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Functionalized Cellulose-Reinforced CMC-Based Hydrogels: NaOH-Urea Catalyzed Oxidation and Mechanical Pretreatments, Crosslinking with Citric Acid and Epichlorohydrin, and Characterization

Fonksiyonelleştirilmiş Selüloz Katkısıyla Güçlendirilmiş CMC Esaslı Hidrojeller: NaOH-Üre Katalizli Oksidasyon ve Mekanik Ön işlem Uygulamaları, Sitrik asit ve Epiklorohidrin ile Çapraz Bağlanma ve Karakterizasyon

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Abstract

To improve the performance of carboxymethylcellulose (CMC)-based copolymer hydrogels with low gel strength, additives like natural cellulose are extensively utilized but its structural limitations restrict successful integration into CMC-based hydrogels without modification. In this study, it was examined the effects of wood pulp with and without treatments as additives on the performance of hydrogels. Pretreatment of cellulose was carried out using hydrogen peroxide oxidation catalyzed by NaOH-urea, as well as mechanical pretreatment using PFI or colloid mills. In the cross-linking of these semi-synthetic polymers, either epichlorohydrin (ECH) or citric acid (CIT) were used. FTIR spectroscopy, DSC, and electron microscopy techniques, as well as swelling and water absorption tests, were used to analyze the chemical, physical, and morphological properties of hydrogels. The successful cross-linking by both agents was verified by FTIR spectra. For all hydrogel groups, regardless of the cross-linking agent used, the swelling ratio in alkaline solutions was higher than that in neutral and acidic environments. CIT-crosslinked hydrogels displayed a swelling rate 16 times greater at pH 7 than the control group. Enhanced swelling performance was observed in solutions with Na^+ and K^+, but hydrogels demonstrated a 50–70% reduction in performance in the presence of Mg^{2+} and NH_4^+. DSC curves demonstrate that crystallinity diminished due to alkaline oxidation pretreatments, and the thermal stability of ECH-crosslinked hydrogels exceeds that of CIT by 40%. SEM images show different patterns and fractures in ECH samples, while CIT samples reveal smoother hydrogel surfaces and the presence of fibers.

Özet

Düşük jel mukavemetine sahip karboksimetilselüloz (CMC) bazlı kopolimer hidrojelin performansını iyileştirmek için, doğal selüloz gibi katkı maddeleri yaygın olarak kullanılmaktadır, ancak bunların yapısal sınırlamaları, modifikasyon olmadan CMC bazlı hidrojellere başarılı bir şekilde entegre edilmesini engellemektedir. Bu çalışmada, katkı maddesi olarak işlenmiş ve işlenmemiş odun hamurunun hidrojel performansı üzerindeki etkileri incelenmiştir. Ön işlemler, NaOH-üre ile katalize edilen hidrojen peroksit oksidasyonunun yanı sıra mekanik ön işlem olarak PFI veya kolloid değirmenler kullanılarak gerçekleştirilmiştir. Bu yarı sentetik polimerlerin çapraz bağlanmasında, epiklorohidrin (ECH) veya sitrik asit (CIT) kullanılarak gerçekleştirilmiştir. Hidrojellerin kimyasal, fiziksel ve morfolojik özelliklerini analiz etmek için FTIR spektroskopisi, DSC ve elektron mikroskobu teknikleri ile şişme ve su emme testleri kullanılmıştır. Her iki ajanla çapraz bağlanmanın başarılı olduğu FTIR spektrumları ile doğrulanmıştır. Kullanılan çapraz bağlama maddesinden bağımsız olarak, tüm hidrojellerin alkali çözeltilerdeki şişme oranı, nötr ve asidik ortamlardakinden daha yüksekti. CIT ile çapraz bağlanmış hidrojeller, pH 7'de kontrol grubuna göre 16 kat daha fazla şişme oranı göstermiştir. Na^+ ve K^+ içeren çözeltilerde şişme performansı artmış, ancak Mg^{2+} ve NH_4^+ varlığında hidrojellerin performansı %50-70 oranında azalmıştır. DSC eğrileri, alkali oksidasyon ön işlemleri nedeniyle kristallik azaldığını ve ECH çapraz bağlı hidrojelin termal stabilitesinin CIT'den %40 daha yüksek olduğunu göstermektedir. SEM görüntüleri, ECH numunelerinde farklı desenler ve kırıklar gösterirken, CIT numunelerinde daha pürüzsüz hidrojel yüzeyleri ve liflerin varlığı görülmektedir.

INTRODUCTION

Cellulose, the most common biopolymer in nature, is estimated to be produced by a wide range of biological entities from bacteria to woody plants at a rate of approximately 10^{11} to 10^{12} tons year (Heinze et al. 2018). It displays a complex structure defined by crystalline and amorphous parts. Crystalline parts provide greater resistance to many liquids and chemicals, whereas amorphous parts are generally more reactive. This reactivity is due to the abundance of free functional groups, such as hydroxyl groups. Krassing (1993) and Liebert (2010) revealed that increasing the reactivity and accessibility of cellulose improves its interaction with water and other chemicals.

Methods for manipulating cellulose in order to reduce or eliminate its structural constraints and to realize its potential and properties can be categorized into chemical (esterification, etherification, oxidation, crosslinking, etc.), physical (mechanical, thermal, nanoscale sizing, etc.), and biological (enzymatic hydrolysis, etc.) approaches (Laine et al. 2004, Cabiac et al. 2011). Most of the chemical treatments target to increase the spacing between cellulose chains by adjusting various process parameters (pH, length of time, temperature, etc.), whereas others rely on introducing new functional groups to the cellulose chains. To accomplish this, acids including sulfuric acid, phosphoric acid, formic acid, and acetic acid, alongside bases such as sodium hydroxide, urea, or thiourea, and oxidizing agents like sodium hypochlorite, potassium permanganate, hydrogen peroxide, and periodic acid can be employed (Cabiac et al. 2011).

