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Coupling fiber cationization with hygroplasticization for 3D-formable cellulose-based materials

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Abstract Thanks to their high availability, renewability, and degradability, paper-based materials are promising candidates for partial replacement of less sustainable fossil-based products. A disadvantage of conventional paper is, however, its low strainability and restricted shapeability. Partial chemical modification of the fibers that constitute the paper, along with external

plasticization, could alleviate this shortcoming. In this contribution, partial cationization of lignocellulosic fibers is employed to enhance the strength and strainability of handsheets; the extensibility is further improved by a moisture-induced plasticization. This combination of modification and hygroplasticization resulted in a strainability of 12%, allowing restraint-dried sheets to be formed into simple 3D structures. Dynamic vapor sorption, dynamic mechanical analysis, and small-angle X-ray scattering measurements are employed to gain deeper insight into the molecular and supramolecular mechanisms underlying the potential for 3D structuring of the papers. It can be concluded that cationization enhances the material's moisture sorptivity. This is explained by increased accessibility of the fiber wall upon modification (as evidenced by decreased crystallinity and fibril separation) and by hydration of the functional groups. Moisture sorption is an enthalpically driven, highly exothermic process that results in softening of the material. It can be established that while cationization does not significantly affect the material's temperature response, it does significantly affect its moisture response. Cationization lowers the onset for the fiber material to be softened by moisture, presumably explaining the extended strainability observed for the cationized, hygroplasticized material.

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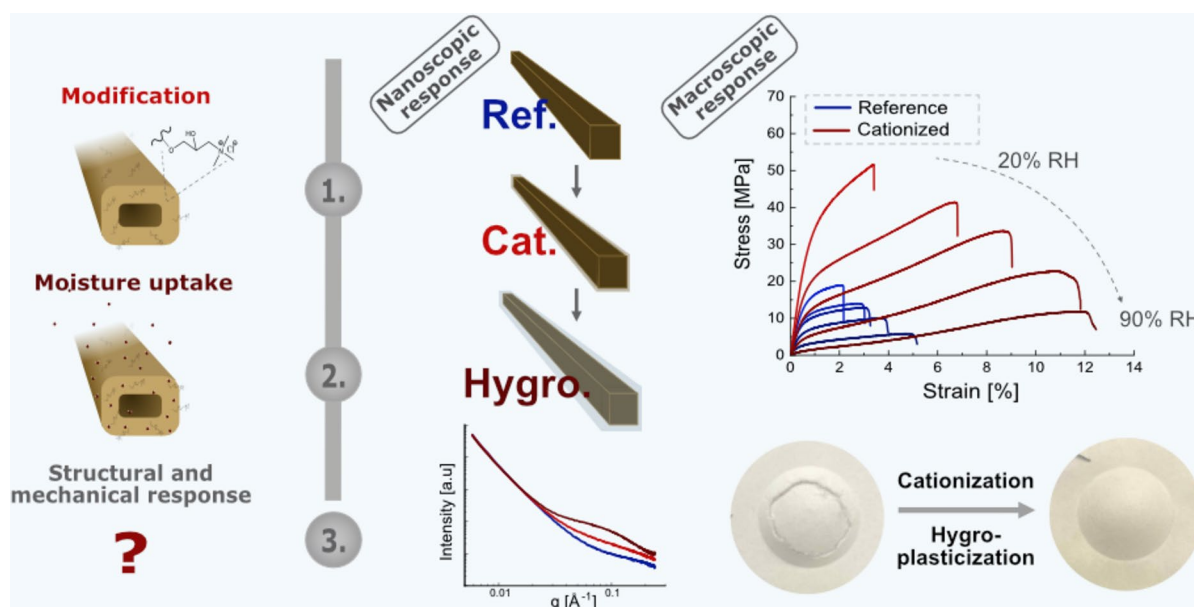
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Graphical abstract



Graphical abstract showing, from left to right; the concept for cationization and hygroplasticization—the material’s response at a nanolevel—the material’s macroscopic response, mechanical properties and potential of 3D forming).

Keywords Cellulose fibers · Cationization · Moisture sorption · Hygroplasticization · 3D formability

Introduction

From a sustainability perspective, cellulose-fiber-based products offer numerous advantages, including renewability, biological degradability, and recyclability with well-developed recycling routes. However, their application possibilities are limited by, among other things, the processes by which fiber- and fibril-based products can be shaped. Due to their comparably low strainability, usually lower than 4%, and high softening temperature, paper has traditionally been limited to use as a flat surface material. When striving to replace fossil-based materials with more sustainable alternatives, a significantly higher degree of formability is often a criterion. As a response to this, original methods, including wet-molding and dry-forming, have been developed for the production of 3D-shaped fiber-based products (Kaplan et al. 2025;

Zhang et al. 2022). From a paper’s perspective, however, 3D formability without feeding material into the die (i.e., using a fixed blank) remains challenging. To boost the strainability of paper materials, advanced refining and structural modification of the fiber web by creping and free drying techniques have been applied (Khakalo et al. 2017a, b; Lahti et al. 2014; Vishtal and Retulainen 2014). While mechanical approaches, such as creping/compaction of the material during sheet making, are promising methods providing the material with stainabilities over 10%, the approach requires the investment in new production units, and the strainability is generally gained at the expense of the strength of the material (Freville et al. 2024; Nordling and Nordström 2018).

The development of fiber-based materials with higher strainability than conventional papers which could be produced using existing production lines, and subsequently be shaped into 3D products at the production site or, preferably, at the customer, closer to the end-user would be a welcome alternative. Restraint-dried sheets with enhanced strainability have been developed by surface treatment of

the fibers, for example, via layer-by-layer adsorption (Marais et al. 2014), and chemical modification of the fibers (Larsson et al. 2014a, b; Larsson and Wågberg 2016; López Durán et al. 2018; Sjölund et al. 2025a). In López Durán et al. (2018) the mechanical properties of handsheets based on fibers carrying a range of different modifications were evaluated. It could be concluded that periodate oxidation and subsequent borohydride reduction, yielding a ring-opened dialcohol functionality, had the strongest influence on the strainability of the material, and at a degree of modification of 31%, a strain-at-break of 12% was reached (Larsson et al. 2014a, b). Although this approach requires additional chemistry and additional process steps, the results demonstrate a promising approach to enhance the strainability, and hence the 3D formability, of handsheets. In the work by Linvill et al. (2017), this was also shown in practice.

Cationization of cellulosic fibers, involving the covalent linkage of positively charged trimethylammonium groups to the cellulose backbone, has also been demonstrated to provide promising effects on the extensibility of fiber-based material without compromising, but rather improving, the strength of the material. It has been shown by Sjölund et al. (2025a) that a strainability of around 7% could be reached at a degree of substitution (DS) of 0.18 (corresponding to a charge of $1000 \mu\text{eq g}^{-1}$). Although these values are lower than those observed for sheets prepared from dialcohol cellulose fibers in Larsson and Wågberg (2016), the functionalization has several advantages over periodate oxidation and subsequent borohydride reduction, including a one-step modification procedure and the use of less harsh, hazardous chemicals (e.g., (3-Chloro-2-hydroxypropyl)trimethylammonium chloride, CHPTAC). Furthermore, the reagent CHPTAC is already used on a large scale for the production of cationic starch, a commonly used paper-strength additive (BeMiller and Whistler 2009; Sharma et al. 2020).

