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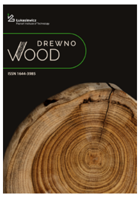

Swelling Capacity in Carboxymethylcellulose – Cellulose Hybrid Hydrogels: The Effects of Oxidation with Zinc Chloride and Refining on Cellulose Used as Reinforcement

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The goal of this study was to address the issue of hydrogels based on carboxymethylcellulose (CMC) having poor gelation strengths when in contact with liquids. To improve this property, cellulose was added to the hydrogels, and their characteristics were then examined. Unlike in previous studies, the cellulose was modified mechanically and chemically before being added. The pulp was refined using a traditional PFI mill or a supermasscolloider as part of a mechanical modification process. In addition, the combination of H_2O_2 and $ZnCl_2$ was chosen for chemical modification of the pulp due to their synergistic effect, where $ZnCl_2$ facilitates fiber swelling, and H_2O_2 enhances Zn^{2+} ions' reactivity, further promoting cellulose oxidation. By creating a cellulosic backbone with higher resistance properties, it is intended to prevent the CMC–cellulose complex from dispersing in water. Epichlorohydrin was utilized in different ratios to crosslink the modified cellulose and CMC in the production of hydrogels. Fourier transform infrared spectroscopy, differential scanning calorimetry, and scanning electron microscopy were used to examine the hydrogels' structural, thermal, and surface characteristics. The results showed that with the addition of modified cellulose, the loss of the hydrogel's swelling and water absorption properties due to the increase in cellulose content can be minimized. The swelling capacity of the samples was significantly preserved by refining the cellulose using a PFI mill. However, refining using a supermasscolloider did not give satisfactory results. In summary, the study showed that modified cellulose reinforcement may be used to produce hydrogels without significantly altering the swelling capacity of CMC-based hydrogels.

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Introduction

Hydrogels, which are linear or branched crosslinked structures that can absorb water or other physiological fluids up to ten to a thousand times their weight [Chen et al., 2010], are widely used in various applications such as hygienic products, agricultural and medical applications, wastewater recovery, and the food industry. In general, they contain functional chemical groups that easily interact with liquids, such as hydroxyl, carboxyl, amine, amide, and sulfonic acid groups [Wang et al., 2017]. An ideal hydrogel is expected to have high gelation resistance and liquid absorption capacity and low human and environmental impact [Zohurian-Mehr and Kabiri, 2008]. Synthetic hydrogels often meet many of these criteria, but also

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have some drawbacks, such as being expensive, toxic, non-biodegradable, and not biologically compatible at the point of use [Chen et al., 2008].

The criteria of toxicity, biocompatibility and biodegradability are crucial for ensuring the safe use of hydrogels in fields such as hygiene, medicine, and the pharmaceutical industry, so as to protect human health [Suo et al., 2007]. Hydrogels made from native polymers such as cellulose, carboxymethylcellulose (CMC), chitin, etc. [Zohurian-Mehr and Kabiri, 2008; Fekete et al., 2010] meet most of these criteria, but their liquid absorption capacity and gelation resistance are lower than those obtained with synthetic hydrogels [Mohy-Eldin et al., 2013]. In studies of native-based hydrogels, the purpose is to improve liquid absorption capacity, gel resistance, cost, biocompatibility, and suitability for usage [Laftah et al., 2011].

Hydrogel manufacturing commonly uses cellulose derivatives as primary native polymers. Compared with other derivatives, CMC is inexpensive, simple to dissolve, and highly reactive [Mohy-Eldin et al., 2013; Wang et al., 2013]. However, due to its weak structure, its gelation resistance is limited when it absorbs water (the structure absorbs water, swells, and disperses). Various processes such as grafting and freeze–thawing [Suo et al., 2007; Chen et al., 2008; Li et al., 2012; Mohy-Eldin et al., 2013; Wang et al., 2013; Wang & Wang, 2016], and polymers such as chitosan, alginate, poly-N-isopropylacrylamide, polyacrylamide, poly(vinyl alcohol) and polyaniline [Ren et al., 2016; Wang & Wang, 2016; Li et al., 2017; Godiya et al., 2019; Su et al., 2020; Feng et al., 2021; Uyanga & Daoud, 2021] can be employed to create composite (or hybrid) hydrogels as a solution to the drawbacks of CMC-based hydrogels.

As the most abundant polymer in nature, cellulose, with three hydroxyl (–OH) groups in each repeating unit, has significant potential to be used in hydrogel production, but obstacles include its high degree of crystallinity and strong intra- and inter-molecular hydrogen interactions that cause a reduction in the water absorption ability of the hydrogel. Generally, it is combined with other materials (typically CMC) as an additive to provide a strong backbone. However, it has been observed that the liquid absorption capacity of hydrogel decreases with increasing cellulose content [Zohurian-Mehr and Kabiri, 2008; Chang et al., 2010; Wang et al., 2017]. If a hydrogel includes cellulose, the reactivity of the cellulose must be enhanced. The higher reactivity of cellulose's amorphous regions is mostly attributed to their containing a larger amount of –OH groups than its crystalline regions. By increasing the percentage of amorphous regions in cellulose, it is anticipated that the bonding of cellulose with CMC and water molecules can be enhanced while the dispersion of the hydrogel in the liquid is prevented. The methods used to make cellulose more reactive (or accessible) are generally classified as chemical, mechanical, and enzymatic processes [Laine et al., 2004; Cabiac et al., 2011]. Increasing cellulose's reactivity makes it easier for it to react and bond with water and other chemicals [Liebert, 2010; Li et al., 2012]. Through mechanical processes, certain natural defects of cellulose may be eliminated. Due to these treatments, the number of functional groups increases as the specific surface area increases; they therefore contribute to improving cellulose's reactivity. This approach involves the papermaking procedures of beating (using a Hollander or PFI mill) and refining using a supermasscolloider (SMC) [Cabiac et al., 2011].

The behaviour of cellulose in solutions prepared from $ZnCl_2$, which is non-toxic and easily recovered, has been studied by various researchers. It was found that solutions comprising 65–76% $ZnCl_2$ and 35–24% water by weight effectively dissolve cellulose; however, only swelling behaviour was observed when the water concentration deviated from that range [Grinshpan et al., 2003]. At $ZnCl_2$ concentrations below 65%, water molecules compete with hydroxyl groups in cellulose for interaction with $ZnCl_2$. Consequently, the dissolving ability of cellulose diminishes, resulting only in swelling. This occurs due to the diffusion of Zn^{2+} ions from aqueous solutions into the amorphous and crystalline parts of cellulose fibres, causing the fibres to swell. This effect may be enhanced by hydrogen peroxide (H_2O_2), a powerful oxidant, which can be expected to elevate the reactivity of Zn^{2+} ions in solution; hence the swelling of cellulose is likely to increase due to the combined effect of H_2O_2 and zinc chloride.

