



Exploring Cellulose-based Hydrogels as Renewable and Eco-friendly Gel Electrolytes

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Abstract

The idea of a useful gel electrolyte membrane made of cellulose-based hydrogels is put forward. Various forms of cellular material have been converted into hydrogels by improved dissolution and bonding processes. For the purpose of examining the binding event and alterations of the cellulose which culminated from the artificial treatment, the structure of the hydrogels' heat stability, flexibility, and extensional stiffness characteristics, correspondingly, the produced gel membranes were examined by the use of Infrared spectroscopy, Scanning electron microscopy, Thermo gravimetric analysis, and machinery evaluation. To determine whether the suggested membranes may effectively be used as gel electrolytes for electrochemical gadgets, the fluid intake capacity and conductive properties of hydrogels that are produced from the ingestion of aqueous electrolytic solutions have been assessed. The cyclic voltammetry experiments have been used to evaluate the redox actions of electro active elements enclosed within the hydrogels, and the results show extremely great reversible change and ion diffusion. The information presented here makes it abundantly evident that cellulose-based hydrogels, which may be made by inexpensive synthetic methods, offer many desirable qualities for usage as gel electrolyte membranes.

Keywords: Sago cellulose-based hydrogel, ion conduction, diffusion, environmentally friendly, and electrolyte

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1. Introduction

In electrochemical energy preservation and transmission systems, electrolyte is essential because it facilitates ionic transit through the two electrodes. The electrolyte has a significant impact on the efficiency of the gadget in terms of electrical conductivity, cycle longevity, and electrochemical stable potential window. Commonly, polymer chains, the solvent and conductive salt dissolved in the solvent make up the components of polymer hydrogel electrolytes. Whereas the charged particles must be conveyed in fluids, the polymer networks may be employed as a platform in a fluid, upon swelling, or completely solid form. In addition to sharing the same benefits of strong ionic conductivity and ion mobility as liquid electrolytes, hydrogel electrodes also address the drawbacks of the restricted interface among the material used for the electrode and the solid-state electrolyte. There is a critical requirement to create sustainable biomass-based substances and related energy storage systems since many hydrogel electrolytes produced by petroleum and other petroleum products have the drawback of being not recyclable and the residue they produce would pollute the surroundings. The gel-state

electrolytes made from biomass-derived bio polymer sources have steadily emerged as a possible substitute for petroleum-based energy sources owing to their benefits of cheap cost, compatibility with the environment, and degradation. The critical demand for environmentally friendly energy storage technologies has recently sparked significant studies into the creation of innovative components for applications requiring energy storage. Due to their superior mechanical properties, higher conductivity of ions, and improved security with respect to conventional liquid electrolytes, gel electrolytes have become known as one of these elements' greatest alternatives [1]. One of the most prevalent polysaccharides found in nature is cellulose, which is found in a variety of natural materials including timber, bamboo, cotton, agricultural straw, spider-based microfibers, sea-silk-based nanofibers, and silkworm-based silk fibers. Cellulose and its byproducts are often utilized in paper, textiles, materials that are useful, medical care, and other industries because they are environmentally friendly, recyclable, toxic-free, compatible with living things, dynamically manipulated, and inexpensive materials. Some of the essential characteristics of a perfect super capacitor divider may be satisfied by the intrinsic qualities of

