption capacity, absorption under load (AUL), centrifuge retention capacity (CRC), absorption rate, and elastic modulus from oscillatory rheology measurements. We hypothesize that a blend of citric acid and BTCA can achieve high AUL and CRC in CMC-based polysaccharide hydrogels by tuning the elastic modulus and the amount of carboxylic groups to an intermediate crosslink density that balances swelling capacity and mechanical stability. This comparative study aims to elucidate the absorption mechanisms in these natural-based systems and to identify design strategies to reconcile the trade-offs between swelling capacity and mechanical stability.

2. Materials and Methods

Hydroxyethyl cellulose (HEC, catalog no. 09368, viscosity 202 mPa·s, estimated viscosity-average molecular weight of 2.5×10^5 g/mol, Sigma-Aldrich), sodium carboxymethyl cellulose (CMC, catalog no. 332641000, average molecular weight 700,000 g/mol, degree of substitution 0.9, $\geq 99.5\%$ purity, Thermo Scientific Chemicals – USA), and native corn starch (Clinton 106 Corn Starch, Product Code 028106, ADM Corporation – Decatur, IL, USA) were evaluated as base polymers. Clinton 106 is an unmodified corn (*Zea mays*) starch with a typical amylose content of 25–28 wt.%. 1,2,3,4-Butanetetracarboxylic acid (BTCA, catalog no. 257303, $\geq 99\%$ purity, Sigma-Aldrich – USA) and citric acid (CA, catalog no. C0759, $\geq 99\%$ purity, Sigma-Aldrich – USA) were used as crosslinkers. All reagents were used as received without further purification. Deionized (DI) water was used for all synthesis procedures.

2.1. CMC - HEC-Based synthesis

The hydrogels were synthesized using two different polymer blends. The synthesis pathway for the crosslinking of each polymer involved esterification reactions, as shown in Figure 1. In the first set, HEC and CMC at a 1:3 weight ratio were dissolved in DI water under stirring at 900 RPM and 25 °C for 1 hour to prepare a homogeneous mixture with a total polymer concentration of 2% (Demitri et al. 2014). The gel was then crosslinked with either citric acid or BTCA for 3 h, followed by heating at 70 °C for 24 h to promote gelation and chemical crosslinking. The hydrogel was stored in a desiccator. The hydrogel was then ground and sieved to a size between 400 and 725 μm . A second formulation was evaluated by dissolving 3.5 wt.% CMC in deionized water under homogenization for 25 min, followed by the

addition of 1.5 wt.% starch. The mixture was mechanically stirred at approximately 900 rpm in a water bath at 60 °C for 3 h. Subsequently, citric acid or BTCA was added, and crosslinking continued for an additional one hour at 60 °C. The hydrogels were put in an oven at 70 °C for 24 h. The samples were ground and sieved to obtain particles in the 400-725 μm size range.

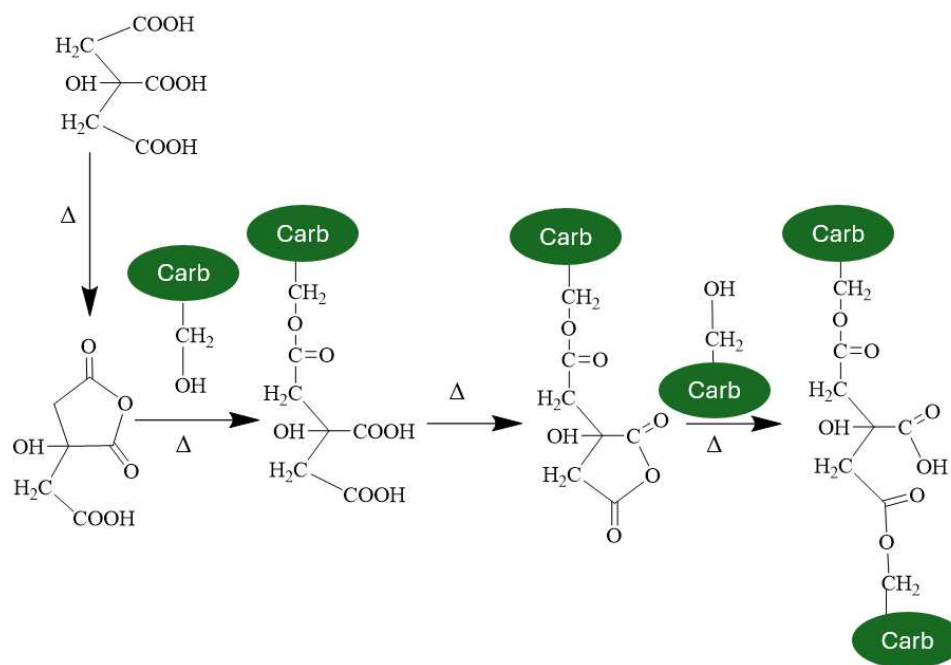


Fig. 1 Esterification of carbohydrates with citric acid via anhydride.

2.2. Solvent exchange

The hydrogels were transferred to a glass beaker and allowed to swell in DI water for 2 hours until equilibrium. Anhydrous ethanol (200 mL) was added to 130 mL of a 20% hydrogel suspension under stirring (IKA-Werk RW 16 Basic S1, at 1600 rpm). The precipitated hydrogel was vacuum filtered using Whatman P2 filter paper in a Buchner funnel. The solid was then resuspended in 200 mL of ethanol and stirred for two hours before filtration. This

washing process was repeated twice (four ethanol batches in total). The final precipitate was dried on filter paper under house vacuum at ambient temperature for 24 h prior to further characterization.

2.3. Free swelling

Dried hydrogel samples (approximately 0.1 g) were added to a tea bag and immersed in DI water or 0.9% NaCl solution at room temperature for 120 minutes. After swelling, excess surface water was removed using paper towels, and the swollen hydrogels were weighed. The swelling ratio was measured every 15 min for two hours. The swelling ratio is given by the slope of the curve in the first 30 minutes. The tests were conducted in duplicates. The swelling capacity was calculated using:

$$\text{Swelling ratio (g/g)} = \frac{W_s - W_d}{W_d} \quad (1)$$

Where W_d is the dry weight, and W_s is the swollen weight of the hydrogel.

