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Upgrading Cellulose Networks: Conquering Limitations in Fiber Foams

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CHALMERS UNIVERSITY OF TECHNOLOGY

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THESIS FOR THE DEGREE OF LICENTIATE OF
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ABSTRACT

The battle to create structural materials with low environmental impact demands the investiture of two champions: porous structures and cellulose substrates. The dominant solutions when constructing strong lightweight materials are plastic and metallic foams, while currently, cellulose fiber foams suffer from challenges which hamper their development. Cellulose foams are structurally promising, but are sensitive to humidity and fire, and often have an inferior mechanical performance compared to their plastic and metallic counterparts. In addition, standard foaming techniques for cellulose fiber foams use synthetic sodium dodecyl sulfate (SDS), a surfactant which weakens critical fiber-to-fiber contacts. In this work, two approaches were employed as solutions to strengthen cellulose foams: cross-linking of cellulose fibers, and controlling pore structure formation. Phytic acid (PA), a bio-based polyphosphate, was cross-linked to cellulose fibers with the goal of improving fiber-fiber bonding and generating flame-retardancy in SDS-based cellulose foams. Controlling pore structure formation was separately achieved by dispersing tert-butanol (TBA), a water miscible amphiphile, into cellulose-water suspensions. Addition of TBA induced the formation of hierarchical structures which vastly increased the surface area and mechanical performance of dried foams. The functionalities produced by the two presented solutions expand the potential applications for cellulose foams, and serve to encourage the development of these materials as lightweight competitors in the transportation, construction and packaging sectors.

Keywords: cellulose, lightweight, porous network, flame-retardancy, cellular solid, fibers, cross-linking, pore structure.

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I. Tert-butanol as a structuring agent for cellulose nanocrystal water suspensions

Saül Llàcer Navarro, Eliott Orzan, Ratchawit Janewithayapun, Paavo Penttilä, Anna Ström, Roland Kádár and Tiina Nypelö

Manuscript

II. Catalyst-free phosphorylation of cellulose for bio-based fire-retardant materials

Eliott Orzan, Stefan Spirk, Aitor Barrio and Tiina Nypelö

Manuscript

AUTHOR CONTRIBUTION

I. Co-author; Responsible for conceptualization and planning of experiments with co-authors; Performed scanning electron microscopy investigations and mechanical testing; Participated in writing and editing the manuscript.

II. Main author. Responsible for conceptualization and planning of experiments with co-authors; Performed the experimental work; Wrote the first draft of the manuscript.

Nomenclature

Materials

CA	Citric acid
CMC	Carboxymethyl cellulose
CNC	Cellulose nanocrystal
CNF	Cellulose nanofiber
FR	Flame-retardant
OH	Hydroxyl functional group
PA	Phytic acid
SDS	Sodium dodecyl sulfate
TBA	Tert-butanol

Methods

BET	Brunauer-Emmett-Teller
FTIR	Fourier transform infrared spectroscopy
NMR	Nuclear magnetic resonance
SEM	Scanning electron microscope
SR	Schopper-Riegler
TGA	Thermogravimetric analysis

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1

Introduction

Millions of years of evolution have slowly specialized the structural composition of living beings, adapting macro- to nano-scale features to suit certain functionalities. One of the most intricate repeating themes in nature is found in the formation of hierarchical structures.¹⁻⁴ The build-up of structures within structures creates hierarchies which, almost without exception, are formed of fibrillar networks. Fibrils often consist of polysaccharides or proteins, which bundle together to form structural units such as cellulose in wood or twisted chitin fibrils in crustacean shells.⁵ The structural composition of these fibrils rather than the molecular body, allows them to bear load under impact, elevating their mechanical performance.⁶

Fibrils which enclose a space and form interconnected networks of solid faces and open cells are known as cellular solids (Figure 1.1).⁷ Cellular solids, also referred to as solid foams or porous networks, are known for their superior specific* properties due to their reduced densities. As materials, they are great thermal insulators, excel as energy and sound absorbers, and are valued for their high strength to weight ratios. Applying the concept of hierarchical structuring to cellular solids creates strong lightweight structures such as those found in sea sponges (Figure 1.1c). The cellular skeleton of the sea sponge is itself porous, creating hierarchies of cellular solids within cellular solids. This optimized solution found in nature can serve as inspiration for infrastructural construction and minimizes weight and material need.^{3,6,8,9} Nature's methodology of lightweight construction has been studied and adapted to engineer cellular solids from plastics and metals for use in major industries such as building, transportation and packaging. Lowering the density of materials by creating porous structures significantly reduces material consumption and the energy required for

*Specific is defined as the property value divided by the material density.