cellulosic itself, such as cheap cost, great wettability, size/thermal/chemical stability, and favorable tensile strength. For a while now, cellulose-based films have been used as separator materials in energy storage, particularly cellulose acetate, methyl cellulose, bacterial cellulose, and cellulose-based composites. The poor electrolyte absorption and liquid retention caused by their low porosity, on the other hand, directly hinder ionic transport across the separator and result in low ionic conductivity. The large permeability of the divider foretells the ability to pass of the ions between both electrodes, which may boost the electrolyte's uptake and fluid storage. This speeds up the movement of ions and prevents excessive heat and waste of energy. Due to their widespread accessibility, being biodegradable, and minimal ecological impact, cellulose-based hydrogels specifically have drawn a lot of interest as regenerative and environmentally friendly gel electrolytes. The outermost layers of plant cells include cellulose, the most common biopolymer substrate on the planet, which is a kind of polysaccharide [2]. It is an excellent option for the creation of hydrogel-based electrolytes because of its amazing integrity of structure, hydrophilic nature, and capacity for the formation of complicated networks. A large quantity of a fluid electrolyte may be absorbed and retained by hydrogels having a three-dimensional structure of networks generated by a physical or chemical process interconnecting cellulose strands. Because of their special qualities, cellulose-based hydrogels are well suited for use in technologies for storing energy, such as super capacitors, fuel cells, battery packs, and batteries powered by lithium-ion [3]. Gel electrolytes made of cellulose-based hydrogels have increased security as one of their main benefits. Gel electrolytes, as opposed to traditional fluid electrolytes, remove the risk of leaks, vaporization, and combustibility, lowering the likelihood of dangerous accidents. Additionally, the superior mechanical strength and flexibility of cellulose-based hydrogels enable them to preserve their firmness even when subjected to mechanical strain or distortion [4]. Their implementation in stretchy and adaptable battery packs, which are widely desired for wearable technology and future-oriented technology, is made possible by this characteristic. Because of their interlinked pore walls, cellulose-based hydrogels provide strong conductivity of ions along with their mechanical qualities. Ions may more easily penetrate and diffuse through the matrix of hydrogel due to cellulose's hydrophilic nature, which leads to the effective transportation of ions. Additionally, the hydrogel network's extensive surface area enables a greater number of active species, improving an energy storage device's overall efficiency [5]. From an environmental point of view, using hydrogels made of cellulose as gel electrolyte is a viable substitute for products made of petrol. Cellulose is produced with little impact on the environment since it is made from materials that are renewable, such as plant matter. Additionally, since cellulose-based hydrogels are digestible, less waste that can't be recycled is produced; helping to promote the economy of circularity [6]. The study [7] investigated the interfaces for enhanced energy retention and transfer devices between electrodes and biopolymer-based hydrogel electrolytes from the viewpoints of production, characterization, and efficiency evaluation. The research [8] showed a complete analysis of cellulose-based hydrogels produced and created,

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in addition to their physical and chemical properties, and used in a variety of fields. The aim of [9] is the development of cellulose-based portable technology, and bioelectronics technologies are discussed, along with possible difficulties and prospective possibilities. The study [10] explained the physic-chemical properties of hydrogels made of cellulose and its uses in a variety of scientific disciplines, such as fields of medicine like the delivery of medications, tissue engineering, and healing of wounds, medical treatment, and sanitary goods, and also in textiles and apparel, applications in manufacturing, and agricultural activities as innovative substances. The objective of [11] is Chitin- and chitin-cellulose-based hydro gel electrolytes: production and electrochemical properties. The study [12] examined the origins, varieties, and the hydrogel's production process, along with current advancements in the creation of cellulose-based hydrogels as well as an introduction to its uses in electrical conductivity, insulation from heat, and pharmaceutical administration. Additionally, as novel substances in the coming years, we examined and emphasized the patterns and prospects for improvement of cellulose-based hydrogels. The goal of [13] is cellulose breakdown employed by depending on the binding agents and solvents, and several approaches may be utilized to create biodegradable as well as biocompatible cellulose-based hydrogels. The categorization of various hydrogel kinds was also the subject of research. The research [14] examined the number of conducting polymer hydrogels made from cellulosic hydrogels loaded using -cyclodextrin and embedded in three-dimensional chains with nanostructured polyaniline that have been created. The study [15] demonstrated the mechanical toughness and dependable electrochemical efficiency of the bio waste-derived extremely efficient flexible super capacitors during twisting sessions.

2. Experiment

2.1 Reagents

The following chemicals were obtained from Carlo Erba in Milan, Italy: an OH (>97%), H₂SO₄ (96%), and Na₂SO₄ (99.5%). Bought urea, epichlorohydrin, and "C₆288" cellulose. "Avicel® PH-101", a brand of microcrystalline cellulose. K4 (potassium Ferro cyanide) and K3 (hexacyanoferrate). The labels for "C₆288" and "Avicel® PH-101" celluloses are "C" and "A", respectively