2.4. Absorption Under Load:

AUL tests were conducted in accordance with EDANA WSP 242.2. Four grams of dry hydrogel were placed in a cylindrical cell fitted with a stainless-steel 150 μm mesh at the bottom, under a constant load (6.2 kPa). The cell was immersed in 0.9 wt.% saline (sodium chloride) solution for one hour. The absorbed liquid under pressure was determined by weighing.

2.5. Centrifuge Retention Capacity:

0.2 g of hydrogel was immersed in 0.9% saline solution for 30 min. Swollen hydrogels were placed in a centrifuge tube with a tea bag and centrifuged at 1200 RPM for 3 minutes (Centrifuge - EPPENDORF 5072). The retained water after centrifugation was used to calculate the CRC, expressed as grams of water per gram of hydrogel, after subtracting the weight of the blank tea bag.

2.6. Total Carboxylic Content:

The carboxyl content of the CMC fibers and the cross-linked gels was determined using a conductometric titration method with a pH METER/conductivity S470-KIT (Mettler Toledo GmbH, Greifensee, Switzerland). 0.2 g of ground hydrogels and 60 mL of deionized water were added to a beaker, and the mixture was stirred for 20 minutes. Then, 0.1 M HCl was slowly added to the mixture to set the pH to 2. Then, the suspension was titrated with 0.01 M NaOH at 0.05 mL/min until the mixture reached pH 11. The carboxyl group content of CMC fibers and the cross-linked gels was determined from the plateau of the conductivity curves (Zemljich et al. 2008).

2.7. Oscillatory Rheology:

Rheological analysis was carried out using a TA Rheometer Discovery HR 10 equipped with a 25 mm parallel-plate geometry. The hydrogel was swollen until equilibrium in DI water. First, a strain sweep was performed to determine the Linear Viscoelastic Region (LVR), and a 0.1 % strain was chosen for the frequency sweeps. Frequency sweep tests (0.1 to 10 Hz) were performed at 25 °C to evaluate the storage modulus (G'), loss modulus (G''), and the complex viscosity.

2.8. Scanning Electron Microscopy:

The ground hydrogels were sputter-coated with a thin layer of gold and imaged using a scanning electron microscope (SEM, JEOL 6000) at 5 kV and magnifications up to 1000 $\times$.

2.9. ATR-FTIR spectroscopy

A PerkinElmer Frontier Spectrometer was used to collect spectra from 4000 to 600 cm^{-1} at a resolution of 1 cm^{-1} , using a total of 32 cumulative scans.

3. Results and Discussion

3.1. Crosslinking efficiency, base polymer, and absorbency performance.

Among the key parameters for the development of SAPs, this work focused on (1) the type and concentration of crosslinker and (2) the choice of base polymers. Carboxylic acid-based crosslinkers, such as citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA), are particularly attractive due to their ability to form ester bonds via anhydride intermediates with hydroxyl groups in polysaccharides (Omidian et al. 2024). CMC and HEC are commonly used as base polymers for biobased SAP research due to their water solubility and reactivity (Demitri et al. 2008; Dong et al. 2024), whereas starch has been investigated for its low cost and biodegradability (Prasad et al. 2023). Blends of these polymers were used rather than single polysaccharides to exploit the advantages of a double-network (DN) structure, as previously described by Kang and Yun (2022). The effects of crosslinker type, concentration, and polymer blends on AUL and retention performance are presented in Figure 2.