The modification of cellulose for the improvement of certain properties is usually conducted under optimized conditions. In order to overcome the disadvantages caused by the previously mentioned use of cellulose in CMC, the present study focused on a new way to use cellulose in hydrogels. The inclusion of mechanically and/or chemically treated cellulose as a reinforcement in hydrogels is expected to reduce the problems associated with the use of raw cellulose. This strategy attempts to reduce the negative impact on the excellent liquid absorption capacity of hydrogels. The optimal treatment conditions of cellulose were investigated for chemical (H_2O_2 oxidation reinforced by $ZnCl_2$) and mechanical (refining in PFI or SMC) processes. Hydrogels containing different ratios of cellulose and CMC were produced by crosslinking with the use of ECH. A comprehensive characterization of the hydrogels was performed using FTIR, DSC, and SEM to understand their chemical and thermal behaviour and their structural morphology. Water uptake and swelling ratio measurements further extended the analysis by indicating the hydrogels' capacity to absorb and retain water.

Materials and methods

1. Materials

Spruce sulphite wood pulp (100% bleached) was supplied by Borregaard (Norway). The pulp characteristics were as follows: 924 ml.g^{-1} Intrinsic Viscosity (ISO 5351:2004); ≤ 1 Kappa Number (TAPPI T 236 om-13); 93.1 Brightness (ISO 2470:2009); 95.2% Alpha Cellulose (TAPPI T203 cm-99); 5.8% Alkali Solubility S10 (TAPPI T 235 cm-00); 3.3% Alkali Solubility S18 (TAPPI T 235 cm-00). The pulp was also determined to have 0.1269 mmol.g^{-1} COOH content according to Prsakalo et al. [2009] and Milanovic et al. [2012], a freeness of 12 (SCAN C-20:65), and a water retention value (WRV) of 88.4 according to Chen et al. [2010]. Sodium carboxymethylcellulose (CMC) (Mw ~700000) was purchased from Sigma Aldrich (DS: 0.80–0.95). All other chemicals were purchased from Merck KGaA or Sigma Aldrich and used without any additional treatment.

2. Methods of treatment of cellulose

Chemical and mechanical treatments were applied to induce changes in the chemical and morphological properties of the cellulose fibres, i.e. to regulate the proportions of amorphous and crystalline regions and to form particles at the micro/nano level. The cycle of pretreatments applied was varied for sample groups as shown in Table 1.

3. Chemical treatment of cellulose

An amount of 75 g of cellulose (o.d.) was placed in a beaker, and deionized water was added until the total solution concentration reached 10%. On the basis of the total volume of the suspension, 5% NaOH, 15% $ZnCl_2$, and 5%, 10% or 15% H_2O_2 (by weight) were added to the beaker. The suspension was kept in a water bath at 80 °C for 180 min. After that time, the suspension was washed with deionized water on a 150 mesh sieve. The pulp remaining on the sieve was manually pressed to remove excess water and then collected from the sieve. The samples were stored in a sealed polythene bag in a refrigerator operating at +4 °C. The mechanical treatments were performed only for the samples oxidized with 15% H_2O_2, since this group exhibited the maximum water retention value (WRV) of 150.5%. The addition of 5% and 10% H_2O_2 resulted in WRVs of 127.9% and 126.9%, respectively. After chemical treatment, –COOH content was determined as 0.22, 0.08 and 0.13 mmol.g^{-1} respectively for the lowest, middle and highest H_2O_2 concentrations.

Table 1. Pre-treatment and reaction conditions of the cellulose/CMC Hydrogels

Pre-treatment Step		Sample Code	Cellulose ratio in mixture (%)	CMC ratio in mixture (%)
First	Second			
None	None	Process 0	10	90
			30	70
			50	50
Chemical	None	Process 1	10	90
			30	70
			50	50
Chemical	PFI Refining	Process 2	10	90
			30	70
			50	50
PFI Refining	Chemical	Process 3	10	90
			30	70
			50	50
Chemical	SMC Refining	Process 4	10	90
			30	70
			50	50
SMC Refining	Chemical	Process 5	10	90
			30	70
			50	50

4. Mechanical treatment of cellulose

The conditions of mechanical treatment performed with the two devices are summarized below.

PFI refining: In a PFI mill, cellulose was mechanically beaten between two rotating cylinders at a pulp concentration of 10% and at 4000 rpm in accordance with the TAPPI T248 sp-15 standard.

SMC refining: Cellulose was refined using a Masuko supermasscolloider (MKCA6-2J) with a grit coarseness of 80, with two Al_2O_3 stones, one fixed and the other rotating. The space between the stones was adjustable within a range of 0–250 µ. This gap was set to 20 µ and the samples were passed between the stones five times. The rotation speed of the stones was set to 1,500 revolutions per minute, and the working concentration was kept at 2%.

5. Hydrogel synthesis

Hydrogels were prepared using a crosslinking polymerization process that involved epichlorohydrin (ECH). A number of mixtures were formulated to obtain hydrogels with cellulose ratios of 10%, 30% and 50%. First, 5 g of a blend of cellulose and CMC (in the proportions indicated in Table 1) was weighed out, and was dispersed in a solution consisting of 195 g of 6 wt.% NaOH, 4 wt.% urea, and 90 wt.% water. The resulting suspension was frozen at -20 °C for 12 hours and subsequent thawing. To obtain a clear cellulose/CMC solution, the mixture was subjected to high-speed mixing in an IKA Ultra-Turrax device at 15,000 rpm for 15 minutes to obtain a solution consisting of cellulose–CMC. Then 25 ml of ECH was added to the cellulose/CMC solution, ammonium hydroxide was further added, and the solution was kept at 40 °C for 4 h. After that time the product was poured into ethyl alcohol to stop the reaction, and then washed with deionized water on a sieve. Process 0 was used for the control group; the cellulose for this group was utilized in hydrogel synthesis in its original form without any modifications.

6. Hydrogel swelling measurements

The capacity of the hydrogels to absorb saline solutions, which is a very important property for biomedical applications of such materials, was also investigated. For this purpose, aqueous solutions containing NaCl, KCl, $MgCl_2$, and NH_4Cl salts at 0.9% (w/w) concentration were used. To prepare saline solution at 0.9% concentration, 0.9 g of salt was used per 100 g of solution.

