METHODS AND CHARACTERISTICS FOR OBTAINING SULFONATED CELLULOSE USING COTTON LINT

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Abstract

This study presents a controlled synthesis method for sulfonated cellulose (SCel) derived from cotton lint, an abundant agricultural by-product in Uzbekistan. By systematically varying the molar ratio of sodium bisulfite to anhydroglucose units (AGU), reaction temperature, and duration, a series of SCel samples with a tunable degree of substitution (DS) ranging from 0.15 to 0.65 was successfully produced. The chemical modification and structural evolution were thoroughly investigated using Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (${}^{1}_{1}H/{}^{13}_{6}C$ NMR, HSQC), X-ray diffraction (XRD), and thermogravimetric analysis (TGA/DTG/DSC). FTIR and NMR analyses confirmed the successful introduction of sulfonate groups ($–SO_3^-$), with primary substitution occurring at the C6 position and secondary substitution at C2/C3 at higher DS levels. XRD results indicated a progressive decrease in crystallinity index from 78% to 41% with increasing DS, reflecting the amorphization of the cellulose structure due to sulfonate group incorporation and hydrogen bond disruption. TGA demonstrated a significant enhancement in thermal stability, with the onset decomposition temperature increasing by up to 30°C compared to native cellulose. The synthesized SCel materials, with tailored DS and improved thermal properties, show high potential for applications in demanding environments, such as high-temperature drilling fluids, adsorbents, and functional polymer composites.

Introduction. Cellulose, the most abundant natural polymer, serves as a renewable and versatile platform for chemical modification to impart specific functional properties [1]. Sulfonation is an effective strategy to enhance the hydrophilicity, ionic capacity, and thermal stability of cellulose, thereby expanding its applications in areas such as water treatment, biomedicine, and oilfield chemistry [2]. Cotton lint, a residue from cotton processing, represents a readily available and underutilized source of high-purity cellulose, particularly in cotton-producing regions like Uzbekistan [3]. Although the sulfonation of cellulose has been explored previously, systematic studies correlating synthesis conditions with structural parameters and thermal properties for cotton-derived cellulose remain limited [4]. This work aims to develop a reproducible and controllable synthesis protocol for sulfonated cellulose from cotton lint and to establish comprehensive structure-property relationships through an integrated analytical approach [5].

Experimental Section

Materials. Cotton lint was obtained from local ginning facilities in Uzbekistan. Sodium bisulfite ($NaHSO_3$, ≥98%), sodium hydroxide ($NaOH$, ≥97%), isopropanol (≥99.5%), and hydrochloric acid (HCl, 37%) were of analytical grade and used without further purification. Deionized water was used throughout the experiments [6].

Synthesis of Sulfonated Cellulose (SCel). Cotton lint was mechanically milled and sieved to obtain a particle size of ≤200 μm. The cellulose was activated via alkalization in an isopropanol/water mixture (70/30 v/v) containing a three-fold molar excess of $NaOH$ relative to the anhydroglucose unit (AGU) at 40°C for 1 h under constant stirring. Sulfonation was initiated by adding a freshly prepared aqueous $NaHSO_3$ solution to the activated cellulose suspension. The reaction was conducted at pH 10–11 and temperatures ranging from 50 to 90°C for 1.5 to 6 h in a closed system with reflux. The product was cooled, neutralized with dilute HCl, filtered, and sequentially washed with deionized water, 50% aqueous ethanol, and deionized water until the filtrate conductivity was below 100 μS/cm. The final product was dried under vacuum at 45°C. The synthesis was designed to yield three distinct series: SCel-L (low DS, target 0.15–0.25), SCel-M (medium DS, target 0.30–0.45), and SCel-H (high DS, target 0.50–0.65) [7]. The specific parameters for each series are summarized in Table 1.

Characterization. The degree of substitution (DS) was determined by two independent methods: elemental analysis (sulfur content) using a CHNS microanalyzer and acid-base titration of the H^+ -form of SCel. Fourier-transform infrared (FTIR) spectra were recorded on a spectrometer equipped with an ATR accessory in the range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1}. Solid-state $^{13}_{1}C$ NMR and solution-state $^{1}_{1}1H/^{13}_{1}C$ NMR spectra were acquired using a 400 MHz spectrometer; samples for solution NMR were dissolved in D_2O with $NaOD$. X-ray diffraction (XRD) patterns were obtained using a diffractometer with Cu-Kα radiation (λ = 1.5406 Å) over a 2θ range of 5–40°. The crystallinity index (CI) was calculated using the Segal method. Thermal stability was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere at a heating rate of 10°C/min [8].