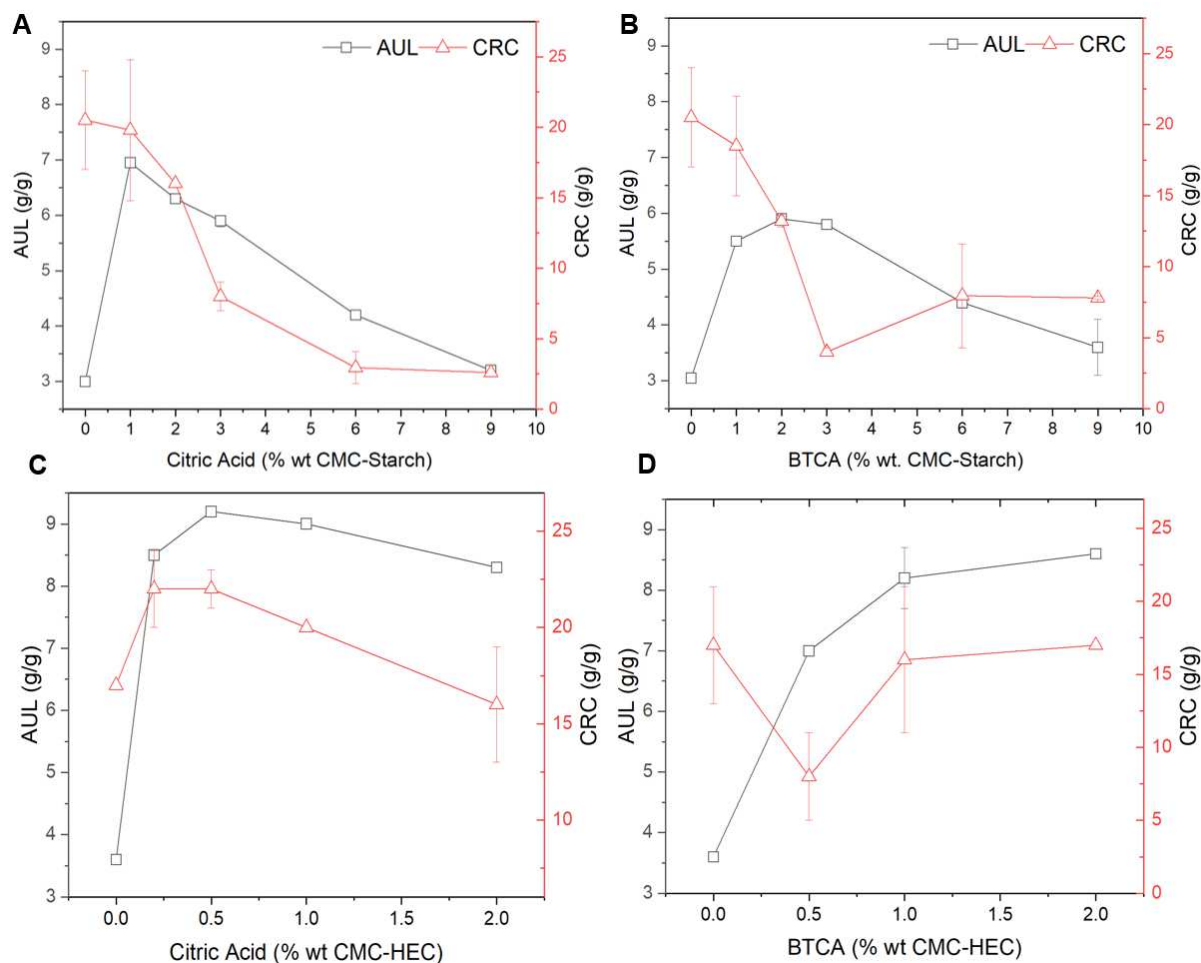


Fig. 2 Effect of Citric Acid and BTCA Concentrations on Absorbency Under Load (AUL) and Centrifuge Retention Capacity (CRC) of (A-B) CMC-Starch and (C-D) CMC-HEC Superabsorbent Polymers.

Figure 2A-D shows that CA and BTCA crosslinkers improved absorbency performance at low concentrations, specifically up to 1% addition of the crosslinker. In Figure 2A, the AUL of CA-Starch base increased to 7 g/g at 1% CA, then sharply declined to below 3 g/g at 9%, suggesting excessive crosslinking restricts polymer chain flexibility. For BTCA-Starch (Figure 2B), AUL showed similar behavior: from 5.5 g/g at 1% to 6 g/g at 2%, then declining to 3.5 g/g at 9% BTCA. The CRC follows a similar pattern. For CA-Starch (Figure 2A),

retention decreases as crosslinker concentration increases. In contrast, low crosslink density yields (below 2% CA) a soft gel that can swell more and retain fluid better. However, at low crosslinker concentrations, the gel can partially dissolve (Ahmed 2015) or deform under load, thereby reducing AUL (Ramazani-Harandi et al. 2009). Ramazani-Harandi et al. (2009) investigated the effect of structural variables on the AUL of acrylic-based SAPs. They found that a crosslinker concentration as low as 0.0025 mol% of N,N'-methylenebisacrylamide (MBA) or triethylene glycol dimethacrylate yielded a high AUL of 6.2 kPa in saline solution. Thus, the goal is to find a moderate crosslink density that maximizes absorption without compromising structural integrity (Nasution et al. 2022).

Interestingly, the CRC curve for BTCA is non-monotonic for both CMC-Starch and CMC-HEC as base polymers. For instance, in Figure 2D, CRC initially drops as the crosslinker increases from 0.5%, but at the BTCA level of 2%, a slight increase in CRC was observed (recovering to 15 g/g). This unusual retention of fluid at high BTCA could indicate that not all added BTCA formed effective crosslinks. Instead, some BTCA may remain unreacted or form pendant acidic groups within the network. Such residual carboxylate groups would increase the ionic osmotic pressure inside the gel (acting somewhat like an internal “soluble” polyelectrolyte) and thus help the gel hold more water. In other words, beyond a particular concentration, additional BTCA may contribute to more hydrophilic groups than crosslinks, thereby offsetting the tightening of the network.

Regarding the base polymer, the AUL for CMC-Starch hydrogels (Figure 2A and B) reached maximum values within the tested range and was independent of the crosslinker addition; the AUL did not exceed 7 g/g. Although starch is generally known for its high-water absorption capacity (Prasad et al. 2023), an amorphous alpha-structure might interfere with

swelling under pressure. On the other hand, the CMC–HEC hydrogels achieved a 30% higher AUL than the starch-containing materials, likely because HEC imparts greater load-bearing capacity to the swollen gel (resisting deformation and the squeezing out of liquid). This is analogous to reports in the literature in which introducing a second polymer network or a reinforcing polymer can enhance SAP mechanical strength, thereby increasing AUL. Kang and Yun (2022) demonstrated this with a double-network hydrogel of CMC–HEC interpenetrated with κ -carrageenan; the DN hydrogel absorbed more than 13 times its weight under 2.0kPa load compared to a single-network CMC–HEC (Kang and Yun 2022).

It is worth noting that, even with these improvements, the absolute AUL and CRC values of our bio-based hydrogels are lower than those of synthetic SAPs. Commercial polyacrylate SAP used in diapers can absorb up to 12 g/g under a 6.2 kPa load and retain 30g/g after centrifugation in 0.9% saline. For example, a recent study of a SAP synthesized with itaconic acid, 2-acrylamido-2-methyl-1-propanesulfonic acid, and acrylic acid (i.e., a partially Bio-SAP), reported an optimized crosslinked surface achieving a CRC of 36g/g and AUL of 27 g/g (2.0 kPa) in saline (Kwon et al. 2022). Those values set a benchmark that today’s bio-based systems have yet to reach. Nonetheless, CMC-based hydrogels herein, with AUL up to 9 g/g and CRC 22 g/g in 0.9% NaCl, are among the better-performing fully natural SAPs reported. (Ismaeilimoghadam et al. 2025; Simões et al. 2025).

3.2. Total Carboxylic Content (TCC) and ester formation

Crosslinking in these hydrogels occurs via esterification between the polyacid blend (CA-BTCA) and polymer hydroxyl groups. However, not all added carboxylic acid groups form ester linkages and remain as free $\text{—COO}^-/\text{—COOH}$ groups (Ghorpade et al. 2018). The

presence of unreacted carboxyl groups can influence swelling behavior, as observed in Figures 2B and D. This happens because the ionic groups contribute to the density charge of the gel, hydrophilicity, and enhance osmotic pressure. Since CMC-HEC exhibited the maximum AUL and CRC in the optimized formulation, the total carboxylic content of this system (Total Carboxylic Content (TCC), in mmol per gram) was quantified via conductometric titration. Figure 3A plots the TCC alongside the AUL and CRC for those samples.