A piece of hydrogel sample of known dry weight was immersed in one of the aforementioned liquids for 12 hours at room temperature. The sample was then placed in a Büchner funnel with filter paper on the bottom to remove excess liquid. Values of water absorption and swelling were determined using the following formulae:

$$\text{Water uptake (g)} = m_1 - m_0 \tag{1}$$

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

where m_1 denotes the mass of the hydrogel sample after immersion, and m_0 is the initial total dry weight of the sample.

7. FTIR analysis

Following Gümüskaya et al. [2003], samples were carefully prepared for FTIR spectroscopic analysis by grinding in a Wiley mill. Samples for testing were produced using the KBr-disc technique. The samples were then subjected to ATR-FTIR analysis using a Schimadzu IRPrestige-21 instrument equipped with a PIKE MIRacle single reflection ATR instrument. A spectral range from 4000 cm^{-1} to 400 cm^{-1} was used, with the spectral resolution set to 4 cm^{-1}. FTIR spectra were obtained from 10% cellulose-reinforced hydrogel samples in each experimental group.

8. DSC analysis

The thermal properties of the hydrogels were investigated using a Netzsch DSC 200F3-Maia instrument. The experiments were carried out in the temperature range 20–500 °C, using a heating rate of 10 °C/min and a nitrogen flow rate of 30 ml/min. Prior to the measurements, the samples were ground in a Wiley mill and then separated using sieves with mesh sizes of 60 and 40. The portion of the samples remaining on the 40 mesh sieve was used for thermal analysis. For each measurement, approximately 5–7 mg of sample was placed in a hermetically sealed aluminium crucible. To ensure the reliability of the results, each measurement was repeated three times, and the instrument's software (Netzsch Proteus Thermal Analysis) was used to calculate the average of the results. Measurements were obtained only from the 10% cellulose-reinforced hydrogel samples in each experimental group.

9. SEM analysis

To determine the surface properties of the hydrogels, the surfaces of samples were imaged using Jeol JSM-6060 and Zeiss Evo LS-10 electron microscopes at 100X, 500X, 1000X and 3000X magnifications. Before SEM imaging, the samples were coated with gold. The operating voltage was 5 kV or 15 kV.

Results and discussion

The aim of the study was to examine the effect of pretreatments of cellulose used in hydrogels, with the goal of reducing the adverse effects related to the characteristics of cellulose utilized to enhance the gel strength of CMC-based hydrogels.

1. Swelling behaviour of samples in different liquids

Swelling ratios of hydrogels are presented in Figure 1 for liquids with pH values ranging from 2 to 10, and in Figure 2 for solutions containing salts (NaCl, KCl, $MgCl_2$ and NH_4Cl).

The swelling behaviour of hydrogels in liquids with various pH values is an essential parameter determining their suitability for many applications. The solutions used in the study had pH values ranging from 2 to 10. Under neutral and alkaline conditions, higher swelling values are expected [Liu et al., 2002; Wang et al., 2013]. A pH of 7 was determined to be the most favourable for swelling, which aligns with earlier research findings. Above pH 7, the swelling behaviour exhibited no consistent pattern of change.

The swelling ratio of hydrogels with 10% cellulose subject to **Process 0** was remarkably high for almost all pH values, although significant decreases were observed as the cellulose concentration was raised. In good agreement with the observations of previous studies [Chang et al., 2010], higher cellulose content in the hydrogel seemed to have negative effects on its swelling ability. The mechanical and chemical treatments applied to the cellulose in this study were intended to reduce these negative effects.

The samples that underwent only chemical treatment (**Process 1**) did not yield the expected results, with nearly all samples exhibiting the lowest values. In this group, no mechanical treatment (PFI or SMC) was applied to the cellulose, to enable a focus on the chemical effects. Zinc chloride ($ZnCl_2$) solutions at high concentration (65–76%) are quite effective in dissolving cellulose. Due to the process of dissolution and side reactions, both water-soluble and insoluble cellulose with a low degree of polymerization (DP) are produced [Cao et al., 1994]. Chen et al. [2020] demonstrated that the process of cellulose dissolution in $ZnCl_2{\cdot}3H_2O$ involves the conversion of **cellulose I** into **cellulose II** by crystal transformation. Cellulose with a high degree of crystallinity will be unable to dissolve in a weak $ZnCl_2$ solution, but this would not be the case for lower molecular weight and amorphous regions of cellulose. By subjecting the cellulose to $ZnCl_2$ treatment, the more accessible fractions are eliminated, resulting in a more stable structure. While this may explain the reduced rate of swelling in hydrogels, an alternative reason may be the replacement of hydroxyl (OH) groups on cellulose chains with zinc (Zn) groups.

Figure 1 shows the impact of changes to the pretreatment cycle on the swelling values of hydrogels in liquids at pH 2, 7 and 10. The cellulose that had undergone PFI refining and subsequent treatment with $ZnCl_2$ (**Process 3**) yielded exceptionally good results in comparison with the other groups of samples. The application of mechanical treatment in the second step (**Process 2**) appears to diminish the impact of chemical treatment. Nevertheless, it is evident that PFI refining provides better results than SMC refining (**Processes 4** and **5**). This means that adverse effects such as hornification of fibres that occur during PFI refining were relatively limited, and this influenced the swelling performance of the hydrogels.

Mechanical pretreatments create changes in the cellulose structure, including enhanced fibrillation, increased surface area, hydration capacity, and reactivity [Laine et al., 2004; Cabiac et al., 2011]. Additionally, they raise the fibre saturation point (FSP) and the volume of pores. Consequently, they enhance the accessibility of cellulose and result in greater absorption of water. However, it is important to remember that extended refining times might have adverse effects, including decreased fibre lengths, the formation of fines, and hornification.