To further enhance the strainability of the material, additional modifications could be an alternative. However, fibers, such as cationized ones, which carry charged functionalities, have an upper limit to their modification due to the buildup of osmotic pressure in the fiber wall, eventually leading to fibrillation of the fiber (Gorur et al. 2020; Karlsson et al. 2020). An alternative approach could be to adsorb or spray polymers onto the structure,

which soften upon heating, thereby further enhancing the strainability of the material (Khakalo et al. 2017a, b; Svensson et al. 2013) or to incorporate an external plasticizer into the system. For example, interesting effects for the softening of fiber-based materials using glycerol or urea as plasticizers (in combination with ultrasonication) have been shown (Eliasson et al. 2023). The most commonly recurring plasticizer for cellulosic materials is, however, water, and softening by moisture can be considered both a blessing and a curse, as the softening, connected to increased strainability, is achieved at the expense of the mechanical properties of the material (Benson 1971; Marin et al. 2020). This has also been shown for dialcohol fibers (Linvill et al. 2017). To the authors' knowledge, neither moisture sorption data nor the mechanical response at corresponding humidities have been reported for cationized fibers or materials derived from them. There are, however, reasons to anticipate that such material would be prone to extensive moisture sorption. Earlier studies have demonstrated a strong tendency for cationized fibers and fibril material to adsorb water (Benselfelt et al. 2019; Pei et al. 2013; Sjölund et al. 2025b). It has also been demonstrated that the increased accessibility of the fiber wall, which can be expected from the incorporation of the comparably bulky trimethylammonium group, enhances moisture uptake in the material (Garg et al. 2021; Hill et al. 2009; Li et al. 1989). This, together with the already observed improvement in extensibility of handsheets based on cationized fibers under standard conditions, leads us to hypothesize that highly strainable materials could be obtained by combining cellulose cationization with hygroplasticization via moisture adsorption.

To address the identified knowledge gap, this contribution presents a detailed study of the effect of moisture on cationized fiber material. The study encompasses investigating the thermodynamics of the sorption process and the concomitant nanostructural response, as well as exploring its effect at the fiber network level. The aim of the work is hence twofold: both to provide a fundamental understanding of how high moisture uptakes affect cellulosic fibers in general and cationized fibers in particular, and to demonstrate how a combined modification and hygroplasticization might be used to achieve a fiber material with enhanced strainability. This strategy

Table 1 Dosages of pulp and chemicals for the cationization modification. C:G corresponds to the CHPTAC to glucose residue ratio

Dosages of CHPTAC and NaOH are given both as ratios and as added mass

Sample	Pulp dry (wet) (g)	CHPTAC C:G-ratio (mass (g))	NaOH NaOH:C-ratio (mass (g))	Water (g)	HCl 1M (mL)
Reference	50 (242)	0 (0)	0 (0)	0	0
200 $\mu\text{eq g}^{-1}$	50 (242)	0.5 (48.4)	1.2 (7.4)	231.7	50
400 $\mu\text{eq g}^{-1}$	50 (237)	1.0 (96.8)	1.2 (14.8)	209.9	100
1000 $\mu\text{eq g}^{-1}$	50 (237)	2.0 (193.5)	1.2 (29.6)	156.3	200

adds another approach to achieving 3D formability in fiber materials. The results were analyzed by equilibrium dynamic vapor sorption (DVS) measurements, from which the thermodynamics of sorption could be derived. The changes in the molecular and supramolecular structure of the fiber with moisture were studied using small- and wide-angle scattering (SAXS and WAXS) of both reference and cationized fibers. The softening behavior of the fiber-based material was established by combining the DVS data with dynamic mechanical analysis at controlled relative humidity (DMA-RH). The indications of a more efficient softening could also be demonstrated through tensile testing in a controlled environment. Lastly, 3D shapeability, enabled by the enhanced hygroplastic deformability of the material following cationization and subsequent hygroplasticization, was demonstrated through press-forming of double-curved structures using a fixed-blank setup.

Material and methods

Materials and chemicals

The fibers used were from a fully bleached, never-dried, softwood Kraft pulp provided by Stora Enso AB (Skoghall pulp mill, Karlstad, Sweden). The cationization reagent, 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTAC), sodium hydroxide (pellets, purity > 98.5%, AnalR NORMAPUR® Reag. Ph. Eur.), hydrochloric acid (ACS reagent, 37%), and silver nitrate (ReagentPlus®, ≥ 99.0%) were purchased from Sigma Aldrich (Burlington, MA, USA). Chemicals were used without further purification to prepare solutions with appropriate concentrations.

Modification

Before modification, the fibers were thoroughly washed according to an earlier method described by Wågberg and Björklund (1993) to remove metal ions other than sodium and dissolved colloidal substances that might interfere with or affect the efficiency of the modification. Once this was done, a washed, never-dried sample containing 50 g of dry fibers was transferred to a polyethylene plastic bag and soaked in an alkali solution of a given concentration for 30 min at room temperature. The reagent, CHPTAC, was added to the plastic bag, and the reaction mixture was kneaded by hand for at least 5 min to ensure proper mixing; exact dosages are listed in Table 1, sample names correspond to the approximate charge of the fiber. The dosages were normalized such that the final solids content of the fibers was always kept constant at 10 wt%. The reaction bag was sealed and immersed in a 60 °C water bath for a preselected time of 4 h. Any remaining reagent was quenched by diluting the fibers with deionized water; thereafter, the material was transferred into a Büchner funnel, and hydrochloric acid was added to the diluted reaction mixture to neutralize its pH. The fibers were dewatered and repeatedly washed with deionized water until the conductivity of the filtrate dropped below 5 $\mu\text{S cm}^{-1}$. The material was collected in air-tight bags and stored at 4 °C until further use. Solids contents were measured in triplicate.

Characterization

The fibers, unmodified and cationized, have been characterized by FT-IR, NMR, lignin and carbohydrate analysis, and fiber dimensions in previous works by Sjölund et al. (2025a, b).

Degree of substitution (DS)

The DS was determined using conductometric titration according to the same method as described earlier by Sjölund et al. (2025b), assuming a 1:1 ratio between chloride ions and cationic groups in the sample. In short, never-dried cationized fibers were suspended in deionized water to a final concentration of 0.5 wt% and a volume of 100 mL. Measurements were performed by adding 1.0 mL of 0.01 M AgNO₃ every minute and reading the corresponding conductivity. The dry mass of the material was determined by filtration of the suspension over a pre-weighted filter paper, the filter paper and fibers were then dried overnight in a 105 °C oven before being weighed. Measurements were performed in triplicate. The DS was calculated according to Eq. 1 and then converted to charge (Q) using Eq. 2.

$$DS = \frac{n_c}{n_G} = \frac{V_s C_s M_G}{m_{\text{fib}} + V_s C_s (M_{\text{cNO}_3} - 1)} \quad (1)$$

$$\text{Charge} = \frac{DS}{M_G + M_{\text{cCl}} DS - DS} \quad (2)$$

where n_G and n_c correspond to the number of glucose residues and cationic groups, respectively. V_s corresponds to the volume of AgNO₃-titrant required to consume all chloride ions in the sample, and C_s is the concentration of said titrant. M_G corresponds to the molar mass of the glucose residue, M_{cNO_3} and M_{cCl} correspond to the molar mass of the cationic group with a nitrate and chloride counterion, respectively. $M_G = 162.1 \text{ g mol}^{-1}$, $M_{\text{cNO}_3} = 177.1 \text{ g mol}^{-1}$, and $M_{\text{cCl}} = 150.5 \text{ g mol}^{-1}$. m_{fib} corresponds to the dry mass of the sample.