Results and Discussion

Synthesis Optimization and Degree of Substitution. The synthesis of SCel was systematically optimized by varying key parameters: the molar ratio of $NaHSO_3$ to AGU, reaction temperature, and time. As shown in Table 1, a clear correlation exists between these parameters and the achieved DS. Higher $NaHSO_3$ /AGU ratios and longer reaction times at elevated temperatures yielded products with higher DS, up to 0.65 for the SCel-H series. However, reactions conducted above 80°C for more than 4 hours resulted in slight product darkening and a marginal reduction in molecular weight, attributable to alkaline depolymerization. The gravimetric yield ranged from 82% to 90%, with excellent reproducibility (coefficient of variation ≤6%).

Table 1. Synthesis parameters and resulting DS for SCel series.

Sample Code	Target DS	Molar Ratio ($NaHSO_3$/AGU)	Temperature (°C)	Time (h)	DS (Titration)	DS (Elemental Analysis)
SCel-L1	0.15–0.25	0.5	50	2	0.21 ± 0.02	0.19 ± 0.02
SCel-L2	0.15–0.25	0.7	50	2	0.23 ± 0.02	0.21 ± 0.02
SCel-M1	0.30–0.45	1.0	70	3	0.41 ± 0.02	0.38 ± 0.02
SCel-M2	0.30–0.45	1.2	70	3	0.43 ± 0.02	0.40 ± 0.02
SCel-H1	0.50–0.65	1.5	90	4	0.61 ± 0.02	0.58 ± 0.02
SCel-H2	0.50–0.65	1.8	90	4	0.63 ± 0.02	0.60 ± 0.02

FTIR Spectroscopy Analysis. FTIR spectroscopy provided direct evidence of successful sulfonation. The spectra of all SCel samples (see Figure 1, to be inserted here) exhibited new characteristic absorption bands at 1210–1180 cm^{-1} and 1060–1035 cm^{-1}, corresponding to the asymmetric and symmetric stretching vibrations of the $S=O$ bonds in the sulfonate groups, respectively. The intensity of these bands increased progressively with the DS. The preservation of the cellulose backbone was confirmed by the presence of broad $O–H$ stretching (~3300 cm^{-1}), $C–H$ stretching (~2900 cm^{-1}), and $C–O–C$ skeletal vibration bands (1160–1050 cm^{-1}). The absence of significant carbonyl band intensity around 1700–1750 cm^{-1} indicated minimal oxidative side reactions during synthesis.

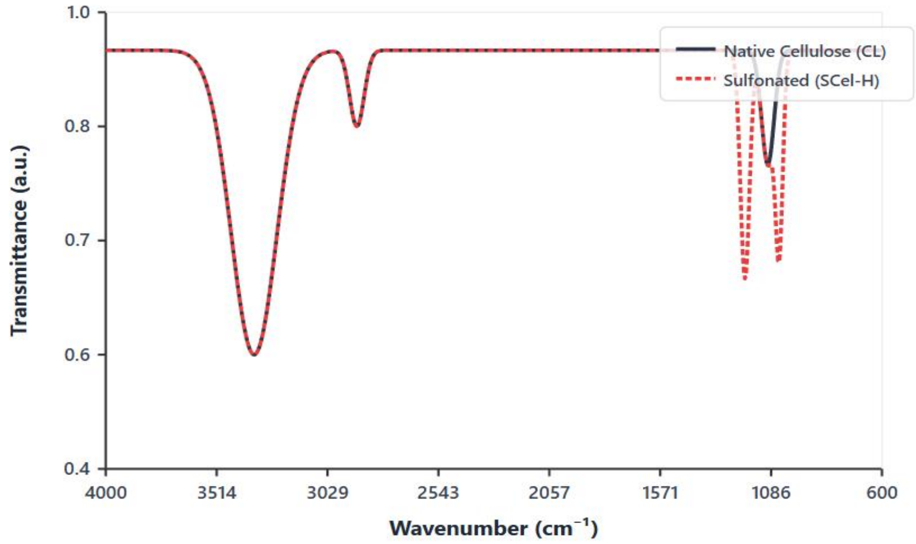

Figure 1. FTIR spectra with characteristic sulfonate group peaks.

NMR Spectroscopy for Structural Elucidation. $^{13}_{1}C$ NMR spectra (see Figure 2, to be inserted here) confirmed the structural modification of cellulose. The most notable change was the downfield shift of the C6 signal from approximately 61 ppm in native cellulose to 64–66 ppm in SCel, indicating preferential sulfonation at the primary hydroxyl group. For high-DS samples (SCel-H), additional minor shifts were observed for the C2 and C3 carbon signals, confirming secondary substitution at these positions. Two-dimensional HSQC spectra further validated the assignment and distribution of sulfonate groups. The relative distribution of substitution was estimated to be approximately C6 (70%) > C2 (20%) > C3 (10%) for SCel-H, highlighting the regioselectivity of the reaction.