SMC is highly effective in altering the physical and chemical characteristics of cellulose, and is a key method employed in the manufacture of micro- and nano-fibrillated cellulose. The reduction of cellulose to micro- or nano-size potentially affects its reactivity (number of released –OH groups) and hence its

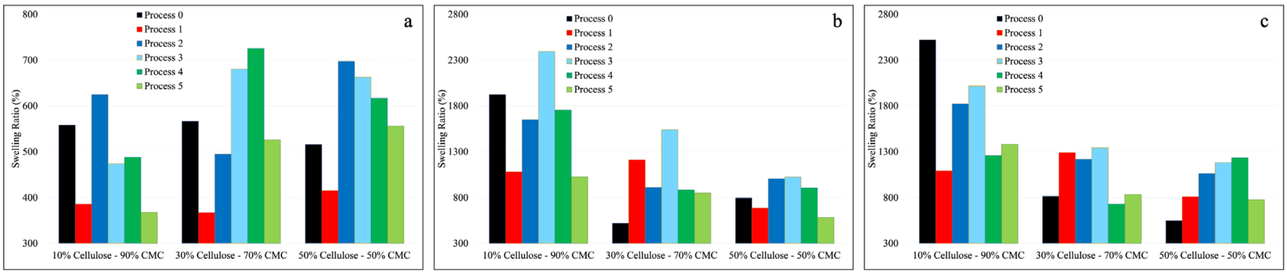

Fig. 1. Swelling behaviour of hydrogels in liquids at pH 2 (a), pH 7 (b) and pH 10 (c) depending on the cellulose content

association with water or other chemicals [Laitinen & Niinimiaki, 2014]. The results indicated that the water absorption ability of hydrogels was significantly influenced by SMC refining (**Processes 4** and **5**), particularly when the cellulose content in the hydrogels was higher. However, it was observed that **Processes 2** and **3** were more reliable than refining using SMC. The decreased swelling ratios resulting from **Processes 4** and **5** were linked to an increase in the quantity of micro- and nano-scale particles. The rise in the quantity of particles at these levels possibly caused the closure of micropores in the hydrogel, diminishing the penetration of liquids.

Salt solutions offer valuable insights into behaviour in liquids with different properties. This methodology assists the identification of specific fields in which hydrogels can be utilized. The impact of salt solutions on hydrogel swelling is dependent on solution characteristics such as ion strength, hydration capacity, and ion size. Figure 2 presents the results of tests of the impact of different salt solutions on the swelling characteristics of hydrogels containing CMC and cellulose reinforcement.

$MgCl_2$ is utilized in nutrition for enhancing wellness and supporting the health of athletes. It contains magnesium ions with a charge of $^{2+}$ [Bock et al., 1999; Xu et al., 2023], which leads to a larger concentration of ions in water solutions, causing a reduced swelling effect. The higher ionic strength can result in interaction between polymers within the hydrogel structure, thereby restricting water absorption. Magnesium ions (Mg^{2+}) can restrict the interaction between hydrogel and water by generating a greater attractive force on the surrounding water molecules, compared with other ions. As a result, the swelling rate of hydrogels in such liquids is limited (Figure 2c). In contrast, Na^+ ions penetrate the cell wall of cellulosic fibres more easily due to their smaller size, increasing cell volume and swelling (Figure 2a). The swelling performance of hydrogels is generally reduced by increasing the cellulose content, except when exposed to NaCl solution. This exception is presumed to be caused by the influence of the size of Na^+ ions. For solutions in which Mg and NH_4 salts were used, it was determined that **Process 3** gave the highest result regardless of the cellulose ratio used in the hydrogel. NH_4Cl (ammonium chloride) can also be used in medical and biomedical applications, in the agricultural and food industries, and in refrigeration systems and packaging materials. Similarly to Mg^{2+} ions, ammonium ions can form strong hydrogen bonds with water molecules, affecting the hydrogel in a similar way. Again, the possibility of easy interaction with carboxylate groups ($–COO^-$) in hydrogels due to the high ion charge and size can make their effect on swelling behaviour similar to that of Mg^{2+} ions.

The swelling rate of **Process 0** samples in Na solution decreased by approximately two-thirds as the cellulose

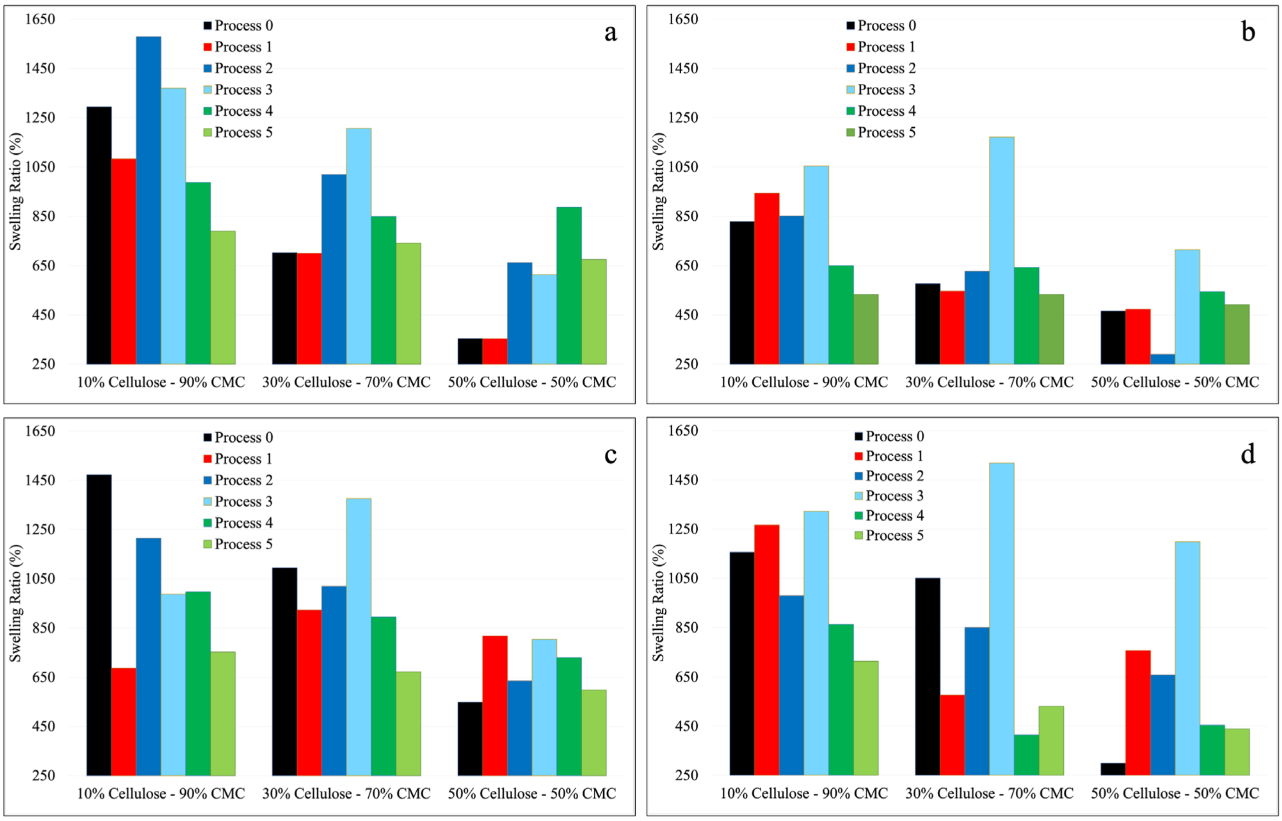

Fig. 2. Swelling ratio of hydrogels in different salt solutions: (a) NaCl, (b) KCl, (c) MgCl2, (d) NH4Cl