The dissolution and subsequent regeneration of cellulose in solvent systems such NaOH-urea, dimethyl acetamide/lithium chloride, or dimethylsulfoxide-tetrabutyl ammonium fluoride result in molecular reorganization and a loss of crystalline structure (Pääkkö et al. 2008). Besides, oxidative treatments in moderate conditions are recognized to enhance the prevalence of carboxylic acid and/or aldehyde groups on the surfaces of cellulosic fibers (Hubbe et al. 2013).

In addition to chemical treatments, mechanical pretreatment methods are employed to modify cellulose. The beating is a crucial application in the paper making process, since it provides the spesific qualities to the fibers. Within the framework of mechanical processes, particularly the mechanical processing of cellulosic fibers, including hollanders and refiners, is carried out on special machines. PFI (Papirindustriens Forsknings Institut) mills are utilized at the laboratory scale (Gharehkhani et al. 2015). Variations in the applied stresses and their combinations induce morphological, physical, and chemical changes in the fibers. These might be related to physical and morphological aspects, including structural disintegration (peeling) of the primary wall and S1 layer, an increase in internal and external fibrillation, hydration, fiber particles formation, fiber shortening and flattening, along with alterations in chemical properties such as crystallinity and the composition of the fiber's outer surfaces. Cellulosic fibers obtain distinct properties by the modification of parameters in chemical and mechanical processes.

Modified cellulose has received attention as an option for structural issues in CMC-based hydrogels (Chang et al. 2010, Li et al. 2017). Cellulosic fibers are employed for preserving the structure of the hydrogel in the liquid, enhance liquid penetration into the hydrogel, and prevent the blockage caused by the expansion of lower size hydrogel particles (Hubbe et al. 2013). Cellulosic additives that have various physical and chemical properties, from mechanical wood pulps to nanofibrillated cellulose, have been utilized experimentally in the manufacture of hydrogels.

Bao et al. (2011) determined that an increase in cellulose content within CMC-based hydrogels results in a decrease in the hydrogel's water absorption capability. The reduction is due to the diminished ratio of crystalline to amorphous cellulose regions regarding liquid absorption capacity relative to CMC, and it is expected that an increase in cellulose content within the hydrogel results in a decrease in water absorption by the hydrogel. The previously discussed modification methods can be employed to solve the problem and enhance the reactivity and accessibility of cellulose.

Oxidation reactions with hydrogen peroxide in a NaOH-urea solution (which is recognized for its capacity to dissolve cellulose under specific conditions) may reduce the crystallinity of cellulose. Mechanical pretreatment with a PFI mill or supermasscolloider (SMC) can also generate various chemical and physical changes in cellulose. Furthermore, the combination of various combinations of these systems may reduce the challenges associated with cellulose integration into CMC-based hydrogels. This work investigated copolymer hydrogels composed of cellulose and carboxymethyl cellulose (CMC) crosslinked by epichlorohydrin (ECH) or citric acid (CIT) to elucidate the impacts of these pretreatments. The physical (water absorption, swelling), chemical (structural investigation using IR spectra), thermal, and morphological (hydrogel surface topography assessed through electron microscopy) properties of the synthesized hydrogels were evaluated.

MATERIALS AND METHODS

Materials

100% bleached spruce sulfite pulp (Super Aceta) supplied by Borregaard, Sarpsborg/Norway was used as cellulose source for hydrogel production. The properties of the pulp supplied are as follows: an intrinsic viscosity of 924 ml/g (ISO 5351:2004), a kappa number of ≤1 (TAPPI T 236 om-13), a brightness of 93.1 (ISO 2470:2009). Alpha cellulose content of 95.2% (TAPPI T203 cm-99), and alkali solubility values of 5.8% for S10 and 3.3% for S18 (TAPPI T 235 cm-00) were determined. The methodology described in the research by Milanovic et al. (2012) was employed to calculate the carboxyl (COOH) content of the pulp. It was found as 0.1269 mmol/g. The pulp exhibited a freeness of 12°SR (SCAN C-15:62 standard) and a water retention value (WRV) of 88.4, according to Chen et al. (2010). Sodium carboxymethyl cellulose (CMC-Na) with a molecular weight of about 700,000 and a degree of substitution between 0.80 and 0.95 was purchased from Sigma Aldrich. All chemicals were obtained from Merck KGaA or Sigma Aldrich and utilized without further purification.

Pretreatment of Wood Pulp

The study involved pretreatment applications designed to eliminate or diminish structural barriers in cellulose, conducted in two separate steps (Table 1). The following table presents the variables employed to the wood pulp in the investigation. The control group samples (ECH Control n and CIT Control n) underwent no pretreatment at any point. If epichlorohydrin was used as a crosslinker, the code of the sample was identified as ECH Oxi SMC 10.

Oxidation Stage

In this study, a short preliminary system was carried out to determine the optimum concentration of the oxidizing agent in the NaOH/urea system (Figure 1). The quantities of H_2O_2 utilized were 5.0, 10.0, or 15.0%. The method used for oxidation of cellulose was simply schematized in Figure 1. After the washing, the samples left on the sieve (150-mesh) were manually compressed, thoroughly squeezed, then gathered from the sieve. The collected samples were placed in a zip-lock bag and stored in a refrigerator maintained at +4°C.

The WRV and -COOH content values of the pulp post-oxidation were measured using the previously described methods. In the system using 5.0% H_2O_2, the -COOH concentration of cellulose was measured at 0.1184 mmol/g, and the WRV value was 133.7%. In the system utilizing 10% H_2O_2, these properties were measured at 0.1360 mmol/g and 145.50%, whereas for cellulose treated with 15% H_2O_2, the values were 0.1552 mmol/g and 139.1%. Considering the correlation between water absorption capacity and WRV values of polymers designed for specific applications such hydrogel and superabsorbent, the pulp oxidized with 10% H_2O_2, exhibiting the greatest WRV value in this investigation, was utilized in hydrogel synthesis.