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their transportation.^{10,11} However, the pressures placed on the environment due to the exponentially growing need for these non-renewable materials demands bio-based solutions which can compete in the market. Therefore, it is necessary to turn back to the most abundant source of low-cost renewable cellular hierarchies: wood.

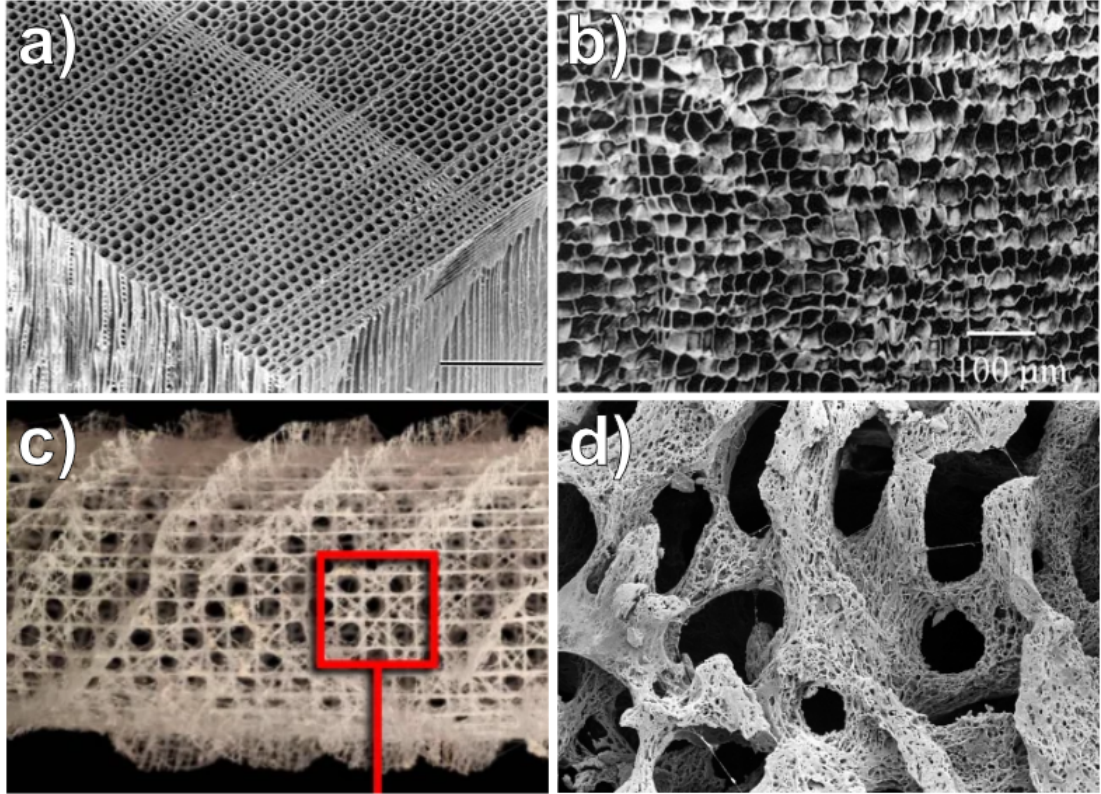


Figure 1.1: Examples of cellular solids with hierarchical structures found in nature a) wood[†], b) cork[‡], c) sea sponge[§], d) bone[¶].

The primary base structural unit of wood is cellulose, a polysaccharide chain of β -1,4-linked glucose units. Cellulose chains link together to form fibrillar hierarchies, giving wood fibers their signature strength. Each glucose unit features three hydroxyl (OH) groups, making cellulose particularly hygroscopic and thus sensitive to humidity. In addition, the poor fire resistance and poor thermal processability of cellulose fibers has created challenges which have limited their applications beyond paper and textiles. On the other hand, the presence of OH moi-

[†]Credit: C.-L. Huang et al. Springer Nature licence number: 5541851320910

[‡]Credit: Isabel Miranda et al. Springer Nature licence number: 5541861002311

[§]Credit: Matheus C. Fernandes et al. Springer Nature licence number: 5541850837784

[¶]Credit: David Gregory, Debbie Marshall. Licence: Attribution 4.0 International