Material testing

Unless otherwise stated, material testing was performed using handsheets with an approximate grammage of 100 g m⁻², prepared using a Rapid Köthen sheet former (Paper Testing Instrument, Laakirchen, Austria) according to the ISO 5269-2:2004 standard and dried for 15 min at 93 °C under a reduced pressure of 95 kPa. The prepared sheets were stored in a controlled climate of 23 °C and 50% RH for at least

24 h before further use. The density of the sheets was determined at a climate of 23 °C and 50% RH, the grammage was determined using an analytical balance, and the structural thickness of the sheets was determined according to the SCAN-P 88:01 standard using an STFI structural thickness equipment.

Mechanical testing at controlled humidity

Mechanical testing was performed using an L&W (code 064, 066) horizontal tensile tester (Lorentzen & Wettre/ABB AB, Kista, Sweden). Test pieces with a width of 15 mm were used; the gauge length was set to 100 mm, and the samples were strained at a rate of 10 mm min⁻¹. Testing was performed at a temperature of 23 °C and RHs of 20, 50, 65, 80, and 90% in a walk-in-sized climate chamber where the RH (and temperature) was monitored continuously throughout the measurements to ensure target conditions. The samples were conditioned in the given climate for at least 16 h (overnight) before being tested, and a total of 10 measurements were performed for each sample at each RH. The moisture uptake of the samples was accounted for as the mass difference between the conditioned sample pieces and the bone-dry samples after overnight drying at 105 °C.

Formation of double-curved structures

3D forming was performed using a Fontijne TP400 press (Fontijne Grotnes, The Netherlands) equipped with a custom-made forming tool (Supporting Information Fig. S1, (Larsson et al. 2014a, b)). Circular, restraint-dried papers, with a diameter of 50 mm, were clamped on top of the female die using a circular ring held in place by four springs to ensure firm clamping and uniform load distribution. The male die was attached to the top part of the press by a magnet, and the double-curved structure with a nominal strain of 12% was formed by pressing the dies together with an operational force of 20 kN. Before pressing, the material was conditioned for at least 16 h (overnight) at either 20 or 76% RH. During the forming process, the sheets were placed between two thin, low-modulus polyethylene films to retain the moisture in the film.

Dynamical vapor sorption

Dynamic vapor sorption (DVS) experiments were performed using a DVS resolution instrument (Surface Measurement System, London, UK). Humidity was changed in 10% increments from 0 to 90% and back to 0% RH for sample sheets weighing approximately 10 mg. Each humidity step was run until moisture content variations $< 0.001\% \text{ min}^{-1}$ were reached, with a minimum step time of 30 min. Measurements were performed at target temperatures of 25, 44, and 58 °C.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) experiments were performed using a Discovery DMA 850 (TA Instrument, New Castle, DE, USA), with a humidity accessory. Test pieces with a width of 5 mm were used, and the clamp spacing was set to about 10 mm. The test was conducted at a frequency of 1 Hz. To minimize the influence of humidity-induced variations in specimen length during the experiment and ensure the acquisition of low-noise data, a dynamic strain of 0.01% was employed, corresponding to an applied load of approximately 0.2 N. The RH was changed from 0 to 90% in increments of 10%, both during sorption and desorption. The duration of each step was set to 3 h, based on the DVS results. In addition, to eliminate dried-in strain, preconditioning steps consisting of humidification at 90% RH and drying at 0% RH for 3 h each were performed before the stepwise changes. Measurements were performed at target temperatures of 25, 44, and 58 °C.

X-ray scattering experiments

Wide- and small-angle X-ray scattering (WAXS and SAXS) patterns were acquired at room temperature using a SAXSLAB Mat:Nordic (Xenocs, Grenoble, France) equipped with a 003+ high brilliance micro-focus Cu-radiation source ($\lambda = 1.5418 \text{ \AA}$; Rigaku, Tokyo, Japan). The WAXS measurements used a Pilatus 100 K detector system (Dectris, Baden-Daettwil, Switzerland) and a sample-to-detector distance of 130 mm, providing a q -range from 0.3 to $2.3 \text{ \AA}^{-1}$,

while the SAXS measurements used a Pilatus 300 K detector system (Dectris, Baden-Daettwil, Switzerland) with a sample-to-detector distance set to 1078 mm, providing a q -range from 0.005 to $0.3 \text{ \AA}^{-1}$. The acquisition time was set to 1800 s for both WAXS and SAXS.

WAXS measurements were performed in vacuum, while the SAXS measurements were performed at controlled humidities ranging from 0 to 90% RH. Such controlled sample environment was achieved using a custom-built, sealed sample chamber with an inlet and an outlet for gas (Supporting Information Fig. S2). The samples were taped to the sample holder and covered with Kapton film before the chamber was closed. Air with a controlled RH was pumped through the system for at least 3 h to condition the material before acquiring the data. The 0% RH measurements were performed in vacuum, without the Kapton films. The relevant backgrounds were acquired separately at the same sample-to-detector distance and acquisition time. The SAXS data were normalized using the Porod invariant, and the relevant background was subtracted for all samples. The WAXS data were normalized by the grammage of the sheets.

Results and discussion

Cationization and material characterization

Fibers carrying a range of different charges from -50 (non-modified, anionic, reference) to $+ 1050 \mu\text{eq g}^{-1}$ were prepared by altering the reagent dosage according to Table 1. The corresponding charges of the material are presented in Table 2. It has previously been demonstrated by Sjölund et al. (2025a) that the reaction efficiency is enhanced by limiting the presence of water in the system during the modification process. In the present study, a feasibly high solids content of 10 wt% was used, and the cationized fibers were obtained at a high gravimetric yield. The corresponding reaction efficiency ranged from 6 to 10%, and higher efficiency was observed with increasing reagent dose, accompanied by a higher degree of modification. A possible explanation for this is increased accessibility of the reagent to the fiber wall,

Table 2 Summary data from fiber cationization and sheet preparation

Sample	Charge ($\mu\text{eq g}^{-1}$)	Reaction efficiency (%)	Gravimetric yield (wt%)	Dewatering time (s)**	Sheet density (g m^{-3})
Reference	– 50*	–	–	11	627 ± 26
200 $\mu\text{eq g}^{-1}$	194 ± 13	6.5	>95	12	663 ± 36
400 $\mu\text{eq g}^{-1}$	392 ± 23	6.8	>95	12	684 ± 31
1000 $\mu\text{eq g}^{-1}$	1053 ± 25	10.3	>90	13	792 ± 24

*Data from Sjölund et al. (2025b), ** Time to form the wet sheet on the forming wire during sheet preparation.

arising from the higher alkali dose, which enhances fiber swelling, as well as gradual fiber swelling as the reaction proceeds. Since the reaction is heterogeneous in nature (solid cellulose and CHPTAC in solution), it is expected to occur on the fibril surfaces throughout the fiber wall. However, the exact homogeneity across the modified fiber wall is yet to be established.