2.2 Generating hydrogels with cellulose

Starting with A and C celluloses, which have different MW and DP values, two different forms of hydrogels have been created. Detailing both in an aqueous solution of weight percent composed of 7 grams of sodium hydroxide, 3 grams of urea, and 90 milliliters of pure water, several forms of cellulose have been solubilized. At low temperatures, dissolution took place via a series of freezing-thawing cycles until a clear four-weight percent cellulose solution was attained. After that, the solution was emptied onto a Petri plate, and ECH 5 vol. % was incorporated gradually while being stirred magnetically at room temperature (RT). The Petri plate was frozen at 30 °C for 20 hours after 1 hour had passed. In 24 hours of freezing the

solid at room temperature, the hydrogel was produced. In order to eliminate the remaining chemicals, the produced hydrogel membrane was rinsed in extremely pure water. When the final rinsing liquid hit pH 7, the washing process was complete. Hydrogels made from either C or A cellulose as a starting material have been designated as HC or HA, correspondingly.

2.3 Analysis

FTIS stands for "Fourier Transform Infrared Spectroscopy". "Attenuated total reflectance" was utilized to evaluate 300 scans which were dried in the vacuum hydrogel samples, while KBr disks were used to investigate cellulosic granules and fiber. Thermo gravimetric evaluation. Both cellulosic powdered and dehydrated hydrogels that are were used in TGA/SDTA8511e Mettler-Toledo's investigation on the hydrogels' thermal conductivity. With an atmospheric nitrogen stream of 60 mL/min, the material underwent heating between 30 to 490 °C at 11°C /min. SEM, LEO1450VP (LEO Electron Microscopy Ltd) SEM at 20 kV was used to investigate the structure of hydrogels. Before being examined by SEM, objects were spray-coated with gold and dried in the freezer to prevent the deformation of the pore structure in the SEM pressure chamber. Tests on machinery. A Perkin Elmer DMA8000 was used to test the preserving elastic at 1Hz in the so-called "tension" mode on tiny strips of vacuum-dried hydrogels that were approximately 15×5× one mm³ in size. In fresh (test samples taken immediately following synthesizing) samples, their shear modulus was evaluated at the exact same frequencies in the 22–44 °C range of temperature. In this instance, samples were examined in the "shear" mode, where a shear strain was placed on the single end-face of the container. Additionally, the shear modulus was tested at the ambient temperature as an indicator of frequencies. Samples were obtained from cleaned hydrogels and dried using a vacuum for 24 hours before being placed in a corked Falcon® tube with 0.5 M Na₂SO₄ solution. The hydrogel was used to support the swelling weight, and wet filter paper was used to clean away any extra fluid. EIS stands for "Electrochemical impedance spectroscopy". Hydrogels that had been electrolytically swelled for 24 hours were measured for their electrical conductivity using impedance spectra from a "frequency response analyzer". In open-circuit circumstances, spectra were captured between 1 kilohertz and 1 Hertz frequency width with a five mV pulse level. In order to maintain a stable cell shape, the hydrogel part and polytetrafluoroethylene (PTFE) compounds with holes punched in the center to attack the hydrogel compound were inserted in between the obstructing electrode of the ethylene cell. In order to provide a satisfactory connection to the electricity while preventing excessive distortion of the sample, the thickness was slightly less than the hydrogel compound. Each conductance result has a small amount of error due to unknowns with the procedure for fitting and sample geometry. CV, or cyclic voltammetry. Two platinum-coated electrodes that meet the copper electrodes make up a T-cell. Hydrogel disks that were dissolved in 0.50 M of both solutions for 24 hours swelled. As a fictitious comparison electrode, a platinum wire that was inserted between the two hydrogel disks was employed.

3. Result and discussion

Since it is possible to directly acquire knowledge about the primary alterations that take place in cellulose under a variety of both physical and chemical treatments, FTIS have widely employed in the research of materials made of cellulose. Figure 1 displays the ATR-FTIS hydrogels-cellulose in comparison to their original cellulose.