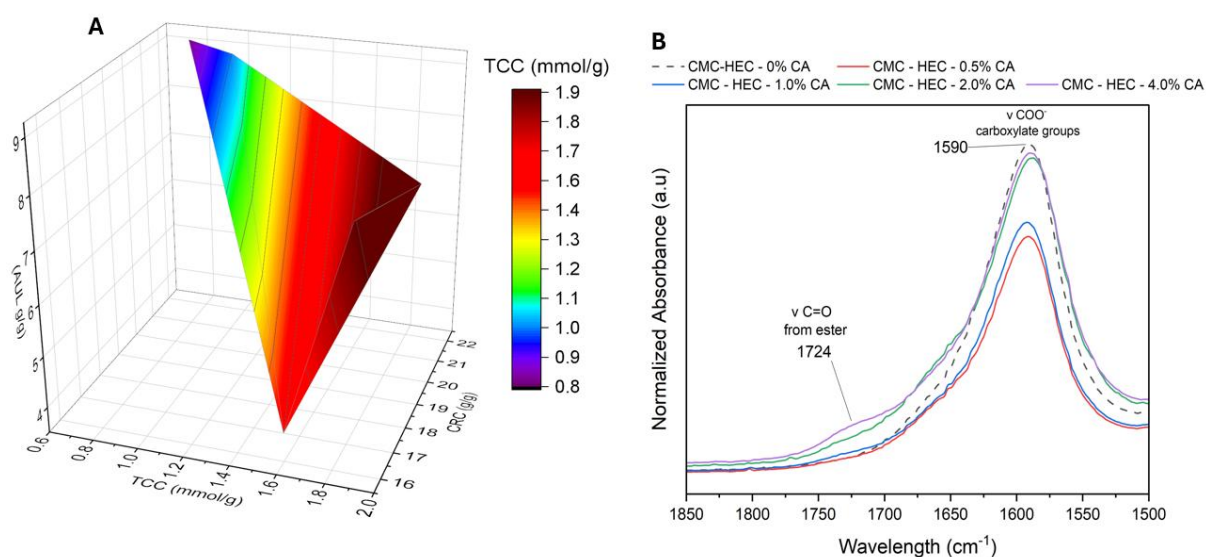


Fig. 3 (A) Correlation between total carboxylic content (TCC, mmol/g) and absorbency performance (AUL and CRC) of Carboxymethyl Cellulose–Hydroxyethyl Cellulose (CMC- HEC) hydrogels crosslinked with citric acid and BTCA. (B) ATR-FTIR spectra of CMC–HEC hydrogels at different citric acid concentrations.

Figure 3A shows that the lowest TCC (0.7 mmol/g) coincides with the highest performance (AUL 9.0 g/g, CRC 22 g/g). This optimum was observed in the CMC–HEC hydrogel containing 0.5% CA. As the CA loading increased to 2%, TCC rose to 1.9 mmol/g; the AUL

was only modestly affected (8.3 g/g), but the CRC declined appreciably from 22 to 16 g/g. This indicates that beyond a certain crosslink density, additional carboxylate groups no longer improve fluid retention. Once the network is overly crosslinked, which tends to accompany higher CA addition, the gel's stiffness and reduced swelling capacity dominate the behavior (Kim et al. 2021), offsetting the benefit of additional ionic groups.

Table 1 Absorbency performance of CMC-HEC Hydrogels with CA and BTCA Crosslinkers.

Crosslinker			
wt.% polymer	TCC (mmol/g)	AUL (g/g)	CRC (g/g)
0.0% CA -Control	1.5 ± 0.2	3.6 ± 0.0	17 ± 3
0.5% CA	0.7 ± 0.1	9.0 ± 0.0	22 ± 1
1.0 % CA	1.0 ± 0.1	9.0 ± 0.5	20 ± 0
2.0% CA	1.9 ± 0.2	8.3 ± 0.0	16 ± 3
0.5% BTCA	1.2 ± 0.2	7.0 ± 0.0	8 ± 3
1.0% BTCA	1.9 ± 0.1	8.2 ± 0.5	16 ± 5
2.0% BTCA	2.1 ± 0.1	8.6 ± 0.0	17 ± 0

Interestingly, the CRC did not linearly decrease with TCC. At 1.9 mmol/g of carboxylic groups (dark red areas in the graph), the CRC rose even as AUL remained low. This supports the idea that excess unreacted acid can increase the ability of the gel to retain water (via osmotic effects) even though the crosslinked network is stiff. In Table 1, it is noted that BTCA-crosslinked samples at the same crosslinker level (i.e., 2.0 wt.%), even at high loadings, exhibit larger fractions of acid remaining unreacted (because BTCA has more carboxyl groups per molecule). This likely explains the non-monotonic CRC behavior noted earlier in Figure 2D for CMC-HEC-BTCA hydrogels, where the rebound in CRC at 9%

BTCA coincided with a high TCC (an excess of carboxylate groups acting as internal osmolytes). This observation was also verified by previous research on CMC-PEG-CA hydrogel systems. The researchers found that a higher proportion of unreacted carboxylic groups (4.95 mmol/g) led to greater free swelling in water (Ghorpade et al. 2018)

In Figure 3B, the ATR-FTIR spectra of CMC-HEC hydrogels are shown. The characteristic shoulder at 1724 cm^{-1} is attributed to the C=O stretch from esters, alongside a band at 1590 cm^{-1} , which indicates the carboxylate groups (Reddy and Yang 2010). The samples were washed with NaOH (0.1 M) to avoid potential overlapping between the carboxylic group of the ester and the carboxylate. The peak at 1590 cm^{-1} increases with the CA addition (Capanema et al. 2023; Ghorpade et al. 2018). The 0.5% CA sample shows no visible ester signal at 1724 cm^{-1} , despite demonstrating excellent swelling properties. This implies that at such a low crosslinker concentration, the gel may have formed near the gelation threshold, a scenario in which only a small fraction of polymer chains are covalently linked, yet sufficient to create a continuous network.