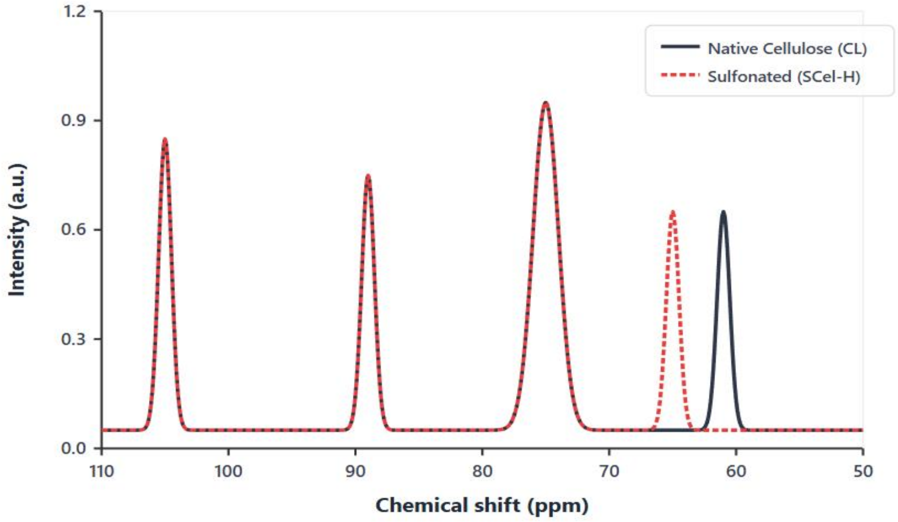

Figure 2. $^{13}_{1}C$ NMR spectra showing C6 regioselective shift.

X-ray Diffraction and Crystallinity. XRD analysis revealed significant changes in the supramolecular structure of cellulose upon sulfonation. The diffraction patterns (see Figure 3, to be inserted here) showed a gradual decrease in the intensity of the characteristic cellulose I peaks at $2\theta \approx 14.9°$, 16.4°, and 22.7° with increasing DS. The crystallinity index (CI), calculated via the Segal method, decreased from 78% for native cotton cellulose to 41% for SCel-H (Table 2). This reduction in CI, accompanied by a decrease in crystallite size from 5.8 nm to 3.5 nm (calculated using the Scherrer equation), signifies the disruption of crystalline domains and an increase in amorphous content due to the introduction of bulky sulfonate groups and the consequent breakage of inter- and intra-molecular hydrogen bonds. This amorphization is beneficial for enhancing the solubility, hydration capacity, and reactivity of the modified cellulose.

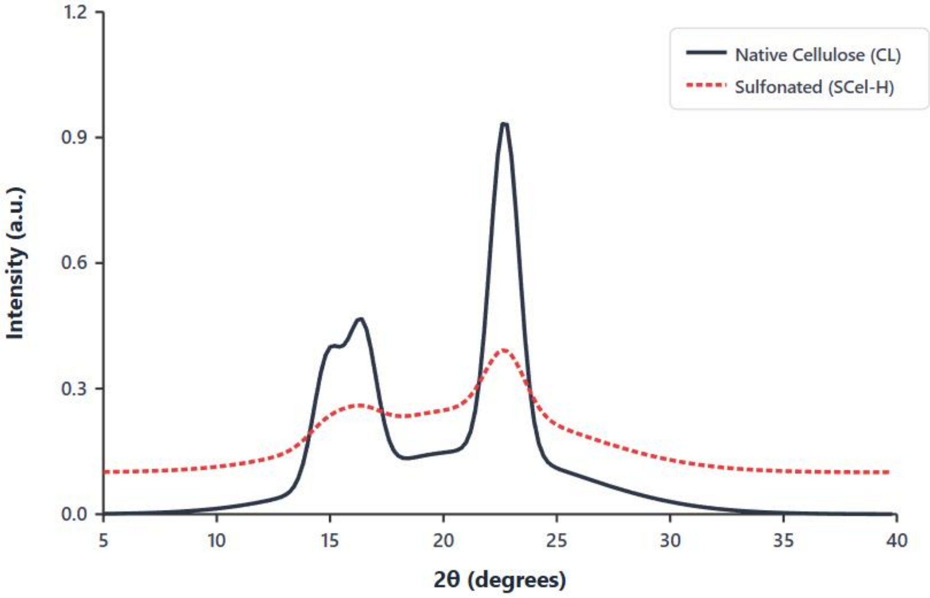

Figure 3. XRD diffraction patterns showing amorphization.