In the differentiation to pure celluloses, the hydrogel's spectra show that (1) the highest rate of the band at 1430 cm significantly dropped in extent, (2) the band at 1328 cm significantly grew, and (3) the bands at 1162 and 1111 cm²¹ vanished. Additionally, it can be shown by evaluating the hydrogels' spectrum at 1635 cm⁻¹ is stronger in HA than HC. The use of alkaline solutions is responsible for a change in cellulose's crystal structure, which is what is causing the spectral modification in the range of 1500-899 cm⁻¹. Point (3) specifically suggests that cellulose I to cellulose II has undergone a crystal transition in the hydrogels. In addition, a drop in the crystallization level of cellulose is reflected in the reduced strength of the band at 1435 cm⁻¹ (also known as the "crystalline band") mentioned in point (1). Point (2) is connected to the cellulose's chemical interaction with ECH, which results in an ether-based bond and is a subliminal indicator of how well the solubility stage worked. The tangling of the cellulose chains competes with the ECH process with hydroxyl groups of cellulose at RT. HC is believed to be more significant since the actual bonding is connected to cellulose DP. Physically more interconnected than HA. In fact, in contrast to cellulose "A," the reaction with ECH revealed the commencement of gelation in the substrate "C." This is in line with the greater extent at 1635 cm⁻¹ in the HA spectra, which indicates a higher degree of hydrophobicity in HA than HC as a result of the predominance of chemical bridging over physical bonding. TGA reaction was used to assess the thermal characteristics of the produced hydrogels in comparison to the beginning celluloses, as shown in Figure 2. Figure 2(a) contrasts the curves of the comparative dried hydrogels (HC and HA) to the ones from the original celluloses (C and A). The related first-derived curves are shown in Figure 2(b). From these curves, the temperature at which decomposition begins (Td) and the onset temperature (TO) of destruction have been calculated, the former derived from the point where both lines of curves intersect and to the extreme low. Reduction in weight at above 99 °C is about 3.0 percent, and the starting temperature of C and A is 290 °C, correspondingly. The hydrogels' thermal performance varies amongst them and in comparison to their original celluloses. The weight loss above 90 °C is larger in HA (8%) than in HC (4%), and this finding suggests that HA is more hydrophilic than HC (as shown by FTIR spectra as well). TO and TD for HC are 220 °C and 320 °C, and 245 °C and 347 °C, respectively. (i) The hydrogels both have lower TO sets as compared to pristine celluloses, although the difference is bigger for HC than for HA; (ii) TD is 31 °C lower for HC than for C and four °C higher for HA than for A. Because of cellulose's reduced level of crystallization, the starting temperature has decreased in hydrogels.