According to the Flory–Stockmayer theory of step-growth gelation, there is a critical conversion (or crosslinker ratio) at which an infinite network first forms. Near that point, the network contains many “dangling” chains and looped structures, and a large portion of the crosslinker’s functional groups remain unreacted (Stockmayer 1943). The 0.5% CA sample likely represents a near-critical gel: it has barely enough ester bonds to form a macroscopic gel, with the remainder of network integrity coming from physical entanglements, hydrogen bonding, and other non-covalent interactions. This would explain why it performs well (it swells a lot because the network is very loosely connected) and shows no strong FTIR ester signal (few covalent bonds). We hypothesize that the 0.5% CA sample would have a lower

gel fraction (due to a soluble component), whereas higher CA samples are highly crosslinked. While this 0.5% CA showed the highest absorbance, in practice, one must ensure the gel remains stable in the intended environment.

3.3. Rheological Behavior and Network Structure

To further elucidate the network structure of the hydrogels, oscillatory rheology was performed on selected samples. Figure 4 and Table 2 summarize the key rheological parameters. We focus here on the storage modulus G' (elastic response) measured at 1Hz frequency for various crosslinker levels. The G' is related to the polymer network's crosslink density and can also be used to estimate the molecular weight between crosslinks (M_c), and the distance between two entanglement points or mesh size (ξ). To complete the rheological characterization, the viscoelastic behavior of CMC-HEC shows the frequency dependence of G' and $\tan(\delta)$ (G''/G') under a constant strain (0.1%).

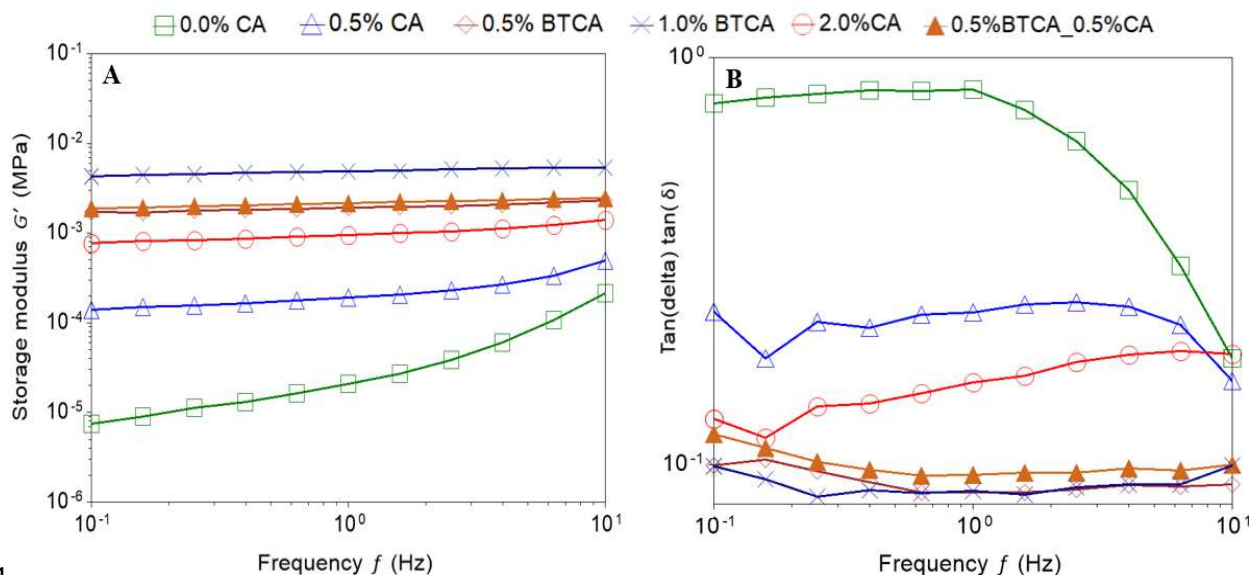


Fig. 4 Frequency sweep rheological measurements of CMC–HEC hydrogels crosslinked with citric acid (CA) and BTCA at different concentrations. (A) Storage modulus (G') as a function of frequency. (B) Tan (δ) ($\tan \delta$).

Figure 4A shows the storage modulus (G') as a function of frequency for HEC–CMC hydrogels crosslinked with BTCA, CA, and a blend of CA + BTCA. The G' values increase with crosslinker concentration. This indicates a stiffer and more elastic network structure. In Table 2, the 2.0% CA sample exhibits the highest G' (949 ± 1 Pa) at 1 Hz among the hydrogels crosslinked with Citric Acid, which supports the results shown in Figure 2 and indicates that a highly crosslinked, rigid gel may restrict swelling. In contrast, the 0% CA sample shows the lowest G' (21 Pa), suggesting a weak, loosely structured gel with poor mechanical integrity. The 0.5% CA sample exhibits an intermediate G' (187 Pa), which correlates with a more balanced network, firm enough to retain its structure yet flexible enough to swell. Wei et al. (2024) showed a similar modulus for CA - Crosslinked Starch with values around 318 Pa (Wei et al. 2024), while commercial polyacrylate shows around 2000 Pa (Supplementary S2).

In Figure 4B, the phase shift ($\tan \delta = G''/G'$) was less than 1 for the hydrogels with crosslinkers, indicating that the elastic properties prevailed over the viscous properties and that the SAP exhibited mechanical rigidity (Zhang et al. 2015). Therefore, although not visible in FTIR (Figure 3B), rheological analysis suggests that CMC-HEC 0.5% CA presents a chemically cross-linked network.

3.3.1. Calculation of Network Parameters

A typical viscoelastic curve shows a rubber-elastic plateau in the intermediate frequency region. Here, the larger molecule chains cannot slide by one another, since the relaxation ability of the segments is smaller than the stress velocity (Seidel et al. 2001). In the linear viscoelastic range, the network parameters can be determined using the rubber elastic plateau G' , the density ρ , the gas constant R , the temperature T , and the Avogadro number N_A . Network parameters for the examined hydrogels were calculated from the values for the storage modules G' at a frequency of 1 s^{-1} (Seidel et al. 2001).

$$\text{Molar mass between two entanglement points: } Me = \frac{\rho RT}{G'p} \quad (2)$$

$$\text{Crosslinking density: } \nu e = \frac{G'pNA}{RT} \quad (3)$$

$$\text{Distance between two entanglement points/ mesh size: } \xi = \frac{1}{\sqrt[3]{\nu e}} \quad (4)$$

For a swollen hydrogel, however, the ratio of swollen polymer volume in the mixture with the solvent needs to be considered. The swelling process corresponds to an isotropic expansion of the network that includes a reduction in network entropy (Gluck-Hirsch and Kokini 1997).

$$\text{Molar mass between crosslinks (swollen state) (g/mol): } Mc = \frac{c^{1/3} \rho^{2/3} RT}{G'} \quad (5)$$

Where ρ is the unswollen polymer density, and c is the weight concentration of the hydrogel in the swollen state. Since there are approximately two cellulose chains per crosslinking agent, it is then possible to calculate an average value of the number of crosslinks (N_c) based on the molecular weight of glucose and the molecular weight between crosslinks. According to the equation (Gluck-Hirsch and Kokini 1997):

$$\text{Number of crosslinks (a.u.): } Nc = \frac{M_w}{M_c} \quad (6)$$

M_w of CMC is 700000 g/mol

Table 2. Network characteristics of Bio-SAP at different CA/BTCA concentrations.