This study uses restraint-dried sheets prepared in a Rapid Köthen sheet former. The modification of the fibers did not significantly affect the dewatering time of the sheets (Table 2), a crucial factor to consider when evaluating the feasibility of producing cationized-fiber-based papers on a large scale using conventional paper machines. An increase in density is observed at higher charges, consistent with earlier work using cationized cellulose and other cellulose modifications, such as TEMPO-mediated oxidation or periodate oxidation followed by borohydride reduction (López Durán et al. 2018). This can primarily be explained by the enhanced swelling and, consequently, softening of the modified fibers, leading to a more efficient consolidation of the sheet during pressing and drying, and hence a higher joint density (Lindström 1992; Lindström et al. 2005; López Durán et al. 2018; Sjölund et al. 2025a). The densification of the sheets will become important in later parts of the work, as it is expected to affect the material's mechanical properties in both dry and humid conditions.

Structural changes in the material upon cationization and moisture sorption

During modification, functionalization is expected to occur on the surfaces of the fibrils and aggregates thereof. An educated assumption of a 6 x 6 nanofibril cross-section, accessibility to the C2, C3, and C6 hydroxy groups during modifications and a degree of modification of 0.18 (1000 $\mu\text{eq g}^{-1}$) would mean that

33% of all glucose residues constituting the surface of the fibril would carry a functional group (de la Motte et al. 2011; Newman et al. 2013). It is hence to be expected that an effect from the modification would be present at a nanoscopic level. Therefore, X-ray scattering data (Fig. 1), both as WAXS and SAXS, were collected to identify such expected changes in the material.

It is clear from the WAXS data acquired for the dry fibers (Fig. 1a) that cationization influences the degree of crystallinity and possibly also the crystalline structure of the material. Reference fibers exhibit a comparably higher crystallinity and an expected cellulose I structure. The same structure is observed at a low degree of modification. However, for the more highly modified sample, significant structural differences can be observed, with a decreased crystallinity (as indicated by the decreased scattering intensity from the (1 – 1 0), (1 1 0) and (2 0 0) planes). The shoulder observed at $\sim 1.45 \text{ \AA}^{-1}$ could be connected to scattering of the (1 0 2) and (0 1 2) planes of cellulose I β or indicate partial transition to cellulose II. However, since no other characteristic signals for cellulose II can be observed in the scattering patterns, it is suggested that the observed increase in intensity at $\sim 1.45 \text{ \AA}^{-1}$ (relative to scattering of the (1 – 1 0), (1 1 0) and (2 0 0) planes) mainly arises from restructuring of the ordered zones arising from the modification (Supporting Information Table S1 for further information). It is also worth noting that the concentrations of alkali before and during modification were considerably lower than those expected to convert cellulose I to cellulose II (Sobue et al. 1939). However, it is possible that the cationization reagent and the covalent linkage of the bulky side groups to the fibril surfaces influence the ordering of cellulose, leading to a decrease in crystallinity of the material and possibly distortions in the crystal, which can explain the emergence, or rather shift, of the peak at $1.45 \text{ \AA}^{-1}$.

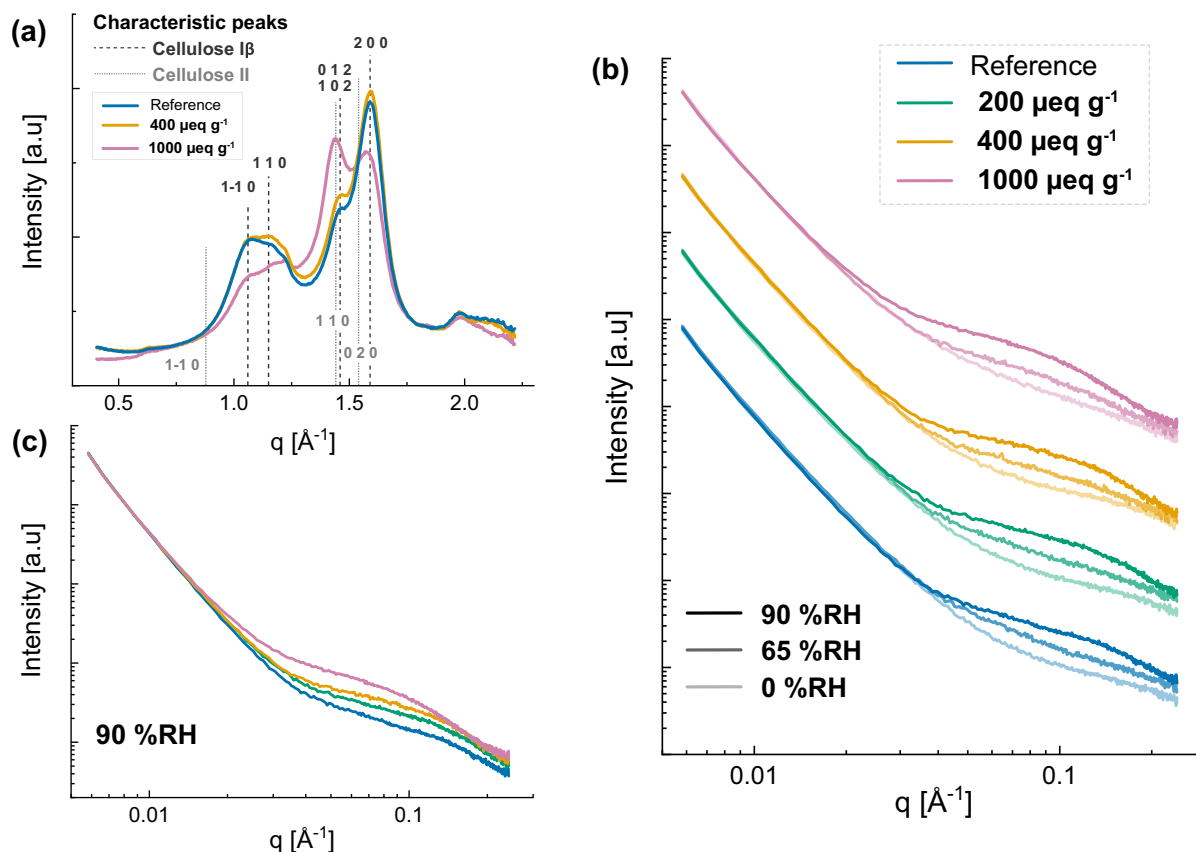


Fig. 1 X-ray scattering pattern of reference and cationized fibers with different charges. **a** WAXS patterns acquired in vacuum **b** SAXS patterns acquired at 0, 65, and 90% RH **c** SAXS patterns acquired at 90% RH