Table 1. The types of crosslinker and pretreatment with cellulose content in CMC hydrogels

Crosslinker Type	Pretreatment Stage		Cellulose Content in Hydrogel (%)
	First	Second	
ECH or CIT	None	none	10, 30 or 50*
ECH or CIT	Oxidation	none	10, 30 or 50
ECH or CIT	Oxidation	PFI Refining	10, 30 or 50
ECH or CIT	PFI Refining	Oxidation	10, 30 or 50
ECH or CIT	Oxidation	SMC Refining	10, 30 or 50
ECH or CIT	SMC Refining	Oxidation	10, 30 or 50

*: The results obtained for the control group were taken from our previous study (Büyüküstün et al. 2025)

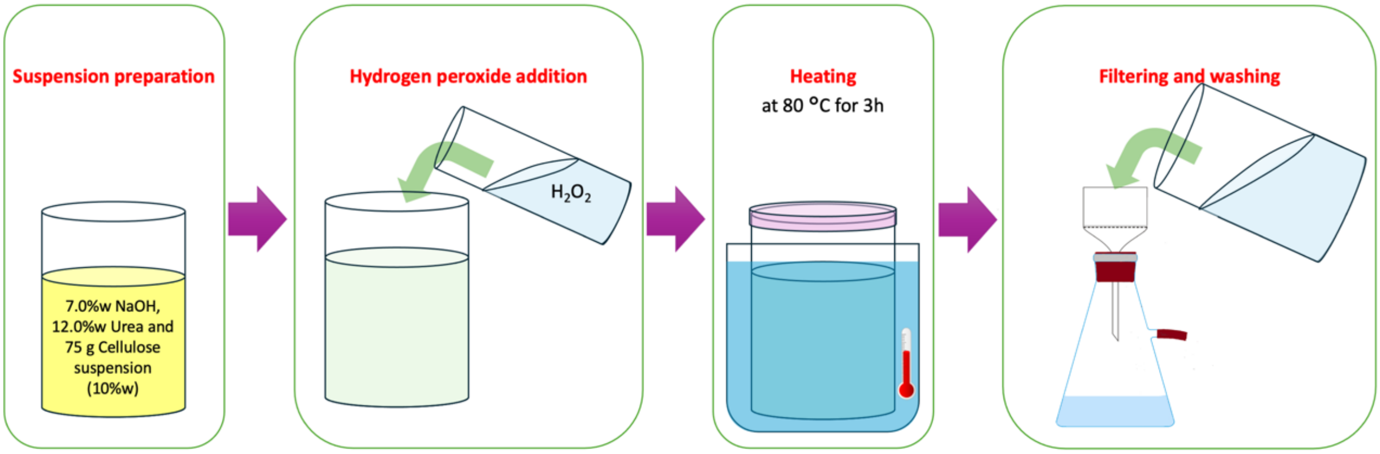

Figure 1. The process used for oxidation of cellulose

Mechanical Treatment

The mechanical treatment was carried out using either a two-roller laboratory-type PFI or a Masuko (Model: MKCA6-2J, SMC) colloid mill. For PFI refining, TAPPI T248 sp-15 standard was employed. The mill was operated at 4000 rpm and the fiber concentration was 10.0%. For SMC processing, the grit coarseness of Al_2O_3 stones was 80.0. The treatment was conducted at ambient temperature and a concentration of 2.0%. The mechanical forces between the stones were exposed by the pulp five times, and the distance between the stones was established at 20 µm. The stones were maintained at a rotational speed of 1500 rpm.

Hydrogel Synthesis

The as mentioned before, epichlorohydrin (ECH) or citric acid (CIT) were utilized as crosslinkers in hydrogel production. So, the crosslinking procedures used in the study were divided to two main sections and the details were given below.

Sythesis Process with ECH

It was carried out in two steps. In the first step, a solution included in cellulose and CMC was prepared by NaOH-Urea solvent system. A homogenized mixture of cellulose (either raw or processed) and CMC in a NaOH-Urea solution (195.0 ml), comprising 6.0 and 4.0 by weight, respectively was dispersed mechanically at 200 rpm for 10 minutes. The cellulose to CMC ratio in the suspension was varied at 10.0-90.0%, 30.0-70.0%, and 50.0-50.0% by weight (Table 1). The suspension was frozen at -20°C for 12 hours in a deep freezer, and the thawed mixture was homogenized using an IKA Ultraturrax at 10,000 rpm for 15 minutes. Subsequently, 25.0 ml of epichlorohydrin (ECH) and 25.0 ml of ammonium hydroxide (NH_4OH) were introduced to the solution to begin the crosslinking reaction. The reaction was performed at 40°C for a duration of 4 hours. Subsequently, the hydrogel was immersed in ethyl alcohol to finalize the crosslinking process. Finally, the hydrogel rinsed with deionized water through a 150-mesh sieve.

Synthesis Process with CIT

Crosslinking by CIT was completed in a single step. In the beginning, cellulose (either raw or pre-treated) was dispersed in deionized water using a mechanical mixer for 10 minutes at 200 rpm. Carboxymethyl cellulose (CMC) was then added to the pulp dispersion and agitated violently with an IKA Ultraturrax at 15000 rpm for 15 minutes. The concentration of cellulose to CMC in the suspension was changed to 10.0-90.0%, 30.0-70.0%, and 50.0-50.0% by weight (Table 1), while also ensuring that the overall mass of the hydrogel remained below 5.0 grams. The suspension was diluted with deionized water to a concentration of 2.0% wt. After that, 5.0% wt citric acid was added depending on the total mass. The mixture, which had a high viscosity, was placed into a beaker and kept at 30°C for 24 hours in order to allow the water to evaporate. It was placed in a water bath at 80°C for 24 hours in order to complete the cross-linking reaction. The hydrogel was then soaked in ethyl alcohol to finish the crosslinking process. After that, it was washed with deionized water using a 150-mesh sieve.