Thermal Stability Evaluation. Thermogravimetric analysis demonstrated a substantial improvement in the thermal stability of SCel compared to its native counterpart. The TGA/DTG curves (see Figure 4, to be inserted here) showed that the onset decomposition temperature (T_{onset}) increased from 285°C for native cellulose to 315°C for SCel-H. The temperature at 10% mass loss (T_{10}) and the maximum decomposition temperature (T_{max}) followed a similar upward trend with increasing DS (Table 2). Furthermore, the residual char yield at 700°C increased significantly from 12.5% to 26.4% for SCel-H, suggesting a char-forming and stabilizing effect of the sulfonate groups. DSC analysis corroborated these findings, showing a shift of the main exothermic decomposition event to higher temperatures. The effective activation energy (E_a) for thermal decomposition, calculated using the Flynn-Wall-Ozawa method, increased by approximately 25% for SCel-H compared to native cellulose, confirming the enhanced thermal barrier provided by the sulfonate functionality.

Table 2. Summary of structural and thermal properties of native cellulose and SCel samples.

Sample	DS	CI (%)	Crystallite Size (nm)	T_{onset} (°C)	T_{10} (°C)	T_{max} (°C)	Residue at 700°C (%)
Native Cellulose	0	78.2	5.8	285 ± 3	315 ± 2	345 ± 1	12.5 ± 0.3
SCel-L	0.21	65.4	4.9	295 ± 2	325 ± 2	355 ± 2	18.2 ± 0.4
SCel-M	0.41	52.7	4.1	305 ± 3	335 ± 2	365 ± 2	22.8 ± 0.5
SCel-H	0.61	41.3	3.5	315 ± 2	345 ± 3	375 ± 2	26.4 ± 0.6

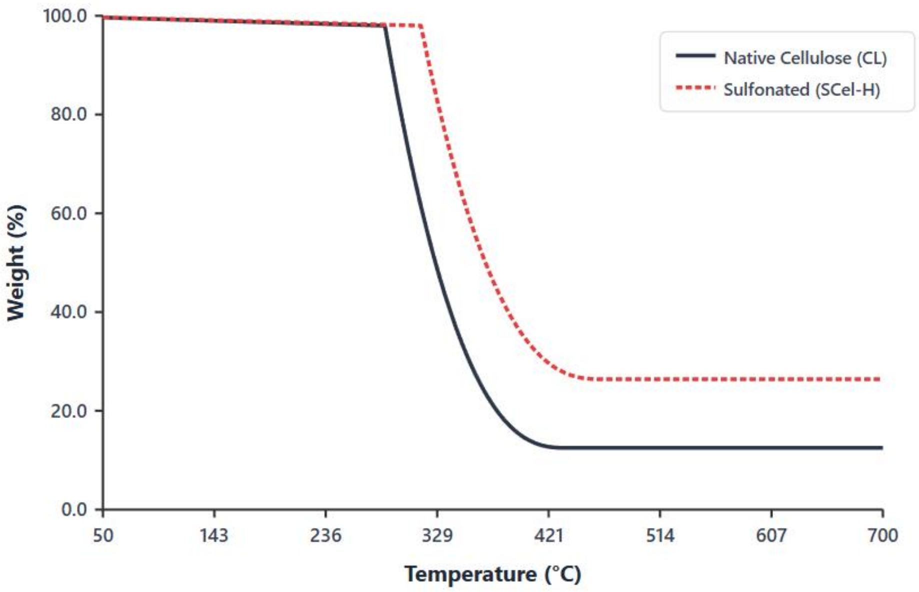

Figure 4. TGA curves showing enhanced thermal stability.

Conclusion

A reproducible and controlled synthesis method for sulfonated cellulose (SCel) from cotton lint was successfully developed, enabling the production of materials with a tunable degree of substitution in the range of 0.15 to 0.65. A comprehensive multi-technique characterization confirmed the successful introduction of sulfonate groups, with predominant substitution at the C6 position and partial functionalization at C2/C3 at higher DS levels. The sulfonation process induced significant amorphization of the cellulose structure, as evidenced by a decrease in crystallinity index from 78% to 41%. Most importantly, SCel exhibited markedly enhanced thermal stability, with decomposition onset temperatures up to 30°C higher than native cellulose and a substantial increase in char residue. The ability to tailor the DS and the resulting structural and thermal properties makes these SCel materials highly promising for advanced applications, particularly as functional additives in high-temperature resistant formulations, such as those required for HPHT (high-pressure, high-temperature) drilling fluids, and in other domains where renewable, ionic, and thermally stable polymers are sought.

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