From the SAXS data, it is possible to obtain information about the arrangement of fibrils in the fiber wall. The SAXS patterns attained for the different cationized materials at different RHs are summarized in Fig. 1b–c, and it is clear that both the modification and moisture sorption affect the structure of the material. The effect can mainly be distinguished as an emerging shoulder in the q -range of 0.02 – $0.2 \text{ \AA}^{-1}$, while the low q -range remains essentially unaffected by modification and moisture sorption. Hence, in the low q -range, a linear fitting could be performed with a power-law exponent close to four, i.e., a value within the same range as found by, for example, Penttilä et al. (2019) for different fiber species in dry and wet state, and by Venkatraman (2024) for dialcohol modified fibers. Such values are indicative of the scattering of dense aggregates, in this case, the cell wall constituents and cavities (Jakob et al. 1996). In the higher q -range, the appearance of a shoulder

can be observed, which grows stronger with increasing degree of modification, as well as with increasing RH. This shoulder is associated with the distance between the fibrils, and a shift to lower q -values indicates an increase in the fibril-to-fibril distance. In Fig. 1b, it can be seen that the SAXS pattern for both reference and modified fibers in vacuum completely lack this feature, which presumably is due to the intimate contact in and between the fibril aggregates in the dry sample, which diminishes the electron density contrast to such an extent that the SAXS measurements cannot distinguish between individual fibrils (Larsson et al. 2022). As the fiber material is subjected to a humid environment, the appearance of a shoulder can be established in the q -range of 0.02 – $0.2 \text{ \AA}^{-1}$, corresponding to long-range repetitive distances in a size range of 3–30 nm. This can be explained by the enhancement in electron density contrast achieved as the fibril surfaces are covered by moisture. For the

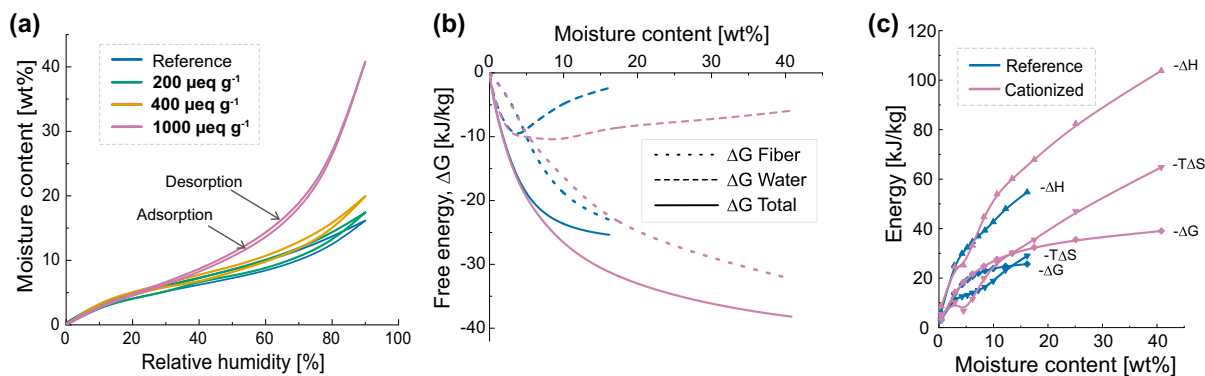


Fig. 2 **a** DVS data, moisture sorption and desorption curves as a function of RH for reference and cationized fibers with different degrees of modification, **b** change in free energy per kilo

fibers as moisture is sorbed, **c** enthalpy and entropy change per kilo fibers connected to the moisture sorption, temperature set to 25 °C

more highly modified fibers, this shoulder is visible at 65% RH, whereas for the reference and less modified fibers, it is only visible at higher humidities, such as 90% RH. By comparing the scattering patterns of the different materials at 90% RH (Fig. 1c), it becomes clear that the onset of the power-law exponent as well as the characteristic shoulder is shifted to lower q -values with increasing degree of modification. This is indicative of increased swelling and a larger fibril-to-fibril distance with an increasing degree of modification. These results are in line with earlier observations made by Venkatraman (2024), who showed that a partial conversion of the cellulose in softwood kraft pulp to dialcohol cellulose increased the characteristic distance between scattering domains, and by Virtanen et al. (2015), who showed that the fibril bundles in the fiber wall of a softwood dissolving grade pulp was loosened up by enzymatic hydrolysis. This emphasizes that modification has an important effect on the nanostructure of the fiber wall. Furthermore, moisture-induced swelling of wood material has been established (Fernandes et al. 2011; Paajanen et al. 2022). From the DVS data in Fig. 2a, it is apparent that cationization enhances the moisture sorption capacity of fibers, which means the more highly modified fibers will hold more moisture than their less modified counterparts at high RH. Using SAXS, Fernandes et al. (2011) showed a 25% (1 nm) increase in fibril distance in spruce wood upon sorption of 25 wt% D₂O, indicating that a high moisture content may have a significant effect on the nanostructure of cellulose-based materials. The results conclusively

indicate that the cationization and the concomitant increased moisture sorption contribute to a loosening of the fibrils in the fibril aggregates and hence a swelling of the fiber wall, which, in turn, is expected to soften the macroscopic fibers and their material.

Thermodynamics of moisture sorption

To better understand the moisture sorption characteristics of the modified material, DVS measurements were performed. Figure 2a shows characteristic sorption isotherms for the different materials (additional isotherms can be found in Supporting Information Fig. S3). Typical sigmoidal-shaped curves are observed, indicating Type II sorption characteristics (Brunauer et al. 1940). At low RHs, the sorption behavior is similar for all materials; however, at higher RHs, it is apparent that the material's sorptivity increases with an increasing degree of modification. Furthermore, all materials exhibit sorption hysteresis, a feature inherent to cellulosic materials. Interestingly, hysteresis is less pronounced at higher degrees of modification, indicating that adsorption occurs into a gradually more softened material (Salmén and Larsson 2018). The initial convex part of sigmoidal-shaped adsorption curves is generally associated with a Langmuir type of sorption and linked to the formation of a monolayer of water molecules on the available surfaces of the cellulosic fiber (Haselton 1954; Simon et al. 2022). Earlier studies using cotton fibers have shown that monolayer adsorption to accessible fibril aggregate surfaces corresponds to ~3.2

wt% moisture uptake (Morrison and Dzieciuch 1959); higher values, up to 5.1 wt%, have been reported for materials such as Sitka spruce fibers (Hill et al. 2009). Interestingly, up to these moisture contents, the sorption behavior is similar across the different materials, indicating that the initial sorption is not governed by the fiber modification. However, at moisture contents greater than ~4 wt%, corresponding to humidities above 25% RH, the sorption behavior begins to differ among the samples, with the more highly modified materials adsorbing more moisture. Following monolayer moisture adsorption to the fibril aggregate surfaces, sorption into the fibril aggregates and onto the individual fibril surfaces is expected (Larsson et al. 2013; Sjöstedt et al. 2015). The results from Larsson et al. (2013) and Sjöstedt et al. (2015) indicate that the dry fibril aggregates have dimensions around 30 nm, whereas the fibrils have dimensions around 4 nm. Assuming a density of the cellulose material of 1.5 g cm^{-3} , these dimensions give a specific surface area of 89 and $667 \text{ m}^2 \text{ g}^{-1}$ for the fibril aggregates and fibrils, respectively. Approximating the size of a water molecule to be $2.8 \text{ \AA}$, the monolayer coverage of water molecules can be calculated to correspond to 3.4 and 25.4 wt% for the fibril aggregates and liberated fibrils, respectively.