Characterization of Hydrogels

Liquid Absorption Capacity

It is usually determined by measuring the change in weight after the sample is submerged in liquids that have different characteristics. For the swelling experiments, we used pH solutions at 2, 7, and 10, as well as several salt solutions, including NaCl, KCl, $MgCl_2$, and NH_4Cl. Each of the salt solutions was made with a concentration of 0.9%. Simply, the solutions were prepared by diluting 0.9 grams of salt with water to create a total volume of 100 ml. A hydrogel sample (o.d.) was immersed in the liquids for 12 hours at ambient temperature. Upon the end of the period, the residual liquid was removed from the sample by a paper towel, and the following formulas were employed to calculate the liquid absorption and swelling rates of the hydrogels:

$$\text{Liquid uptake (\%)} = m_1 - m_0 \tag{1}$$

$$\text{Swelling rate (\%)} = (m_1 - m_0) \times 100/m_0 \tag{2}$$

Here, it presents the mass of the hydrogel after immersion (m_1), while the mass of the sample before immersion is expressed by (m_0).

Fourier Transform Spectroscopy (FTIR)

KBr-disk method was used for Fourier transform spectroscopy (FTIR) analysis. In this method, the samples were carefully ground in a Wiley mill and KBr-disks were prepared form milled samples. A Schimadzu IRPrestige-21 instrument supported by a PIKE MIRacle ATR instrument was used for the measurements. Operating range was from 4000 to 400 cm^{-1} and the spectral resolution was set to 4 cm^{-1}. The measurements were performed for the samples with 10% cellulose content.

Electron Microscopy

Jeol JSM-6060 and Zeiss Evo LS-10 electron microscopes were utilized for obtaining SEM images. The magnifications were 100x, 250x, 500x, 1000x, 2500x and 5000x. The imaging voltage ranged from 5 to 15 kV. The samples were gold-coated before imaging, and images were obtained for the samples exhibiting the highest swelling rate.

Differential Scanning Calorimetry (DSC)

DSC was used to evaluate the thermal properties of the hydrogels under varying temperatures. For the measurements, 5-7 mg of air-dried and sieved samples (40 and 60 mesh) exhibiting the highest swelling rate were placed in aluminum crucibles. Thermal signals of the samples were collected using a NETZCH DSC 200F3-Maia equipment, and NETZCH Proteus Thermal Analysis software was utilized for result evaluation. The measurements were performed within a temperature range of 20-500°C, using a heating rate of 10°C/min and a nitrogen flow rate of 30 ml/min.

RESULTS AND DISCUSSION

This study aimed to identify the major properties of CMC hydrogels obtained by either treated or untreated cellulose. FTIR spectroscopy was applied to evaluate chemical transformations and detect functional groups in hydrogels. The results were presented in Figure 2. The FTIR spectra indicated C-O stretching vibrations in CMC within the 1020-1160 cm^{-1} range, indicating the presence of hydroxyl functional groups (Wang et al. 2017). The -C-O- functional group was distinctly noted at around 1041 cm^{-1}, signifying the extent of crosslinking within the hydrogel network (Cui et al. 2019, Kundu et al. 2022). The signal intensity in this area indicated variations in crosslinking effectiveness, exhibiting a little stronger absorption band in the ECH spectra relative to other crosslinkers. Furthermore, signals corresponding to OH groups in CMC were detected at approximately 1320 cm^{-1} (Qiu and Yu 2008).

The characteristic vibrations at about 1435, 1589, 1593, and 1616 cm^{-1} were attributed to the COO^- functional groups of CMC (Ma et al. 2007, Seki et al. 2014, Uyanga and Daoud 2021). Previous studies demonstrated a correlation between the width of these peaks and the water absorption capacity of the hydrogel (Barbucci et al. 2000).

The FTIR spectra of samples cross-linked with ECH have greater peaks indicating of carboxylate groups, characterized by multiple peaks, whereas the ones utilizing CIT exhibit narrower peaks with an individual peak. In hydrogels crosslinked with citric acid, functional groups in the 1320 cm⁻¹ band were clearly detected, but no vibrations were noted in this region for samples crosslinked with ECH. An absorption peak was observed at approximately 1666 cm⁻¹, attributable to carbonyl groups (Pasqui et al. 2012). The 1700-1750 cm⁻¹ range exhibited distinctive vibrations associated with C=O stretching band (Kumar et al. 2019; Büyüküstün et al. 2025). This band, which is more prominent for acyclic anhydrides such as citric acid, appears as a shoulder in the FTIR spectrum and supports the formation of cross-linking structures (Demitri et al. 2008).