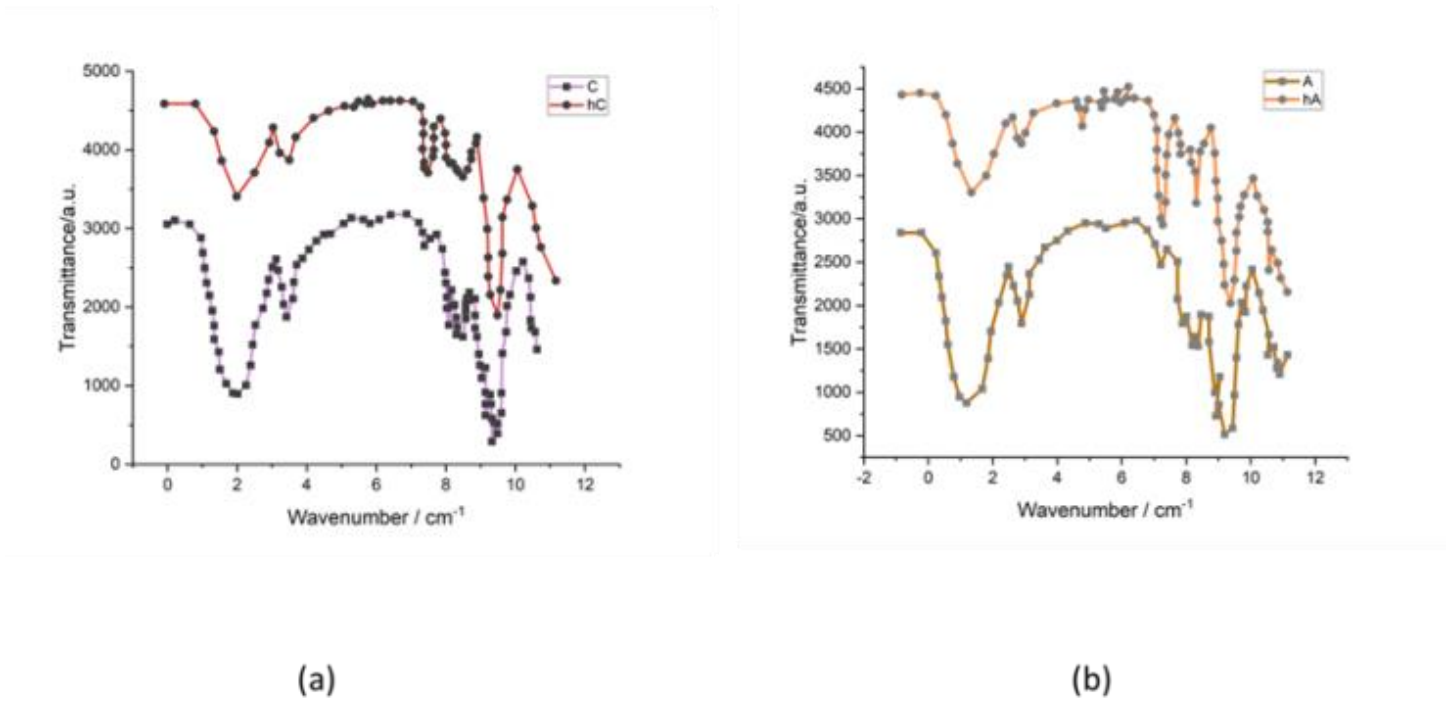


Figure 1: Correlate the FTIR spectra of the hydrogels made from the initial celluloses

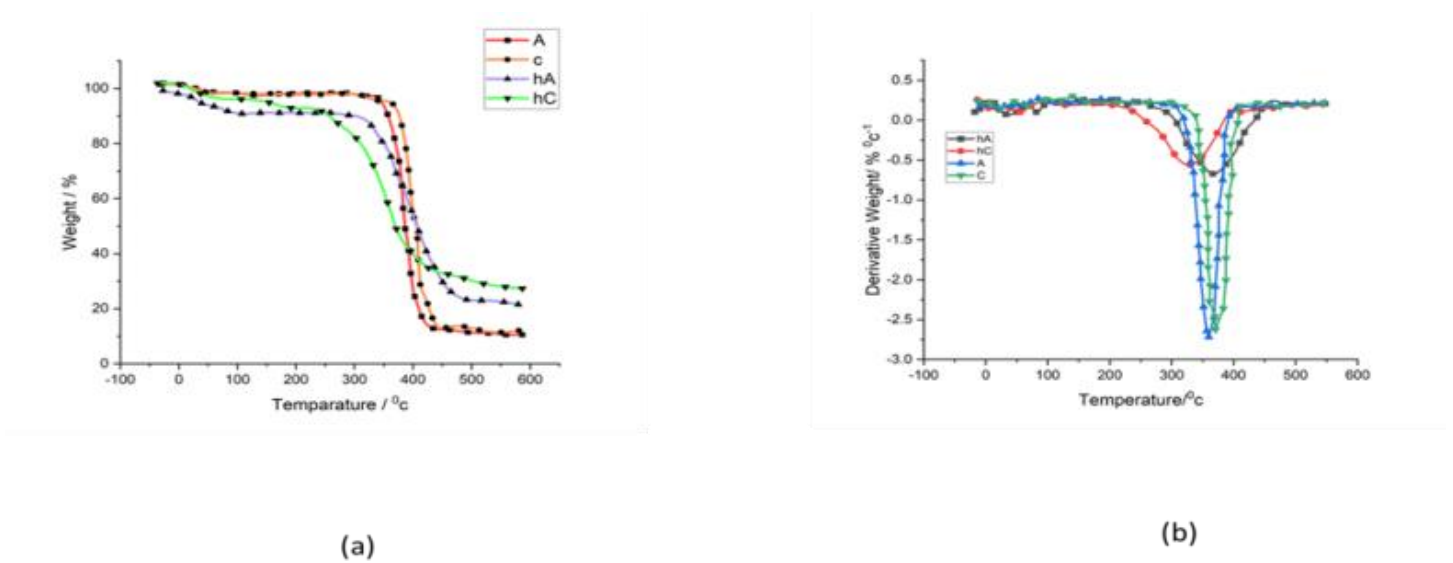


Figure 2: (a) Curves of cellulose and of corresponding hydrogels, (b) derivatives of the mass curves.