From the SAXS data shown in Fig. 1b, an enhancement of the electron density contrast can be observed at higher RH, which indeed supports that moisture penetrates into the fibril aggregates and acts as a spacer “freeing” the fibrils inside the aggregates. Earlier studies also show that cellulose fibers with a lower degree of crystallinity are more prone to adsorbing moisture, due to greater accessibility of the fiber wall (Jeffries 1964; Mihranyan et al. 2004). From the WAXS patterns in Figure 1a, a loss of crystallinity is clearly visible in the most highly modified fibers, which could partly explain the enhanced sorption, as moisture can penetrate into the less ordered regions (Kocherbitov et al. 2008). In addition, the literature suggests that chemical modification and even the choice of counterion in a modified system can influence sorption behavior (Berthold et al. 1994; Salmén and Larsson 2018). López Durán (2018) performed DVS measurements using cellulose nanofibril films with various functionalities and found that materials with charged groups (anionic, carboxylic groups) were comparably more prone to adsorb moisture, a tendency that increased with the increasing

amount of charges present. Just like the carboxylate functionalities, the trimethylammonium groups on the cationized fibers are expected to enhance the material’s water interactions, and the corresponding salt, tetramethylammonium chloride, is highly soluble in water (ROTH 2025). It is therefore hypothesized that hydration of the quaternary ammonium group and its counterion significantly contributes to the high sorption capacity of the modified fibers.

To better understand and characterize the sorption process, the total Gibbs free energy (ΔG_{tot}) was calculated from the adsorption isotherm (Supporting Information Section S4 for calculations (Hollenbeck et al. 1978)). The sorption process depends on two factors: the free energy change of the sorbed water (ΔG_{water}), governed by the difference in chemical potential of water in the adsorbed and pure liquid state, and the free energy change of the fiber (ΔG_{fiber}), governed by, among other things, structural changes in the fiber wall upon moisture sorption. The results are shown in Fig. 2b. Furthermore, by separating the total Gibbs free energy into entropic and enthalpic contributions (Fig. 2c, Supporting Information Section S5 for calculations), further insight into the thermodynamics can be gained. It should be noted that the values calculated for the reference material agree well with those calculated by Hollenbeck et al. (1978) for microcrystalline cellulose. However, to the authors’ knowledge, corresponding data have not yet been presented for either cationically charged cellulose or other modified cellulose materials.

At low moisture contents, the total Gibbs free energy change upon moisture sorption is high. A considerable reduction in enthalpy (negative ΔH) indicates that the initial monolayer adsorption is a strongly exothermic process, while a steady decrease in entropy (negative ΔS) indicates an increased ordering of the system as moisture is adsorbed to the fiber. It can hence be concluded that moisture sorption is an enthalpically driven process, occurring spontaneously due to favorable interactions between the moisture and the fibers, as well as energetically favorable deformation of the fiber wall.

Interestingly, it can be established that the total Gibbs free energy release, enthalpy and entropy changes, as well as the two separate contributions ΔG_{water} and ΔG_{fiber} , are essentially the same for the reference and modified material up to about 4 wt%. This suggests that the initial moisture sorption occurs

at energetically homogeneous surfaces with a similar effect on the fiber wall. According to the earlier calculations, this adsorption most likely occurs on the available surfaces of the fibril aggregates. However, perfect monolayer adsorption is probably not expected, due to the dramatic decrease in entropy such sorption characteristics would entail (Kocherbitov et al. 2008). Instead, a gradual transition from monolayer adsorption on the fibril aggregate surfaces to adsorption onto the individual fibrils is probably to be expected. Indeed, the SAXS patterns (Fig. 1) support that moisture penetrates into the fibril aggregates at higher moisture contents. It should also be noted that ΔG_{water} approaches zero at moisture contents above 4 wt%, indicating that the driving force for further sorption is decreasing, which can be attributed to the formation of additional water layers on the available surfaces. This behavior is more pronounced for the reference material, whereas for the highly modified material, ΔG_{water} remains negative even at moisture contents above 25 wt%, indicating that favorable interactions between water and the modified fibers persist beyond the calculated monolayer adsorption onto the fibrils. This suggests that the functional groups become hydrated and/or that the fibril surfaces are more swollen, thereby increasing the available surface area for the cationically modified fibers/fibrils.

Regarding equilibrium moisture sorption capacity, the enhanced sorptivity of the modified material can be understood by studying the contributions to the total Gibbs free energy. At moisture contents above 4 wt%, the increase in ΔG_{water} is compensated by a continuous decrease in ΔG_{fiber} , which initially ensures a decrease in the total Gibbs free energy and sorption beyond 4 wt%. ΔG_{fiber} reflects energetic transitions in the fiber wall, such as the relaxation of built-in stresses upon moisture sorption, and the value is similar for both the modified and reference material. However, since the fiber–moisture interactions (ΔG_{water}) are more favorable for the modified material, sorption becomes more thermodynamically favorable. This ultimately results in a higher equilibrium moisture sorption capacity of the modified material. On a similar note, the enthalpy change is larger for the modified material at moisture contents exceeding 4 wt%, which supports that cationization enhances fiber–water interactions (Digaitis et al. 2024). While the enthalpy change is dominant at low moisture contents, its

dominance gradually decreases at higher moisture contents as the entropy contribution increases, gradually leading to an energetic equilibrium at which the sorption ceases. Owing to the larger enthalpic driving force, a steeper slope for ΔG (i.e., driving force for moisture sorption) can be established for moisture sorption to the modified fibers at comparable moisture contents, which explains why the modified material exhibits a higher sorption capacity.

Based on the shape of the sorption isotherm and calculated thermodynamics, it might be hypothesized that the underlying mechanism for the enhanced moisture sorption in the modified material is twofold. Firstly, moisture can more easily penetrate the fiber wall and adsorb on fibril aggregates as a consequence of an increased disordering of the fibril surfaces. Secondly, moisture sorption beyond monolayer sorption will be more energetically favorable due to hydration of the functional group.

Moisture sorption and mechanical response

Dynamic mechanical properties of hygroplasticized, cationized fibers

Moisture sorption is known to soften cellulosic materials (Benson 1971; Salmen 1982). From Fig. 1, it can be expected that moisture will have a greater effect on the properties of the modified fibers and, consequently, on the fiber network properties. In this respect, DMA-RH measurements can provide important information about the effect of hygroplasticization. In Fig. 3a–b, the relative storage and loss modulus of the material are presented as a function of moisture content (absolute values and corresponding data as a function of RH, see Supporting Information Fig. S12). It can be concluded that the change in relative storage modulus, which describes the material's ability to store energy during elastic oscillatory stress (i.e., its stiffness), is similar for the different materials. The most highly modified material, however, loses a larger fraction of its stiffness due to its higher moisture sorption capacity. It is interesting to note that changes in the loss modulus, which reflect a material's ability to dissipate energy, differ significantly across the samples. It is apparent that all materials' capacity to dissipate energy increases up to a certain moisture content, which is expected as the surface and other less ordered structures, such as cellulose