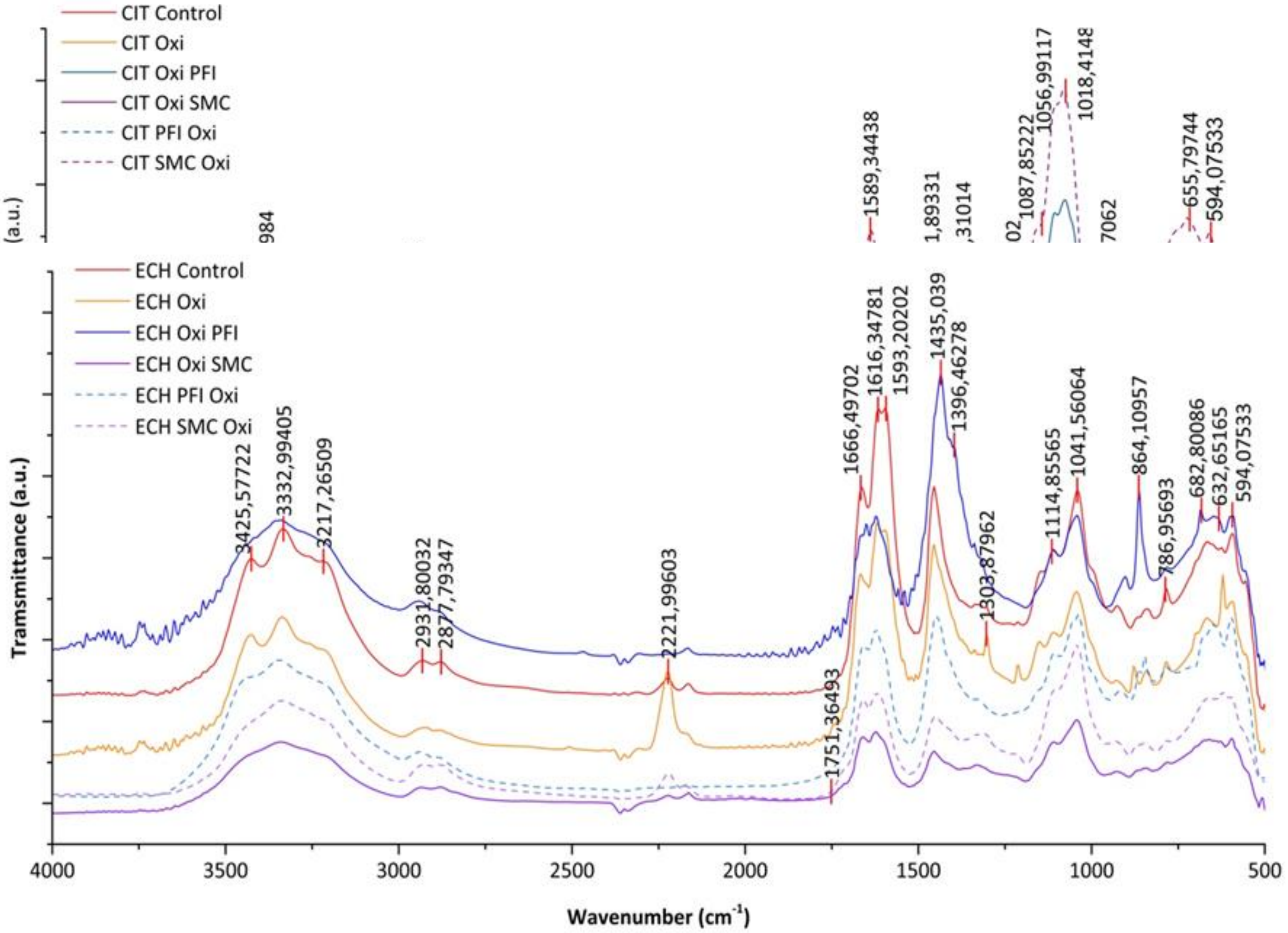

Figure 2. FTIR spectra of hydrogels crosslinked by epichlorohydrin (above) or citric acid (below)

N-stretching vibrations were detected in the 2150-2250 cm⁻¹ range in the ECH crosslinked samples (Pasqui et al. 2012). This indicated a connection between nitrogen-containing functional groups of ECH and it could not be shown for CIT. Similarly, in 786-787 cm⁻¹ range for the spectra of samples crosslinked by ECH, there was a sign which is attributed to out of plane absorption of N-H (Fan et al. 2012). The extensive band detected in the 3000-3600 cm⁻¹ region was ascribed to -OH stretching vibrations, which are essential in hydrogen bonding interactions (Kurtuluş et al. 2024). The strength of this band fluctuated based on the extent of crosslinking. An elevated concentration of free OH groups led to an augmentation in signal intensity and a simultaneous decrease in crosslinking efficiency. The purified cellulose samples demonstrated a reduced intensity in this range, reflecting the effects of mechanical and chemical treatments on the hydroxyl groups.

Figure 3 illustrates the swelling characteristics of the produced hydrogels in different pH solutions. The results obtained from the hydrogels synthesized with ECH (Figure 3a) indicated that the swelling capacities, particularly in acidic pH ranges, were comparatively diminished. Similarly, Chang et al. (2010) found a reduction in the swelling capability of cellulose-based hydrogel concerning pH. Besides, for all groups, an elevation in the cellulose content of the hydrogel matrix led to a reduction in swelling capacity. This trend was particularly evident in the control group. This finding also aligns with prior research (Hubbe et al. 2013).

Furthermore, when comparing groups with equivalent cellulose content, it is evident that pretreatments applied to cellulose substantially minimize the adverse impacts on swelling behavior. For example, the ECH PFI NaOH Urea 30 sample exhibited approximately fourfold more swelling capacity than the ECH Control 30 sample. The samples containing equal quantities of cellulose and CMC exhibited an obvious enhancement in swelling performance due to the effects of the pretreatments. The primary functions of employing fluff pulp (untreated cellulosic fibers) in absorbent materials are to enhance their durability and allow liquid movement (Schuchardt and Berg 1991). The incorporation of fluff pulp is considered effective in preventing the obstruction of gels caused by fully saturated superabsorbent polymer (SAP) particles, which restrict fluid transmission and lack enough separation by the fibers (Hubbe et al. 2013). However, the existence of fines and/or micro- and nano-scale cellulose particles over the acceptable limit creates a paradox. Spagnol et al. (2012) indicated that the absorption capacity of the hydrogel diminished with an increasing nanoscale cellulose ratio, concurrently resulting in an increase in pore size. With SMC treatment, commonly employed in nanocellulose manufacturing, it is probable that a greater quantity of micro- and nanoscale cellulose is generated compared to alternative methods. These events may elucidate the reduction in liquid absorption efficacy of cellulose-based hydrogels subjected to SMC treatment.