Sample	G' (Pa)	Mc (swollen) g/mol	Nc (a.u)	ve (1/m ³)	ξ (m)
0.0% CA	21±1	1.2E+06	0	5.1E+21	5.8E-08
0.5% CA	187±4	1.4E+05	3	4.5E+22	2.8E-08
2.0% CA	949±1	2.7E+04	13	2.3E+23	1.6E-08
0.5% BTCA	1446±468	1.8E+04	20	3.5E+23	1.4E-08
1.0% BTCA	3489 ±1400	7.4E+03	47	5.8E+23	1.2E-08
0.5% BTCA/ 0.5 % CA	2406±240	1.1E+04	33	8.5E+23	1.1E-08

The storage modulus G' is the elastic component of the hydrogel and reflects its stiffness or solid-like behavior. A higher G' indicates a more rigid, crosslinked network that stores more energy elastically. In the hydrogels, G' increases with crosslinker content and type, ranging from 21 Pa in the non-crosslinked sample to 187 Pa at 0.5% CA, and up to 3489 Pa at 1.0% BTCA. This trend shows that adding crosslinkers, especially the tetra-functional BTCA, stiffens the gel. Gel stiffness correlates inversely with free swelling but directly with stability under load. A low G' means the network lacks integrity, leading to dissolution or collapse under pressure, resulting in an AUL of 3.0 g/g at 6.2 kPa. Conversely, high G', e.g., 949 Pa for 2% CA, or >1000 Pa for BTCA-crosslinked gels, implies a tight network that resists swelling expansion, yielding lower capacity or retention. These results are supported by previous work, in which the increase in G' was linear with the AUL (Ramazani-Harandi et al. 2009). The optimal absorbency herein occurred at an intermediate G' of 150–200 Pa for

the 0.5% CA gel, which was strong enough to retain its shape but soft enough to swell significantly.

A blend of CA and BTCA has not been reported previously in the literature for polysaccharide-based SAPs. We investigated this combination under the hypothesis that balancing crosslink density and residual carboxylic groups could favorably influence performance. This blend produced networks with intermediate M_c and the smallest ξ among the formulations tested, while delivering the highest CRC of all single-crosslinker and blend variants, suggesting that the improved performance arises from balancing crosslink-density-driven elasticity with residual carboxyl content rather than from increased mesh size. This suggests that mixed crosslinking strategies may represent a promising avenue to tune the elasticity–swelling trade-off in bio-based SAPs.

M_c represents the average polymer mass between two effective crosslinks and is inversely related to crosslink density (ve). In the uncrosslinked sample (0% CA), M_c is higher than in the other SAPs (1.2×10^6 g/mol), reflecting unbound or loosely entangled chains. Adding 0.5% CA reduces M_c to 1.4×10^5 g/mol, indicating the formation of a sparse but continuous network. At 2% CA, M_c decreases further to 2.7×10^4 g/mol, consistent with a denser network restricting chain length between junctions. BTCA produces much tighter networks even at low concentration: 0.5% BTCA yields M_c 1.8×10^4 g/mol, and 1% BTCA drops sharply to 7.4×10^3 g/mol, the smallest among all samples, reflecting a very rigid crosslinked structure. The CA–BTCA blend shows an intermediate M_c 1.1×10^4 g/mol, shorter than pure CA but longer than pure BTCA at 1%. These values directly correlate with the swelling: higher M_c (longer chains, as in 0.5% CA) permit higher CRC (22 g/g) and better AUL (9 g/g).

Mesh size (ξ) refers to the average distance between two entanglement points (Seidel et al. 2001), i.e., the size of pores or voids in the polymer network. It is also inversely related to crosslink density: a tightly crosslinked hydrogel has a smaller mesh size. The 0% CA sample (no chemical crosslinks) has the largest mesh size, reflecting a very open network (dominated by entanglements or hydrogen bonds). Introducing 0.5% CA reduces ξ to approximately 2.8×10^{-8} m. BTCA-crosslinked hydrogels exhibit even smaller mesh sizes with a trend that more crosslinker and higher functionality produce a finer mesh. This scale agrees with previous work in which the synthesized carbohydrate-based hydrogels were on the order of 10^{-8} m (Seidel et al. 2001). In practical terms, a larger mesh allows more water to enter and be held (higher swelling capacity), whereas a smaller mesh constrains the swelling. For example, the loosely crosslinked 0.5% CA hydrogel can swell more freely (contributing to its high CRC). In comparison, the densely crosslinked 1% BTCA gel, with its small spacing between connection points, permits only limited expansion. Moreover, mesh size affects fluid diffusion and absorption rates, which are essential factors in hygiene products. Hydrogels with larger pores imbibe fluid faster but may also release it under pressure. In contrast, those with tiny meshes swell more slowly and hold water more tightly, a threshold that should be considered when formulating SAPs. Studies in hydrogel science have quantified this inverse relationship (Peppas et al. 2000).

At the nanometric scale observed in this work ($\xi \sim 10\text{--}60$ nm), the hydrogels are classified as non-porous with respect to swelling kinetics. Fluid uptake in such dense networks occurs mainly by molecular diffusion and convection, which is suitable for biomedical applications requiring controlled release and transparency, such as drug delivery systems or contact lenses (Ganji et al. 2010). However, this mechanism is inadequate for hygiene products, which

require rapid fluid uptake enabled by interconnected pores in the 0.1–1.0 μm range (Ganji et al. 2010). For carbohydrate-based hydrogels, slow swelling kinetics remain a limitation, as current approaches in the literature yield dense networks with very small pores. R&D focus on increasing porosity while retaining the elasticity of the gel represents a significant opportunity to make bio-based hydrogels competitive with synthetic SAPs in hygiene applications.