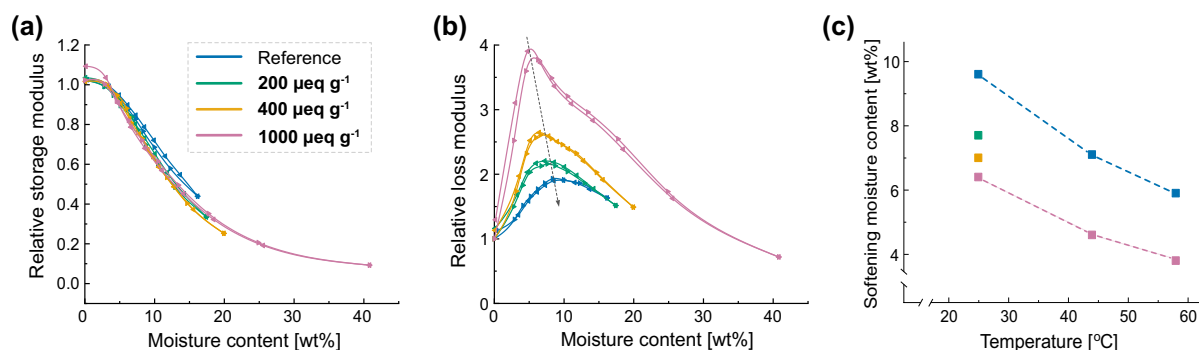


Fig. 3 Dynamic mechanical analysis at different moisture contents and temperature for reference and cationized fibers with different degrees of modification, **a** relative storage modulus,

and **b** relative loss modulus as a function of moisture content, measured at 25 °C, **c** the softening moisture content as a function of temperature

molecules (and any residual hemicelluloses), in the fiber wall become gradually more mobile as moisture is adsorbed. However, once a certain moisture content is reached, the loss modulus decreases again as the polymers' viscous nature becomes dominant. The peak of the relative loss modulus can hence be considered the softening moisture content of the material (Salmén and Larsson 2018). Figure 3b shows a clear difference in peak position for the loss moduli of the different materials, indicating that the modification has significantly altered the softening properties of the material, as cationization decreases the softening moisture content. Hence, it can be concluded that the fiber material is more prone to moisture-induced softening after functionalization with quaternary groups. This is also supported by plotting $\tan\delta$ (i.e., loss modulus/storage modulus) as a function of moisture content (Supporting Information Fig. S13), where the modified materials show a greater response to moisture. It has previously been demonstrated that the degree of crystallinity of cellulosic materials has a significant impact on the onset of hygroplasticization (Salmen and Back 1977). In the case of cationized cellulosic fibers, efficient softening is likely a combined effect of the loss of ordering at the fibril surfaces, which facilitates the mobility of individual polymer segments, and the added functionality acting as a spacer, which further facilitates the separation of the lamellar structure of the fiber wall.

To better understand the softening behavior, DMA-RH measurements (and correlative DVS measurements, Supporting Information Fig. S3) were performed at three different temperatures (25, 44, and 58

°C). The DVS measurements show that an increase in temperature results in lower sorption values for all samples, which is expected and can be explained by the sorption process being enthalpy driven (Fig. 2c and Hollenbeck et al. (1978)). In Figure 3c, the softening moisture content is shown as a function of temperature; the values have been extracted from the peak of the loss modulus curves collected at different temperatures (Supporting Information Fig. S14). This representation again emphasizes that the modification significantly enhances the material's response to moisture. It is also apparent that an increasing temperature decreases the threshold moisture content, a consequence of temperature affecting molecular mobility in the material in a manner similar to that of moisture (Salmen 1982). The effect of temperature is similar for reference and modified material, i.e., the onset moisture content decreases by ~40% as the temperature increases from 25 to 58 °C. These observations can be compared to those made for sheets prepared from dialcohol cellulose fibers, a known thermoplastic-like material. In the case of dialcohol cellulose, it was found that the effect of temperature on the softening moisture content was significantly more pronounced, suggesting a synergistic effect of moisture and temperature on the material's softening (Salmén and Larsson 2018). The absence of this effect for the cationized material suggests that the modification does not provide significant thermoplasticity, but mostly hygroplasticity, to the material. From the experiments performed, it is not possible to separate whether moisture uptake leads to softening of the individual fibers or the fiber–fiber joints. It can,

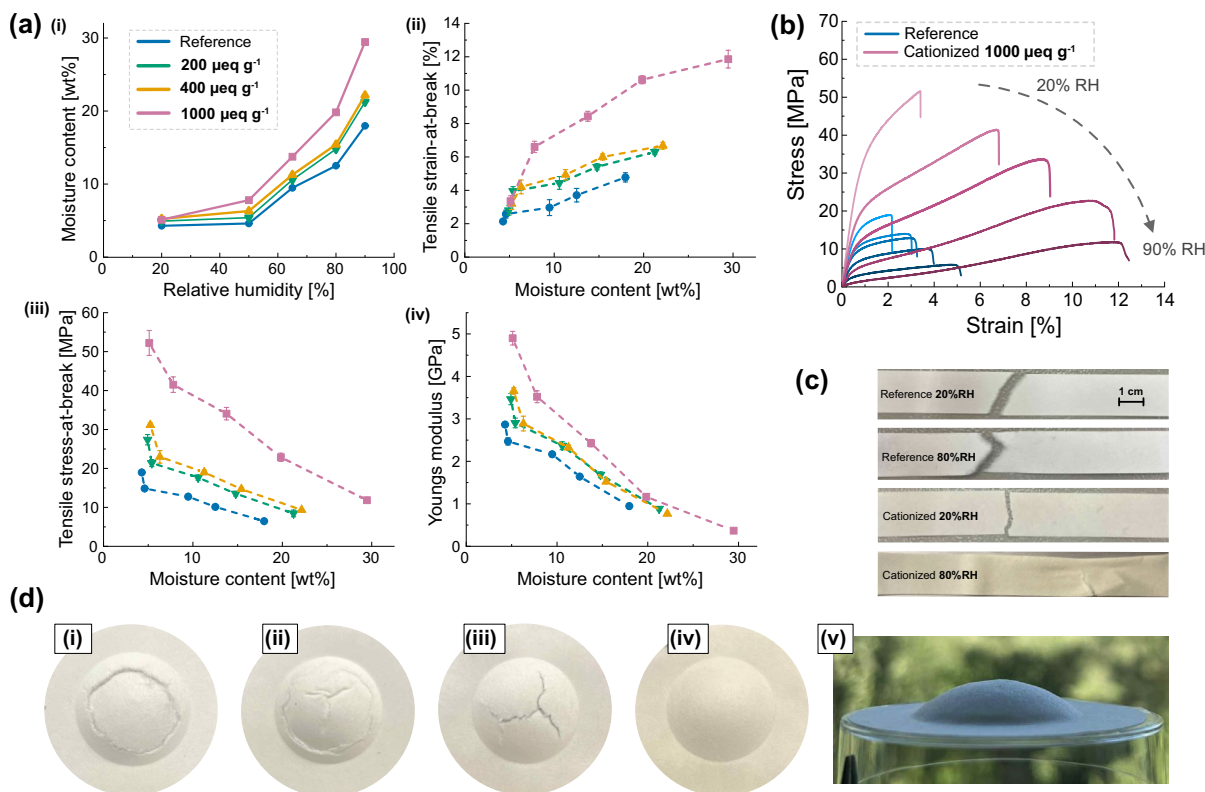


Fig. 4 **a** Moisture uptake and mechanical properties of reference sheets and sheets prepared from cationized fibers, measured at different RH; (i) moisture uptake and (ii–iv) tensile strain-at-break, tensile stress-at-break, and Young's modulus of the sheets. **b** Representative stress–strain curves for sheets made from reference fibers and cationized fibers. **c** Photos of

the failure surface of reference material and cationized material (1000 $\mu\text{eq g}^{-1}$) after being strained to failure at 20 and 80% RH. **d** Double-curved structures formed by 3D forming of restraint-dried sheets; (i–ii) reference sheets and (iii–iv) cationized sheets conditioned at 20 and 80% RH, respectively, (v) side-view of the successfully formed structure shown in (iv)

however, be expected that subjecting the cationized fiber sheets to moisture will improve the material's overall strainability.