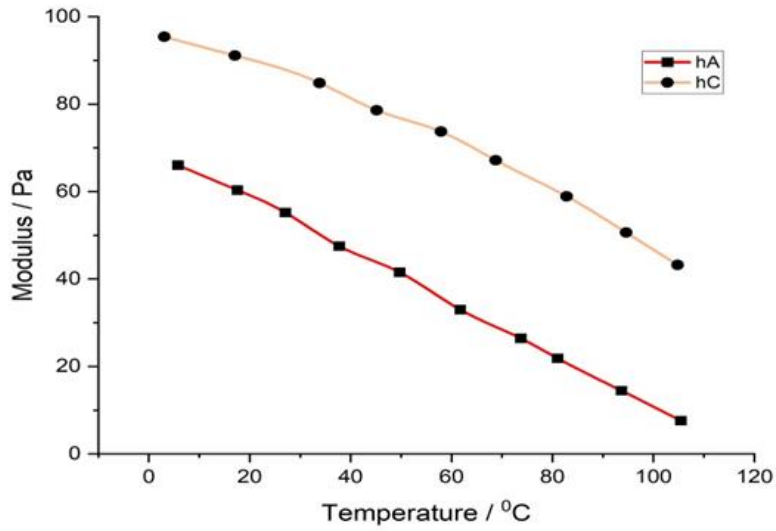


Figure 3: The stiffness of dried HA and HC varies with temperature.