content increased (Figure 2a). Other samples exposed to the same solution exhibited inconsistent effects from an increase in cellulose content, with some samples even showing an increase. These findings are particularly important for medical, agricultural and food industry applications where Na-based solutions are used. The treatments may be effective in this particular scenario, but **Process 5** was found to give the lowest results for all groups in this solution. This is probably explained by the fact that fragments formed by the breakdown of cellulose as a result of the treatments block the pores in the hydrogel structure. The accessibility of cellulose increases significantly in **Process 1**, where the cellulose added to the hydrogel has been subjected to chemical treatment without mechanical treatment, as evidenced by the results obtained with Na solution. This may be attributed to the fact that the width of the fibres increases as a result of the treatment method used for **Process 1**. The fibres in hydrogels produced by **Process 1** maintain their original shape because the pulp is not subjected to mechanical treatment. The hydrogel's capacity to incorporate liquid increases as the fibre width increases.

Products containing KCl are utilized as electrolyte alternatives for topical usage and to enhance wound healing processes [Choi et al., 2024]. In potassium salt solution, for all samples, a similar downward trend in the swelling ratio was observed as the cellulose content increased. The mechanical processes resulted in favourable outcomes for these solutions. It was determined that the losses in swelling ratio as the cellulose ratio increased were smaller in the case of refining with PFI or SMC than in the case of **Processes 0** and **1**.

It is observed that among all sample groups, the highest values in salt solutions are attained with the use of PFI as in **Processes 2** and **3**. When all processes are ranked, it is found that those with PFI (**Processes 2** and **3**) are in first place, the control group (**Process 0**) in second place, the samples reinforced with cellulose with only chemical pretreatment (**Process 1**) in third place, and the hydrogels reinforced with cellulose following SMC refinement (**Processes 4** and **5**) in last place. In the pretreatment of cellulose with SMC, the fibres are subject to greater forces, and while some new properties can be created, certain other properties are lost. The heat-induced hornification resulting from the treatment with SMC reduces the amount of water uptake and retention and thus the degree of swelling.

2. FTIR analysis

Cellulosic polymers exhibit chemical changes when exposed to mechanical and/or chemical treatments. FTIR spectroscopy is a useful technology to identify these changes. The structures of hydrogels produced from cellulose and CMC were examined by this means, and the results for hydrogels with the addition of 10% cellulose are shown in Figure 3.

The presence of the ester group (–C=O) as an indication of crosslinking through epichlorohydrin is observed as a small peak around 1735–1750 cm^{-1} [Kumar et al., 2019]. Additionally, Capanema et al. [2018] conducted investigations concerning vibrations in the same location related to the ester groups in –COOH. The intensity of the peak at 1440–1450 cm^{-1}, which is related to the stretching of CH bonds in the crosslinks between CMC and cellulose chains, was smaller in the case of samples treated with **Process 4** (10% cellulose content). This suggests that there is less crosslinking in these samples. Major vibrations of –COOH groups are observed at 1620 cm^{-1} and 1450 cm^{-1}. Consistently with findings reported in the literature, the magnitude of the peak observed at around 1600 cm^{-1} declined as the vibration intensity increased, suggesting the occurrence of crosslinking [Barbucci et al., 2000].

The treatment of cellulose resulted in a decrease in the intensity of the peaks between 1620 and 1660 cm^{-1}, which are associated with COOH groups [Chang et al.,

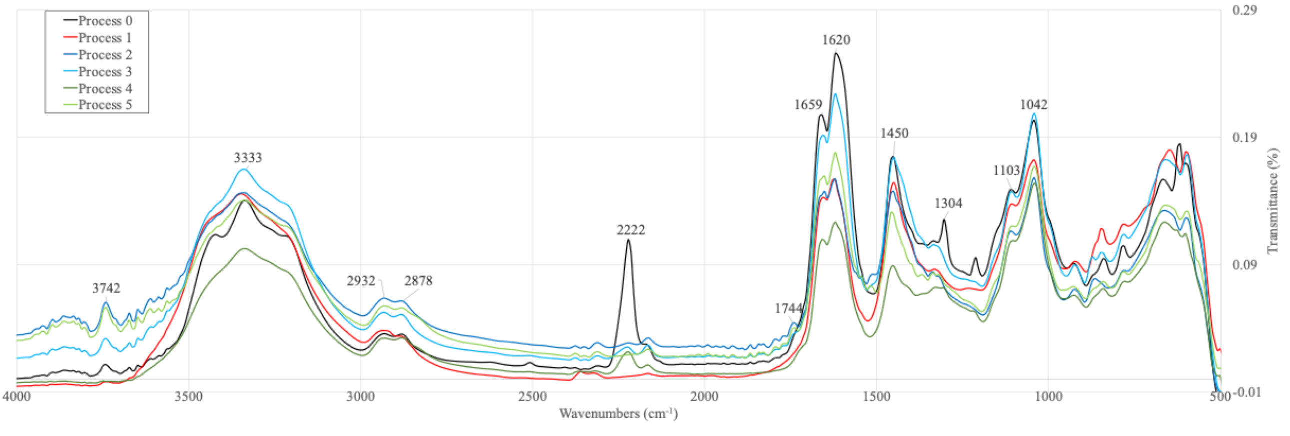

Fig. 3. FTIR spectra of selected hydrogels containing cellulose

2010; Fan et al., 2012]. Replacing carboxymethylcellulose (CMC) with cellulose in hydrogels reduced the magnitude of the peak associated with the total number of carboxyl groups (–COOH). The O–H stretching vibrations for CMC are assigned to the 3100–3600 cm^{-1} band [Buhus et al., 2009]. The location and size of these peaks varied depending on the intensity of the treatments, showing changes in intramolecular and intermolecular hydrogen bonding and hydration capacity.