Tensile properties of hygroplasticized, cationized fibers

In order to quantify the mechanical properties of the sheets, and the influence of moisture, the sheets were subjected to tensile testing under controlled RH (Fig. 4). Since the DMA measurements (Fig. 3), did not indicate any significant thermoplastic response in the modified material (at temperatures below 60 °C), the temperature was kept at standard conditions of 23 °C. Gravimetric measurements of the moisture uptake of the test pieces used for tensile testing indeed show the strong tendency of the modified

material to adsorb moisture (Fig. 4a(i)). Mechanical testing indicates a gradual softening of the sheets as moisture is adsorbed (Fig. 4a (ii–iv)), which can be noted as an increase in the strain-at-break and concomitant reduction in the tensile stress-at-break and Young's modulus of the materials. Previous studies have shown that cationization increases the strainability of the material (Sjölund et al. 2025a), which is also observed in the present work. As indicated by the DMA-RH measurements, the modified material is also more responsive to moisture. This is, for example, shown by the strain enhancement being considerably greater for the modified material. For the highly modified material, the strain-at-break increased from 3 to 12% (a 300% increase) when the humidity was increased from 20% RH to 90% RH. For the reference material, the corresponding increase was only

100%, rising from 2 to 4% strain-at-break. The low- and medium-modified materials fall in between these extremes with an increased strainability of around 150%. One underlying factor is likely the higher concentration of plasticizing moisture in the modified material. However, by presenting the mechanical data as a function of moisture content, it can be concluded that this alone does not fully explain the observed behavior, as the modified material is comparably more strainable also at the same moisture content. For example, upon increasing the moisture content from 5 to 12 wt%, the highly modified sample showed 150% greater strainability, whereas the reference material showed approximately 60% greater strainability. As a matter of fact, the stress-at-break and Young's modulus of the material display similar behavior, where the loss in mechanical strength upon moisture sorption is more extensive for the modified material. The cationization itself, however, increases the sheet strength, an effect attributed to better network formation during sheet making, as highly swollen, cationically charged fibers are used (Sjölund et al. 2025a). The observed increase in strength is partially attributed to higher material density (Table 2). Normalizing the tensile data by grammage (i.e., tensile index, Fig. S15) does, however, yield similar trends in strength, underscoring that the fiber network can withstand higher forces before failure after cationization. It can be concluded that the highly modified material exhibits higher stress-at-break and tensile index values than the reference material, even at high moisture content. The material's higher mechanical integrity may be one explanation for achieving a higher strain-at-break. Figure 4b–c shows representative stress–strain curves as well as images of test pieces strained to failure. The failure surfaces provide valuable insights into the straining and rupture mechanisms taking place when the material is strained. For the reference material, fiber pullouts can be observed at both low and relatively high moisture contents. This suggests that joint strength limits the overall strength of the fiber network. For the samples prepared from cationized fibers, the shape of the tensile curves and the visual appearance of the corresponding test pieces indicate that the failure mechanism changes from a stiff break, with fiber fracture, when dry, to a plastic failure where the fibers are pulled out of the fiber network as moisture is sorbed. It is, however, unfortunately, not

possible to determine to what extent the fibers themselves have been strained.

3D forming

As a proof-of-concept, 3D forming of restraint-dried sheets from cationized and hygroplasticized fibers was performed. Figure 4d shows 3D structures prepared from reference and cationized sheets, conditioned at two different RHs. The humidities were chosen such that the material was tested both below and above their indicated softening moisture content (see Fig. 3). At 20% RH, the moisture content is expected to be similar for the two samples (see Fig. 4a), while at 80% RH, the cationic material will contain considerably more moisture. Only the material prepared from cationized fibers, subjected to 80% RH, could withstand the required deformation without mechanical failure. The fraction mechanisms appear similar to those observed during tensile testing, with fiber pullouts in the reference material and a high degree of fiber fractures in the cationized material. The failure zone is more delocalized for the reference material, and the top part of the double-curved surface has essentially been torn off to make room for the male die. On the other hand, samples made from cationized fibers conditioned at low RH showed that larger deformations could be tolerated before failure, resulting in cracking of the structure.

All in all, the 3D forming trial demonstrates not only the importance but also the power of combining fiber cationization with a simple softening technique to achieve 3D formability of paper. This is a novel approach, which, like methods such as free-drying and creping, efficiently improves the strainability of the paper. The obtained stainabilities, and hence expected 3D formabilities, are within the same range as those reported for free-drying and creping methods, but unlike these methods, sheets can be prepared on conventional paper machines (Strand et al. 2018; Tanaka et al. 2023). Instead, the fibers are chemically modified before sheet-making, altering their bulk properties and the properties of the final paper. While the introduction of cationic groups to the fibers increases the strainability to a certain extent, RH-mediated tuning of the material's softening allows for further control of its strainability. This constitutes an additional advantage over mechanical methods, as the material can be formed at high RH and then subjected to lower RH to

regain mechanical strength. The sensitivity to moisture, however, as with most fiber-based products, is also a limitation for the final product, and a post-treatment might be required to expand its application range beyond dry conditions. This, together with further improvements in strainability, is suggested as a focus area for future studies in the development of fiber-based materials that can replace fossil-based products.

Conclusions

This work demonstrates that it is possible to combine fiber modification and hygroplasticization to obtain a fiber material that can sustain up to 12% strain (at 90% RH), a value 400% higher than the strain of the reference material (at standard conditions 50% RH). This enables the fabrication of sheets using conventional papermaking methods, which can be subjected to 3D forming in a humid climate without experiencing mechanical failure. The present work, hence, constitutes a stepping stone towards the development of fiber-based sheets with the potential to replace fossil-based plastics in applications requiring a high degree of formability.

DVS measurements reveal that the material's moisture sorptivity increases with increasing degree of modification. This is primarily linked to increased accessibility of the fibril surfaces in the fiber wall (as indicated by a decrease in crystallinity) and the hydration of the functional group and its counterion. Thermodynamic calculations indicate that moisture sorption is an enthalpy-driven process where the initial sorption process, with monolayer adsorption to the accessible fibril aggregate surfaces, is a highly exothermic process. Furthermore, DMA-RH measurements revealed that the softening moisture content (as indicated by the peak position of the relative loss modulus) of the material decreases gradually with increasing degree of cationization. This, combined with the enhanced strainability and strength achieved through cationization, ultimately enables the 3D forming of the sheets.

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Data availability Data will be made available upon request.

Declarations

Competing interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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