Figure 3b illustrates the swelling behavior of hydrogels crosslinked with citric acid and the influence of both raw and processed cellulose additions on these structures. In particular categories (e.g. CIT Oxi SMC 10 in pH 7), swelling rate of the hydrogels exhibited increases up to 16-fold relative to the control group. However, hydrogels including cellulose treated by the CIT Oxi PFI group were found to dissolve in liquids. This occurs by an inadequate crosslinking rate (Hubbe et al. 2013). Demitri et al. (2008) stated that utilizing low amounts of citric acid diminishes the degree of cross-linking, hence resulting in an increased swelling rate. The swelling capacity is often greatest at the point at which crosslinking is sufficient to create phase separation (Wach et al. 2001). In the samples of both group, it is evident that the rise in cellulose content similarly restricts the liquid absorption ability of the hydrogel. In general, it was determined that the swelling rate in alkaline solutions were higher than those obtained in neutral and acidic media in all hydrogel groups without affecting from the type of the crosslinker. Consequently, it is unavoidable that specific hydrogels may dissolve in the liquids, while others will demonstrate superior performance characteristics.

Figures 3c and d illustrate the swelling characteristics of hydrogels in various saline solutions. The initial significant observation is the absence of columns indicating the swelling rates of some hydrogels in saline solutions (e.g., ECH Oxi, CIT Oxi PFI). The samples exhibited solubility in the various liquids and lost their structural stability.

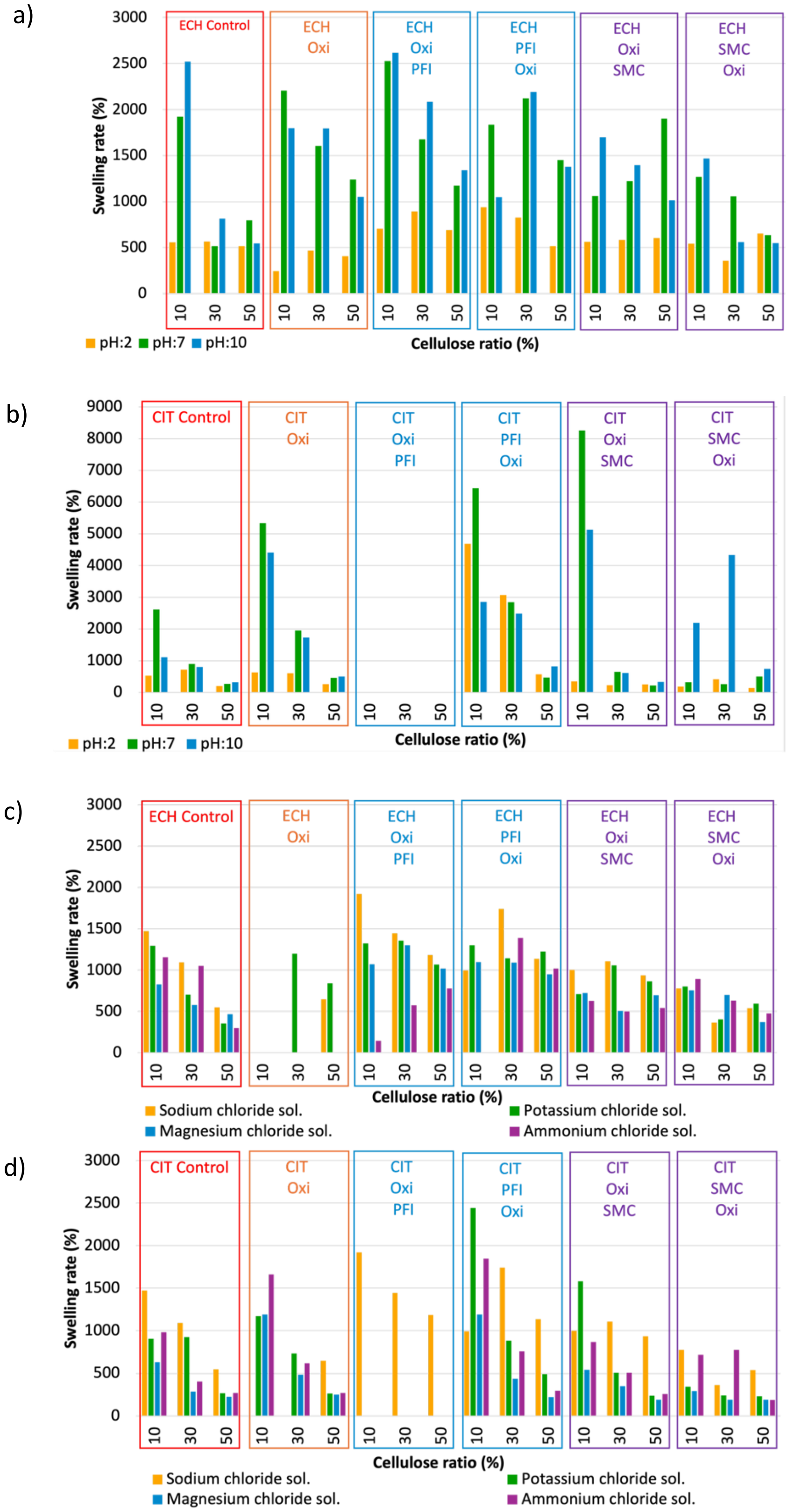

Figure 3. Swelling rate (%) of hydrogels crosslinked by epichlorohydrin (a&c) or citric acid (b&d) in different solutions. a-b) pH solutions, c-d) saline solutions

When each crosslinker is evaluated individually, it is shown that an increase in cellulose content within hydrogels crosslinked with ECH results in reduced liquid absorption and a diminished swelling rate. In comparison to the control group samples with 50% untreated cellulose, the swelling rates of samples having an equivalent quantity of pretreated cellulose were seen to be elevated. A reduction in swelling is anticipated with an increase in valence values, given a constant cation concentration (Hubbe et al. 2013). The swelling rate is expected to be elevated in liquids containing K+ and Na+ cations, but it should be diminished in the presence of Mg^{+2}. The results align with this expectation. The swelling rates of hydrogels in solutions containing $MgCl_2$ salt were low. Despite being comparable to K^+ and Na^+ cations in valence, the swelling rate in liquids formulated with NH_4 salt remained low. This is most likely the result of the larger molecular size in comparison to the other monovalent cations mentioned, which leads to a relatively small penetration of the applied liquids into the hydrogel (Büyüküstün et al. 2025).