3.4. Impact of morphology and solvent exchange on fluid dynamics

As discussed in the previous section, a critical performance requirement for SAPs in hygiene applications is not only the maximum swelling capacity but also the uptake rate. Figure 5 shows the swelling behavior of CMC–HEC hydrogels crosslinked with CA, BTCA, and their blend in 0.9% saline solution, compared with a commercial polyacrylate (PAA)-based SAP. The PAA sample reached its maximum swelling within 15 minutes, confirming the well-known rapid kinetics of PAA SAPs. In contrast, cellulose-based hydrogels required extended times to reach equilibrium, likely due to extensive hydrogen bonding among hydroxyl groups, which slows water diffusion and network expansion.

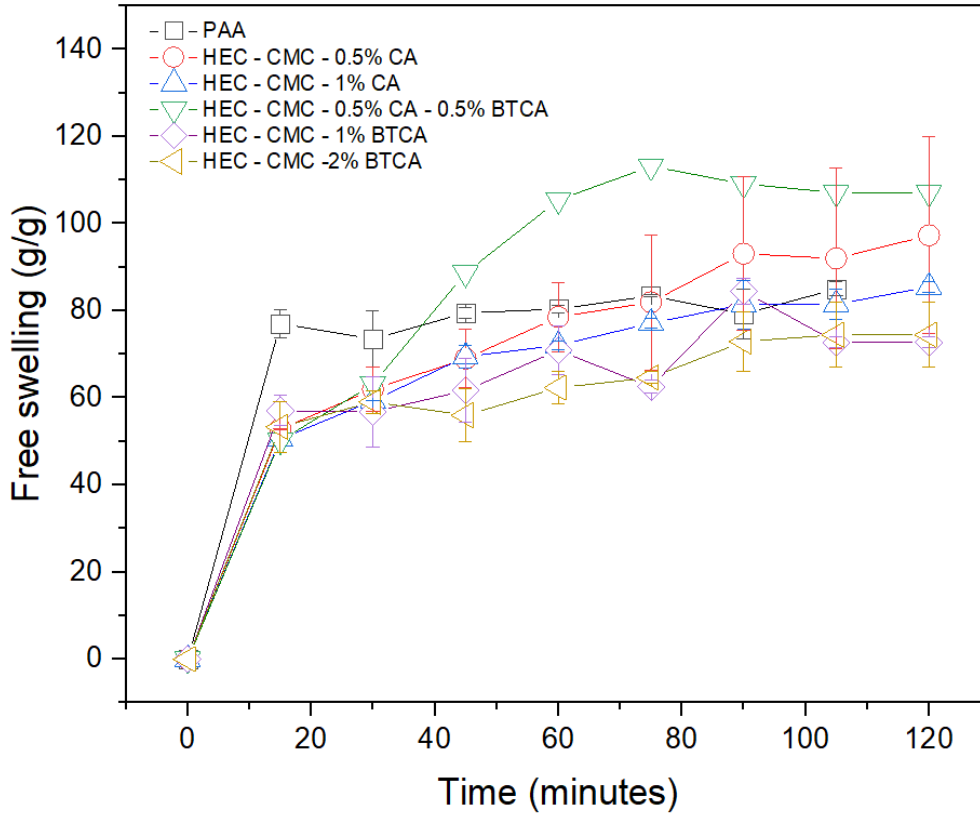


Fig. 5 Swelling kinetics of CMC–HEC hydrogels crosslinked with CA, BTCA, and their blend compared with a commercial Polyacrylate-based (commercial sample) SAP in saline solution.

Among the bio-based formulations, the CA–BTCA blend exhibited the highest equilibrium swelling of 110 g/g after 60 minutes of absorption in saline solution. This indicates that a balance between crosslink density and residual carboxylate groups promoted fluid uptake. Nevertheless, the relatively slow swelling of all carbohydrate-based hydrogels highlights a key limitation: their dense structures restrict rapid fluid penetration. Similar behavior has been reported for other polysaccharide-based SAPs with modified cellulose and epichlorohydrin, showing a retention value in saline water of 118 g/g, exceeding the WRV

of commercial gels by more than 2-fold (40–50 g/g). The absorption plateau, however, occurred at 500+ minutes, and rates were not evaluated (Alam et al. 2019).

As shown in Figure 6A and Supplementary Information S3, cellulose-based SAPs present a compact structure compared with the porous morphology of PAA. Introducing micro- or mesoporous, for example, through solvent exchange techniques, could accelerate fluid uptake by creating larger capillary pathways while retaining the nanoscale mesh that provides elasticity.

A solvent-exchange technique was performed by immersing the hydrogels in ethanol for solvent replacement, prior to drying under ambient conditions. Morphological modifications via ethanol solvent exchange significantly influenced the hydrogel network structure (Figure 6A). Ethanol/air has lower surface tension than water/air, reducing capillary collapse during drying and resulting in a less collapsed porous surface. (El-Tahlawy et al. 2007). Consequently, the final composites also exhibit lower bulk densities. (Patel et al. 2010).