3. DSC analysis

The thermal behaviour of hydrogel samples subjected to different treatments (**Processes 0–5**) under varying conditions was investigated by DSC. The first notable finding is that energy absorption was consistent for all samples. It was found that the hydrogel produced following **Process 3** had the highest energy absorption capacity, while **Process 1** led to the lowest. This can be attributed to the higher cellulose concentration in the sample produced by **Process 1**, since it has a greater amount of cellulose compared with the other samples with 30% cellulose content. An increase in the cellulose content within the hydrogel results in changes to the structure of the hydrogel, such as a rise in the average crystallinity index and modifications in the interaction between water molecules, carbohydrates, and other morphological characteristics. These changes, of course, impact the thermal characteristics. It is well established that cellulose has a higher crystallinity index than CMC [He et al., 2009]. According to Das et al. [2021], the crystalline regions of cellulose serve as a barrier to the transfer of heat, which is a critical factor in the reduction of energy absorption. The proportion of crystalline zones in cellulose is expected to be changed by modification processes. As a result, possible changes in the crystalline structure will have an impact on the energy absorption levels of the samples. In these samples, the endothermic changes beginning at approximately 70 °C reported by researchers such as Dai et al. [2018] and Poletto et al. [2014], which were attributed to water loss, were not observed.

4. SEM analysis

SEM (scanning electron microscopy), which supplies information about the surface morphology, internal structure and network formation of hydrogels, provides important indications regarding their potential areas of application. With this aim in mind, images were used to analyse the surface characteristics of the hydrogel samples with the highest degrees of swelling. These images are shown in Figure 4.

SEM analysis offers a variety of insights into the internal structure, network formation, and surface morphology of hydrogels. Fibrillation, an increase in surface area, a reduction in fibre length, and hydration of the fibres are results of the mechanical forces applied during the refining process. The surface opacity is slightly increased by refining following chemical treatment (**Process 2**). Conversely, when refining is performed initially, as in **Process 3**, fibre clusters and pores are visible. The quantity of small particles (fines) is increased, particularly at the micro and nano scales, by mechanical treatment using SMC (**Processes 4** and **5**). The swelling rates decreased as a consequence of the increased amount of fines, which in turn led to a reduction in micropores.

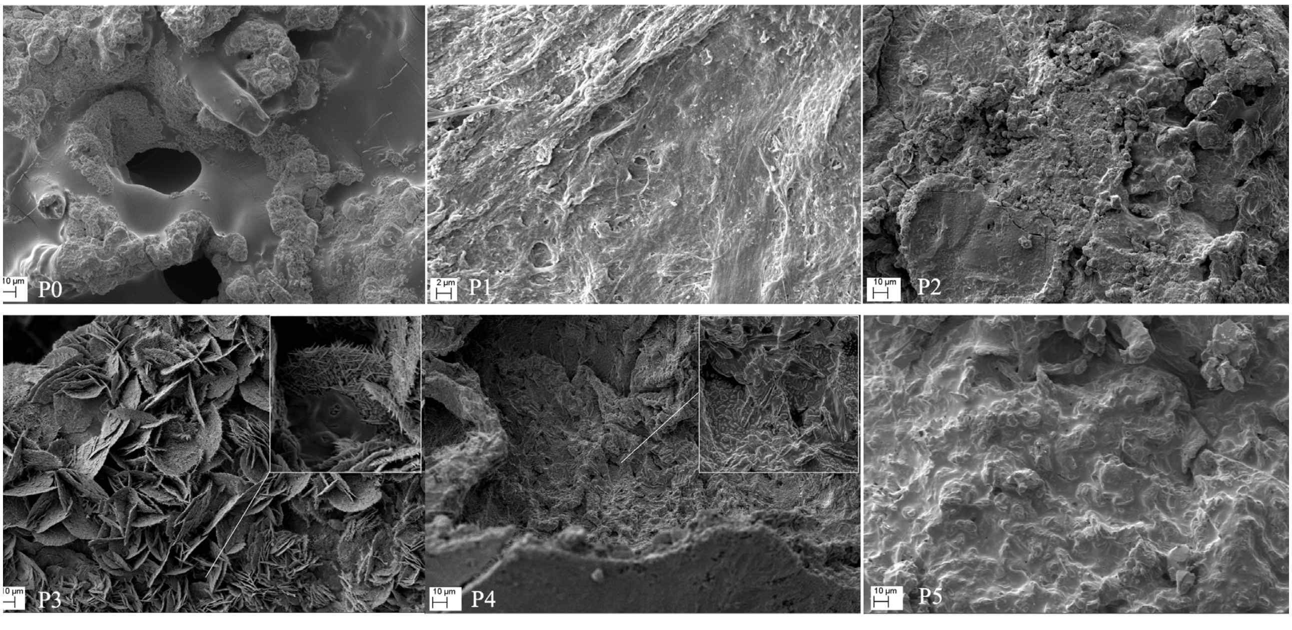

Fig. 4. Selected SEM images of hydrogels. The images were captured at a magnification of 1kx, except for P1, which was captured at 5kx

Conclusions

This study has examined the influence of the pretreatment of cellulose on the characteristics of cellulose/CMC-based hydrogels, with the aim of addressing concerns related to gel resistance, dispersion, and dissolution. The FTIR analyses demonstrated the successful formation of chemical bonds between the molecules, resulting in the crosslinking of the hydrogel. Additionally, the investigation revealed noticeable alterations in the structure of the hydrogel when reinforcements were introduced. The hydrogels exhibited excellent resistance to gelation for all liquids and successfully completed swelling tests without dispersing or dissolving. The hydrogel produced by **Process 1** exhibited the least amount of swelling, whereas the hydrogel synthesized by **Process 3** gave more encouraging outcomes. The swelling characteristics of hydrogels in salt solutions varied depending on the specific type of salt used. The $MgCl_2$ solution produced the lowest rate of swelling due to its strong ionic connections, whereas NaCl had a higher permeability. The DSC investigations revealed notable disparities in energy absorption levels, with **Process 1** leading to minimal absorption curves. Scanning electron microscopy (SEM) images showed that mechanical pretreatments, specifically PFI refinement, increased the surface area of cellulose and influenced its swelling capacity.