The surface morphology of CMC–cellulose hydrogels crosslinked with ECH or CIT is illustrated in Figure 4. Several magnifications from 100x to 5000x were employed to provide enhanced clarity regarding the microstructural characteristics of the hydrogels.

The images demonstrate that the nature of the crosslinker significantly influences the structural properties of the hydrogel network. In the samples crosslinked with ECH, a heterogeneous surface morphology was observed. The cellulosic fibers completely disappeared with surfaces exhibiting noticeable cracks and holes. Conversely, the hydrogels crosslinked with CIT preserved visible fibers and the surfaces of hydrogels largely remained smooth without significant cracks or holes except the fibers. The differences can be partially attributed to the mechanical forces (Johnson et al. 2004, S et al. 2012), such as shrinkage and tension, that arise during the drying phase of hydrogel production. In ECH-crosslinked samples, where covalent bonds create a rigid and extensively interconnected network, mechanical stresses have a more significant impact, resulting in deformation of the surface morphology. Conversely, CIT, an organic acid, forms a less dense network through esterification of cellulose fibers. This flexible network is stronger to resist the mechanical forces generated during drying, therefore maintaining the hydrogel's surface structure.

Furthermore, different chemical environments employed during crosslinking also influence the observed morphological variations. ECH crosslinking is performed in alkaline conditions, whereas CIT crosslinking often takes place in an acidic medium. Alkaline treatment is known to convert cellulose into various allomorphic forms and diminish its crystallinity (Jang et al. 2023). This mechanism presumably undermines the fiber structure, elucidating the lack of visible fibers and changing the surfaces of ECH-treated samples as evidenced by SEM pictures.

Figure 5 illustrates the impacts of modification techniques on cellulose, utilized as a component in composite hydrogels, on the thermal properties of the hydrogels, categorized by the respective crosslinkers. It is known that oxidation process degrades the crystalline structure of cellulose (Siller et al. 2015). A decline in the crystal structure diminishes the thermal resistance of cellulose, leading to lower heat flow values in pretreated samples. The results for both crosslinkers align with the literature (Pedersoli Júnior 2000) and with conclusions from SEM images of hydrogels. The DSC curves of hydrogels crosslinked with CIT did not exhibit any values exceeding 135 mV, which implies that the crystallinity of these structures is inferior to that of hydrogels synthesized with ECH. The thermal stability of hydrogels synthesized using CIT is significantly diminished. The presence of epoxy groups in the ether bonds formed during crosslinking with ECH may be the reason for their enhanced thermal stability. DSC thermograms exhibit a wide endothermic transition between 50-120 °C, particularly in samples created with ECH. This transition is believed to be primarily associated with the elimination of free hydroxyl groups. Nevertheless, the transitions beyond this temperature range cannot be distinctly delineated due to the extensive structure and peak overlap.