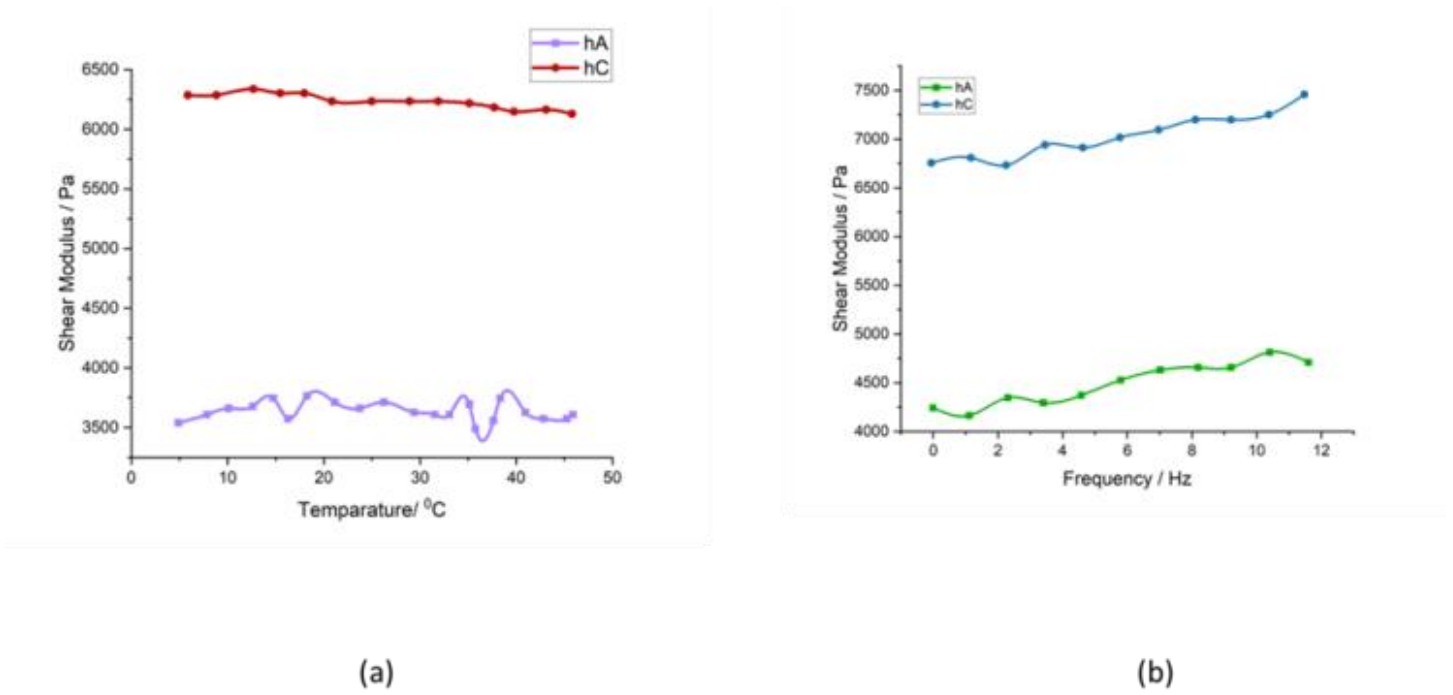


Figure 4: Temperature and the frequency relied upon the shear strain of pure hydrogels are shown in (a) and (b), respectively.