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References

Barbucci, R., Magnani, A., & Consumi, M. [2000]: Swelling Behavior of Carboxymethylcellulose Hydrogels in Relation to Cross-Linking, pH, and Charge Density. *Macromolecules, 33*, 7475-7480. DOI: 10.1021/ma0007029

Bock, C., Katz, A.K., Markham, A., & Glusker, J.P. [1999]: Manganese as a Replacement for Magnesium and Zinc: Functional Comparison of the Divalent Ions. *Journal of the American Chemical Society, 121*, 7360-7372. DOI: 10.1021/ja9906960

Buhus, G., Peptu, C., Popa, M.I., & Desbrières, J. [2009]: Controlled release of water soluble antibiotics by carboxymethylcellulose- And gelatin-based hydrogels crosslinked with epichlorohydrin. *Cellulose Chemistry and Technology, 43*, 141-151.

Cabiac, A., Guillon, E., Chambon, F., Pinel, C., Rataboul, F., & Essayem, N. [2011]: Cellulose reactivity and glycosidic bond cleavage in aqueous phase by catalytic and non catalytic transformations. *Applied Catalysis A – General, 402*, 1-10. DOI: 10.1016/j.apcata.2011.05.029

Cao, N., Xu, Q., Chen, C.S., Gong, C.S., & Chen, L.F. [1994]: Cellulose hydrolysis using zinc chloride as a solvent and catalyst. *Applied Biochemistry and Biotechnology, 45-46*, 521-530. DOI: 10.1007/BF02941827

Capanema, N.S., Mansur, A.A., de Jesus, A.C., Carvalho, S.M., de Oliveira, L.C., & Mansur, H.S. [2018]: Superabsorbent crosslinked carboxymethyl cellulose-PEG hydrogels for potential wound dressing applications. *International Journal of Biological Macromolecules, 106*, 1218-1234. DOI: 10.1016/j.ijbiomac.2017.08.124

Chang, C., Duan, B., Cai, J., & Zhang, L. [2010]: Superabsorbent hydrogels based on cellulose for smart swelling and controllable delivery. *European Polymer Journal, 46*, 92-100. DOI: 10.1016/j.eurpolymj.2009.04.033

Chen, Y., Liu, Y., & Tan, H. [2008]: Preparation of macroporous cellulose-based superabsorbent polymer through the precipitation method. *BioResources* 3(1), 247-254. DOI: 10.15376/biores.3.1.247-254

Chen, Y., Wang, Y., Wan, J., & Ma, Y. [2010]: Crystal and pore structure of wheat straw cellulose fiber during recycling. *Cellulose, 17*, 329-338. DOI: 10.1007/s10570-009-9368-z

Chen, Y., Yu, H., & Li, Y. [2020]: Highly Efficient and Superfast Cellulose Dissolution by Green Chloride Salts and Its Dissolution Mechanism. *ACS Sustainable Chemistry & Engineering*, 8(50), 18446-18454. DOI: 10.1021/acssuschemeng.0c05788

Choi, C. R., Kim, E. J., Choi, T. H., Han, J., & Kang, D. [2024]: Enhancing Human Cutaneous Wound Healing through Targeted Suppression of Large Conductance Ca2+-Activated K+ Channels. *International Journal of Molecular Sciences*, *25*(2), 803. DOI: 10.3390/ijms25020803

Dai, H., Huang, Y.S., & Huang, H. [2018]: Eco-friendly polyvinyl alcohol/carboxymethyl cellulose hydrogels reinforced with graphene oxide and bentonite for enhanced adsorption of methylene blue. *Carbohydrate Polymers, 185*, 1-11. DOI: 10.1016/j.carbpol.2017.12.073

Das, D., Prakash, P., Rout, P.K., & Bhaladhare, S. [2020]: Synthesis and Characterization of Superabsorbent Cellulose-Based Hydrogel for Agriculture Application. *Starch – Stärke,* 73(1-2), 1900284. DOI: 10.1002/star.201900284

Fan, M., Dai, D., & Huang, B. [2012]: Fourier Transform Infrared Spectroscopy for Natural Fibres. In: Salih, M. S. (ed) Fourier transform-materials analysis. InTech, Rijeka, Crotia, pp 45-68. DOI: 10.5772/35482

Fekete, T., Borsa, J., Takács, E., & Wojnárovits, L. [2014]: Synthesis of cellulose derivative based superabsorbent hydrogels by radiation induced crosslinking. *Cellulose, 21*, 4157-4165. DOI: 10.1007/s10570-014-0445-6

Feng, S., Liu, F., Guo, Y., Ye, M., He, J., Zhou, H., Liu, L., Cai, L., Zhang, Y., & Li, R. [2021]: Exploring the role of chitosan in affecting the adhesive, rheological and antimicrobial properties of carboxymethyl cellulose composite hydrogels. *International Journal of Biological Macromolecules*, *190*, 554-563. DOI: 10.1016/j.ijbiomac.2021.08.217

Godiya, C.B., Cheng, X., Li, D., Chen, Z., & Lu, X. [2019]: Carboxymethyl cellulose/polyacrylamide composite hydrogel for cascaded treatment/reuse of heavy metal ions in wastewater. *Journal of Hazardous Materials, 364*, 28-38. DOI: 10.1016/j.jhazmat.2018.09.076

Grinshpan, D.D., Savitskaya, T.A., & Tsygankova, N.G. [2003]: Non-traditional solutions of cellulose and its derivatives and their processing products. *Chemical Problems of the Development of New Materials and Technologies*, 295-326.

Gümüşkaya, E., Usta, M.C., & Kirci, H. [2003]: The effects of various pulping conditions on crystalline structure of cellulose in cotton linters. *Polymer Degradation and Stability, 81*, 559-564. DOI: 10.1016/S0141-3910(03)00157-5

He, X., Wu, S., Fu, D., & Ni, J. [2009]: Preparation of sodium carboxymethyl cellulose from paper sludge. *Journal of Chemical Technology & Biotechnology, 84*, 427-434. DOI: 10.1002/jctb.2057

Kumar, B., Sauraj, & Negi, Y.S. [2019]: To investigate the effect of ester-linkage on the properties of polyvinyl alcohol/carboxymethyl cellulose based hydrogel. *Materials Letters*. *252*, 308-312. DOI: 10.1016/J.MATLET.2019.05.118

Laftah, W.A., Hashim, S., & Ibrahim, A.N. [2011]: Polymer Hydrogels: A Review. *Polymer-Plastics Technology and Engineering, 50*(14), 1475-1486. DOI: 10.1080/03602559.2011.593082

Laine, C., Wang, X., Tenkanen, M., & Varhimo, A. [2004]: Changes in the fiber wall during refining of bleached pine kraft pulp. *Holzforschung 58*(3), 233-240. DOI: 10.1515/HF.2004.036

Laitinen, O., & Niinimäki, J. [2014]: Fractional study of the microfibrillated cellulose. Tappi Journal 13(7), 49-55. DOI: 10.32964/tj13.7.49