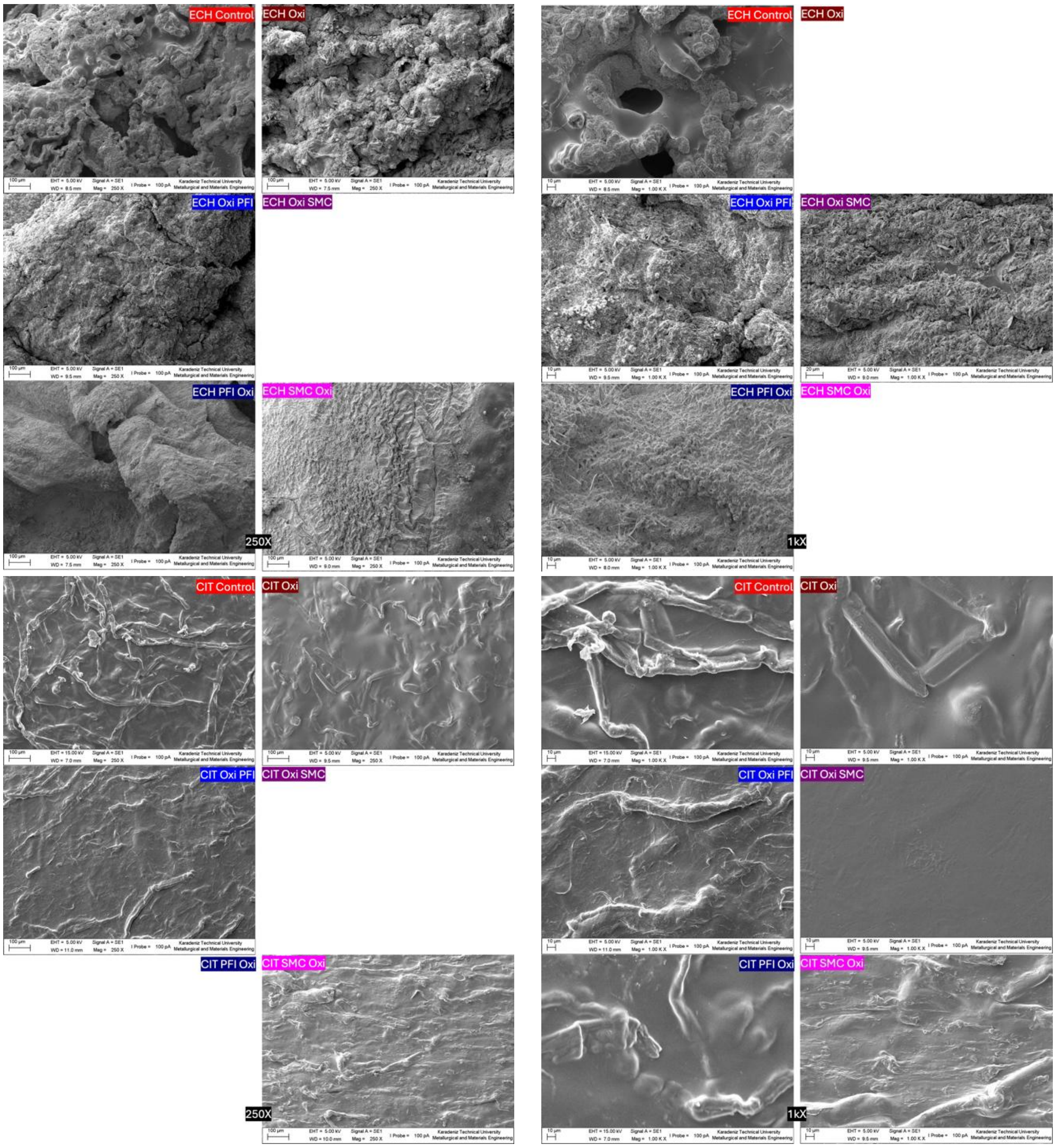

Figure 4. SEM images of CMC-cellulose hydrogels crosslinked with epichlorohydrin and citric acid at 250x and 1000x

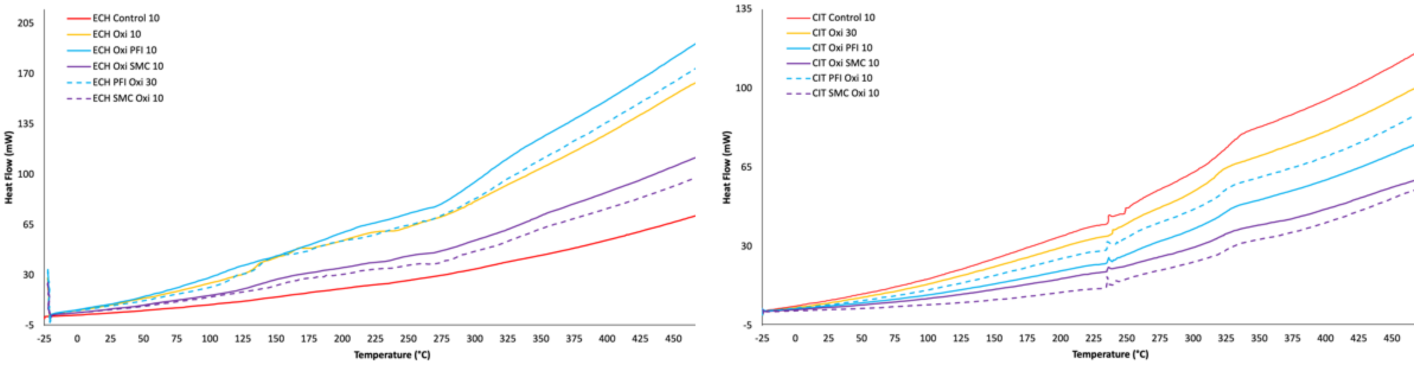

Figure 5. Thermograms of hydrogels (crosslinked by epichlorohydrin (above) or citric acid (below), (endotherm upward)

The phenomena seen between 225-250 °C in the samples treated with CIT likely signifies the heat breakdown of cellulose. Nonetheless, the identical change is not distinctly evident in the samples produced with ECH.

CONCLUSION

This study aimed to minimize or eliminate problems related to the incorporation of cellulose for increasing the gel strength of carboxymethylcellulose-based hydrogels. To achieve this, a sequence of chemical and/or mechanical treatments were carried out to cellulose prior to hydrogel production, and the subsequent modifications in the fundamental characteristics of the hydrogels were examined using FTIR, swelling tests (in various pH and saline solutions), SEM, and DSC studies.

FTIR analysis provided evidence indicating the successful synthesis of the hydrogels. While samples crosslinked with ECH showed peaks belonging to N-containing groups and broader/multiple COO^- peaks, narrower/single COO^- peaks and distinct C=O shoulder peaks were detected in those crosslinked with CIT. DSC analysis indicated that hydrogels crosslinked with ECH possess higher thermal stability compared to those crosslinked with CIT, which is attributed to the presence of epoxy groups in the ether bonds formed with ECH. As a result of the applied pretreatments, it was observed that the liquid uptake and swelling properties of the hydrogels were enhanced or maintained compared to control groups with similar cellulose content. However, in some combinations, it was observed that the samples dispersed in liquids due to an insufficient degree of crosslinking. This phenomenon is explained by the effect of the colloid mill (SMC) application, used in microfibrillated (MFC) and nanofibrillated (NFC) cellulose production, on fiber dimensions. Examination of SEM images revealed that the type of crosslinker used and the application of mechanical treatment altered the surface properties of the hydrogels. Furthermore, it appears that changing the sequence of chemical and mechanical treatments also affects the overall outcomes, including the hydrogel's surface morphology. These findings suggest that subjecting cellulose to pretreatment holds promise for positive outcomes regarding the hydrogel's gelation performance.

In order to improve the results and possible applications of this research for future scholars, subsequent investigations might focus on developing the crosslinking parameters (e.g., concentration, reaction time) specifically for cellulose subjected to the most effective pretreatments, with the objective of minimizing dispersion while maximizing performance, particularly following treatments such as SMC. A thorough study of modifying the sequence of chemical and mechanical treatments, while measuring their effects on morphology, swelling, and particularly on final gel strength, might yield significant design guidance. Furthermore, establishing a clear correlation between the exact sizes of cellulose fibers produced by various pretreatments and the principal hydrogel performance measures could provide profound mechanistic insights for more focused material development.

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