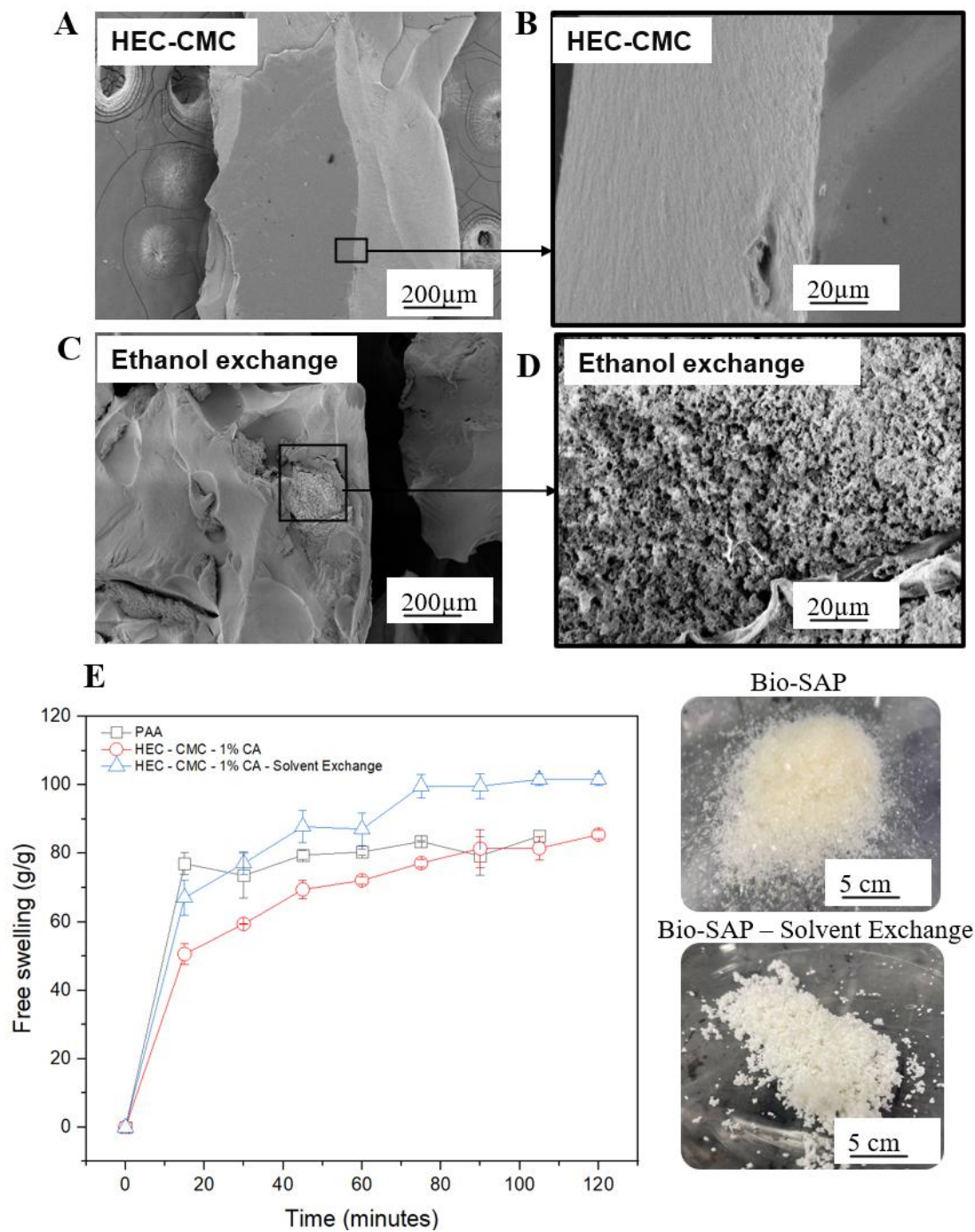


Fig. 6 Morphological and swelling behavior of bio-based SAPs. (A–B) SEM images of HEC–CMC hydrogel crosslinked with 1% CA. (C–D) SEM images of ethanol-exchanged HEC–CMC hydrogel. (E) Swelling kinetics and morphologies before and after solvent exchange treatment.

As expected, the ethanol-dried hydrogel initially absorbed saline solution faster, with a rate comparable to that of the synthetic PAA (78 g/g in the first 30-minute window). We hypothesize that this is due to the porous structure, which allows the gel to swell more freely and uniformly. These findings highlight that morphological engineering is a viable approach to improving absorption rates. However, one must balance this with mechanical considerations: highly porous gels can be weaker. In our case, the ethanol-exchanged gels were slightly more brittle when dry (as expected due to less compact polymer packing), and the AUL values decreased from 9 g/g to 3 g/g after solvent exchange. Under load, if pores are too large, the gel structure may collapse more easily, like a sponge being squeezed. The CRC increased slightly from 22 to 26 g/g, suggesting a shift toward looser, more permeable structures. This highlights a classic trade-off in hydrogel design: enhancing uptake rate often compromises absorption under load. For hygiene applications, this presents a critical challenge, particularly when aiming to match the performance of commercial synthetic SAPs such as polyacrylates.

4. Conclusions

This study demonstrates that fully bio-based SAPs can achieve promising performance when crosslinking and morphology are carefully balanced. Citric acid at a low concentration (0.5%) produced networks with good elasticity and absorption under load, whereas higher crosslinking ($\geq 2\%$ CA or BTCA) led to rigid gels with diminished swelling. A novel CA–BTCA blend provided a favorable combination of high CRC and improved swelling dynamics. Rheological and network parameter analysis confirmed that intermediate G' and mesh size are critical for maximizing absorbency while maintaining mechanical stability.

Morphological modification by solvent exchange significantly enhanced the saline uptake rate, demonstrating the potential of structural engineering to address the slow kinetics of polysaccharide SAPs. However, this came at the expense of reduced retention under pressure, reinforcing the classic trade-off between swelling rate and structural capacity. Altogether, these results show that while bio-based SAPs still lag synthetic polyacrylates in hygiene benchmarks, rational tuning of crosslinker chemistry and morphology can bridge part of this gap. Future work should focus on hierarchical porosity design and composite strategies to achieve the simultaneous goals of fast absorption, high CRC, and AUL, thereby enabling sustainable alternatives in hygiene products.

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Statements and Declarations

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Competing Interests

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Author Contribution

Mirela A. Artner (MAA): Conceptualization, Methodology, Investigation, Formal analysis, Visualization, Writing – original draft. Alfonso J. Dominguez (AJD): Formal analysis, Visualization, Writing – review & editing. Richard A. Venditti (RAV): Conceptualization,

650 Resources, Supervision, Funding acquisition, Writing – review & editing. Joel J. Pawlak
651 (JJP): Conceptualization, Resources, Supervision, Funding acquisition, Writing – review &
652 editing. All authors read and approved the final manuscript.

653 **Data Availability Statement**

654 The datasets generated and analyzed during the current study, including absorbency (AUL,
655 CRC), swelling kinetics, rheological, FTIR, and SEM data, are available from the
656 corresponding author upon reasonable request.

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