Li, Q., Ma, Z., Yue, Q., Gao, B., Li, W., & Xu, X. [2012]: Synthesis, characterization and swelling behavior of superabsorbent wheat straw graft copolymers. *Bioresource Technology, 118*, 204-9. DOI: 10.1016/j.biortech.2012.03.028

Li, J., Fang, L., Tait, W.R., Sun, L., Zhao, L., & Qian, L. [2017]: Preparation of conductive composite hydrogels from carboxymethyl cellulose and polyaniline with a nontoxic crosslinking agent. *RSC Advances, 7*(86), 54823-54828. DOI: 10.1039/C7RA10788A

Liebert, T.F. [2010]: Cellulose Solvents – Remarkable History, Bright Future. In: Liebert, T.F., Heinze, T.J., Edge, K.J. (eds) Cellulose Solvents: For Analysis, Shaping and Chemical Modification, 1st edn. AS Publishing, Washington DC, USA, pp 3-54. DOI: 10.1021/bk-2010-1033.ch001

Liu, P., Zhai, M., Li, J., Peng, J., & Wu, J. [2002]: Radiation preparation and swelling behavior of sodium carboxymethyl cellulose hydrogels. *Radiation Physics and Chemistry, 63*(3-6), 525-528. DOI: 10.1016/S0969-806X(01)00649-1

Milanovic, J.Z., Kostić, M.M., & Škundrić, P. [2012]: Structure and properties of tempo-oxidized cotton fibers. *Chemical Industry & Chemical Engineering Quarterly, 18*(3), 473-481. DOI: 10.2298/CICEQ120114024M

Eldin, M.S., Omer, A.M., Soliman, E.A., & Hassan, E.A. [2013]: Superabsorbent polyacrylamide grafted carboxymethyl cellulose pH sensitive hydrogel: I. Preparation and characterization. *Desalination and Water Treatment, 51*(16-18), 3196-3206. DOI: 10.1080/19443994.2012.751156

Poletto, M., Ornaghi Júnior, H.L., & Zattera, A.J. [2014]: Native Cellulose: Structure, Characterization and Thermal Properties. *Materials, 7*(9), 6105-6119. DOI: 10.3390/ma7096105

Praskalo, J., Kostić, M.M., Potthast, A., Popov, G.V., Pejić, B., & Škundrić, P. [2009]: Sorption properties of TEMPO-oxidized natural and man-made cellulose fibers. *Carbohydrate Polymers, 77*(4), 791-798. DOI:.1016/j.carbpol.2009.02.028

Ren, H., Gao, Z., Wu, D., Jiang, J., Sun, Y., & Luo, C. [2016]: Efficient Pb(II) removal using sodium alginate-carboxymethyl cellulose gel beads: Preparation, characterization, and adsorption mechanism. *Carbohydrate Polymers, 137*, 402-409. DOI: 10.1016/j.carbpol.2015.11.002

Su, C., Liu, J., Yang, Z., Jiang, L., Liu, X., & Shao, W. [2020]: UV-mediated synthesis of carboxymethyl cellulose/poly-N-isopropylacrylamide composite hydrogels with triple stimuli-responsive swelling performances. *International Journal of Biological Macromolecules, 161*, 1140-1148. DOI: 10.1016/j.ijbiomac.2020.06.094

Suo, A., Qian, J., Yao, Y., & Zhang, W. [2007]: Synthesis and properties of carboxymethyl cellulose-graft-poly(acrylic acid-co-acrylamide) as a novel cellulose-based superabsorbent. *Journal of Applied Polymer Science, 103*(3), 1382-1388. DOI: 10.1002/app.23948

Uyanga, K.A., & Daoud, W.A. [2021]: Green and sustainable carboxymethyl cellulose-chitosan composite hydrogels: Effect of crosslinker on microstructure. *Cellulose, 28*(9), 5493-5512. DOI: 10.1016/j.ijbiomac.2021.08.217

Wang, Y., Shi, X., Wang, W., & Wang, A. [2013]: Synthesis, characterization, and swelling behaviors of a pH-responsive CMC-g-poly(AA-co-AMPS) superabsorbent hydrogel. *Turkish Journal of Chemistry, 37*(1), 149-159. DOI: 10.3906/kim-1204-52

Wang, Z., Ning, A., Xie, P., Gao, G., Xie, L., Li, X., & Song, A. [2017]: Synthesis and swelling behaviors of carboxymethyl cellulose-based superabsorbent resin hybridized with graphene oxide. *Carbohydrate Polymers, 157*, 48-56. DOI: 10.1016/j.carbpol.2016.09.070

Wang, L., & Wang, M. [2016]: Removal of Heavy Metal Ions by Poly(vinyl alcohol) and Carboxymethyl Cellulose Composite Hydrogels Prepared by a Freeze–Thaw Method. *ACS Sustainable Chemistry & Engineering, 4*(5), 2830-2837. DOI: 10.1021/acssuschemeng.6b00336

Xu, R., Gao, X., Chen, Y., Peng, C., Zhang, Z., Wang, C., Sun, H., Chen, X., & Cui, L. [2023]: Research advances of the electrolytes for rechargeable magnesium ion batteries. *Materials Today Physics*, 101186. DOI: 10.1016/j.mtphys.2023.101186

Zohuriaan, M.J.M., & Kabiri, K. [2008]: Superabsorbent Polymer Materials: A Review. *Iranian Polymer Journal, 17*(6), 451-477.

List of standards

ISO 2470:2009 Paper, board and pulps — Measurement of diffuse blue reflectance factor. International Organization for Standardization, Geneva, Switzerland.

ISO 5351:2004 Pulps — Determination of limiting viscosity number in cupri-ethylenediamine (CED) solution. International Organization for Standardization, Geneva, Switzerland.

SCAN C-20:65 Drainability of Pulp by the Schopper-Riegler Method

TAPPI T203 cm-99 Alpha-, beta- and gamma-cellulose in pulp. Technical Association of the Pulp and Paper Industry, Georgia, USA.

TAPPI T 235 cm-00 Alkali Solubility of Pulp at 25°C. Technical Association of the Pulp and Paper Industry, Georgia, USA.

TAPPI T 236 om-13 Kappa number of pulp. Technical Association of the Pulp and Paper Industry, Georgia, USA.

TAPPI T248 sp-15 Laboratory Beating of Pulp (PFI Mill Method). Technical Association of the Pulp and Paper Industry, Georgia, USA.