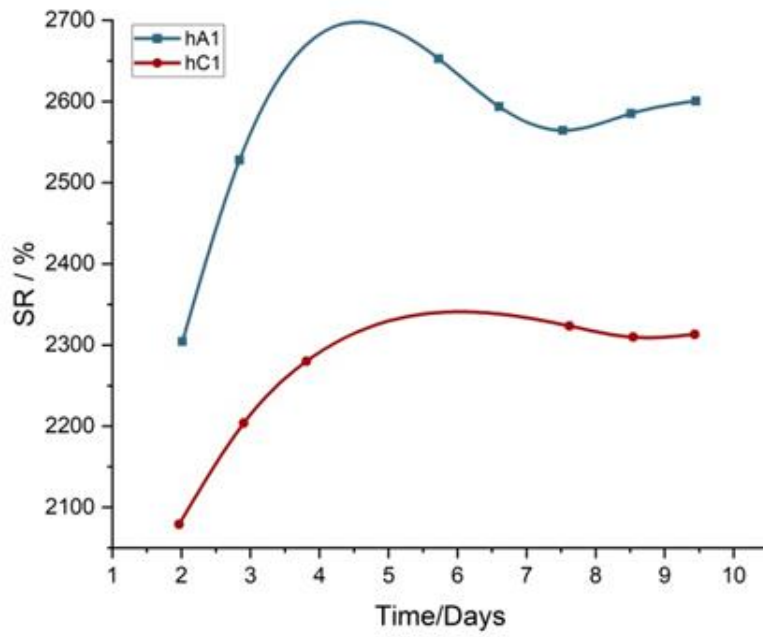


Figure 5: Time-dependent expanding ratio of cellulose-based hydrogels

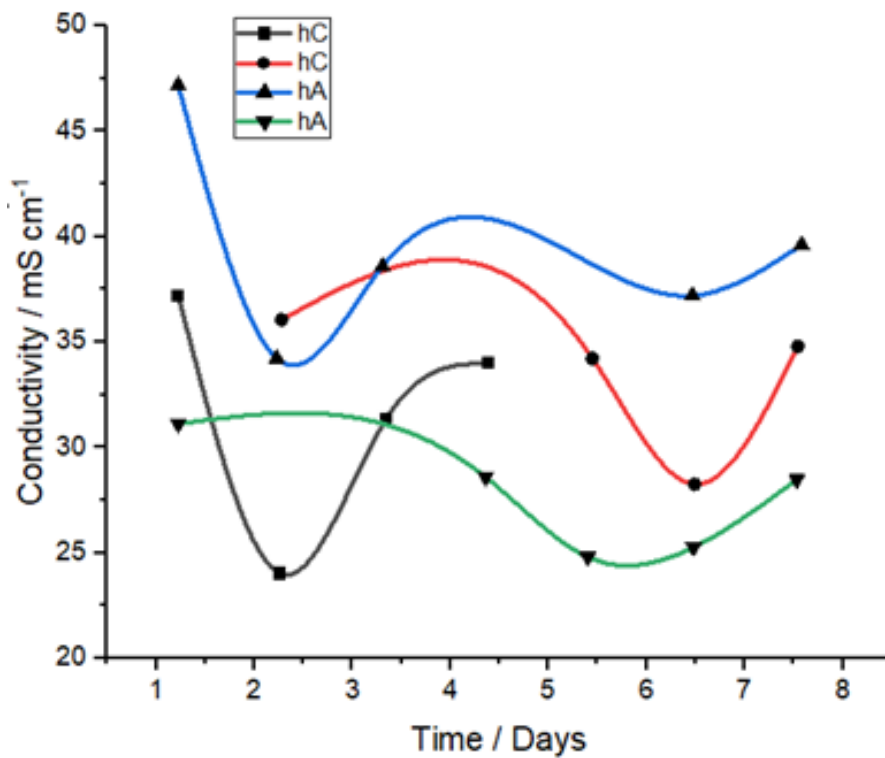


Figure 6: The ion conductivity values for HA and HC at ambient temperature

Chemical crosslinking enhances the heat balance of HA, which restricts the decline of TO and increases TD. The temperature-dependent dependency of the stiffness of the dried HC and HA samples can be seen in Figure 3. In the entire temperature interval, the modulus of HC is greater compared to the modulus of HA. The results for HC and HA at ambient temperature were 9.1108 Pa and 2.3108 Pa, respectively; these values are standard for bonded tridimensional polymer substances. Both of the samples exhibit a monotonous elasticity drop with temperature until the highest degree under investigation, which is around 90 °C. The tensile strength of the hydrogels as they were produced after being synthesized has been tested within 23 and 44 °C and is shown in Figure 4a. The reduction in mass from the transpiration of water in the mentioned range is fairly negligible and shouldn't have a significant impact on the stiffness values. Regarding the dry specimens, HA has a smaller value compared to HC, which may be explained by HA's larger water content than HC's. Both hydrogels' shear modulus is essentially temperature-independent. In addition, shear modulus observations have also been made at ambient temperature as a result of frequency to understand the elasticity properties of the hydrogels. Figure 6b reports observations made between 0.01 and 22 Hz. The shear modulus has a slight frequency dependence for both HC and HA. Each of the polymers exhibits the little elastic modulus increase that occurs as the frequency rises. This variation might be attributed to the various cellulose types and various crosslinks between the polymers. Figure 5 shows the results of time-lapse monitoring of the swelling rate of cellulose-based hydrogels submerged in 0.25 M sodium sulfate solutions at room temperature. The analysis was made using two distinct specimens of every hydrogel. When stored in a sealed package, the hydrogels attain a saturation condition after five days and then continue to retain the liquid that is absorbed solution without leakage or evaporating for an extended period of time. It should be noted that the cell membrane may still reverse accept the swollen solution after the drying process. Both hydrogels have a strong swelling capacity, as predicted by SEM data. The broader extension of the chemical bonding procedure with relation to HC, which means a greater amount of oxygen molecules produced by the etherification process that is accessible for communication with water via hydrogen bonds, might be linked to the greater SR of HA. Since the proportion of swelling is known to rise with a reduction in the solution's ionic capacity, this discrepancy is further understated. Electrochemical impedance spectroscopy was used to demonstrate the hydrogel membranes' capacity to conduct ions on HC and HA specimens that had swollen for one day in a sodium sulfate solution. Figure 6 reports the values of conductivity of time at RT. The According to this investigation, both HC and HA exhibit sufficient extremely open pores architectures which contain well-connected openings that allow for rapid ion movement in response to an induced electrical field.

4. Conclusion

It has been shown that it is possible to effectively manufacture cellulose hydrogels with customizable finished material properties. The kind of cellulose used in this *Ropashree et al., 2023*

process is crucial; with the synthesis method equally effective, it is feasible to regulate the corresponding expansion of both its chemical and physical characteristics. Employing various starter celluloses and a practical bonding agent proportion to crosslink. This enables the hydrogel's competing mechanical qualities and fluid absorption capabilities to be balanced. It has been discovered that synthetic cellulose hydrogels have the capacity to take in and keep a significant volume of electrolytic fluid without leaking. The hydrogels that are swollen in solution exhibit a level of ionic conductivity that is similar to the initial swelled electrolyte. Furthermore, absorbed hydrogels tested using cyclic voltammetry revealed an extremely high diffusion rate and reversible redox activity. The findings of the first testing on the hydrogels' chemical stability in both acidity (pH 1) and alkalinity (pH 12.7) water mixtures are looking extremely promising. The information presented here makes it abundantly evident that cellulose-based hydrogels, which may be made by inexpensive synthetic methods, offer many desirable qualities for usage as gel electrolyte membranes.

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