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eties allows cellulose surfaces to be modified via e.g. acetylation, oxidation or esterification reactions.¹² Therefore, cellulose can be easily adapted to suit certain requirements such as solubility, flame-retardancy, and material compatibility in composites. Developing cellulose fibers into foam materials tuned for structural applications presents additional challenges due to the heterogeneous nature of a fiber network. Surfactants such as SDS are employed, which creates homogeneous pore size and fiber distributions yet weakens fiber-fiber contacts.^{13–18} The fibrous nature of wood pulp requires physical entanglements or other cross-links between fibers to prevent them from slipping past one another in a network under load.^{19,20} To strengthen fiber-fiber bonding, conventional methods involve hot-pressing or curing of citric acid (CA) or 1,2,3,4-Butanetetracarboxylic acid, which establishes covalent bonds between fabric fibers from cellulose.^{21,22}

This thesis focuses on providing solutions to strengthen fiber foam networks. The proposed chemical approach uses a similar method to citric acid cross-linking, introducing phytic acid as an alternative to enhance strength and generate fire-retardancy. Studies have verified the success of phytic acid for promoting flame-retardancy in substrates^{23,24} yet the underlying mechanisms and resulting structures have been poorly elucidated. The second part of the work is focused on the physical strengthening effect of structural arrangements within foams. The use of sodium dodecyl sulfate (SDS) was replaced by introducing tert-butanol (TBA) as a pore structuring agent in cellulose nanocrystal (CNC) suspensions. The ability of TBA to disrupt the hydrogen bond network between water molecules was expected to impact the hierarchical structuring of CNC suspensions and the resulting properties of freeze-dried foams.^{25,26} Therefore, it was hypothesized that modulation of TBA concentration would allow control over the porous network formation and thus properties of cellulose foams.

2

Background

The key components which underline this work are cellulose fibers and the formation of a porous network. To rival the mechanical performance of plastic foams, an understanding of how each of these components influences the structural stability is necessary. Here, the fundamental concepts behind how fiber and pore morphology lend mechanical strength to a cellulose fiber foam are elucidated and solutions are presented.

2.1 Pore formation and structural stability

A foam is defined as a dispersion of gas within a liquid, gel or solid matrix. Two foaming mechanisms are principally used to describe the formation of porous systems: dispersion and condensation methods.²⁷ In dispersion foams, a dispersed phase (e.g. gas) is mixed into the medium via agitation such as shaking, stirring or bubbling. Condensation foams instead rely on the dispersed phase being present as a solute in the medium, where it combines to form the gas. Once a foam has been formed, gas bubbles inside suffer from thermodynamic instabilities and begin coarsening and draining over time.²⁸ Coarsening describes the flow of smaller isolated gas pockets into larger bubbles due to differences in capillary pressure and the drive to reduce surface energy in the system. As bubbles rearrange and grow, the morphology of the final pore network changes, subsequently determining the properties of the dried foam. In an open-cell morphology, pores are inter-connected, allowing gas to pass through the matrix, generating properties which are ideal for thermal and sound insulation (Figure 1.1a). A closed-cell morphology instead describes isolated pores encapsulated in the matrix material, ideal for foam mechanical strength (Figure 1.1b).

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Maintaining smaller pore sizes is typically advantageous for improving foam compressive strength and homogeneity.^{7,18} Broad pore size distributions can create heterogeneous structures and substructures which lead to varied localized deformation behaviors. As a gas bubble increases in size, it is also increasingly affected by hydrostatic pressures from gravity and viscous traction.²⁷ This creates anisotropy in the gas bubbles which is an important consideration for morphological control of foam mechanical properties.⁷ During axial deformation, the compressive modulus, yield stress and shear strength of the pore increases in the direction parallel to the longest cell wall.^{7,29} The mechanical properties on the perpendicular axis suffer as a result of this, and thus control over the orientation and size is crucial when determining which applications each foamed material can be implemented. The most common method to keep pore sizes small is the addition of surfactants or nanoparticles, which help to stabilize the liquid-air interfaces.^{15,16}

Incorporating cellulose fibers as a matrix material creates complexities which are not considered in plastic and metallic foams. The fibrillar network of cellulose fiber foams diminishes the ability for closed-cell pores to form and creates a important reliance on fiber-fiber bonding for strength. The pore size influences the density of fibers aligned in lamella between pores. With larger macropores, less material is distributed around small pores and thus fibers in the cell walls are more tightly bundled, increasing inter-fiber interactions. This causes an increase in Young's modulus, as thicker cell walls resist elastic deformation, yet also causes a decrease in yield stress with higher pore interconnectivity.^{29,30} It is thought that the generation of larger pores in the matrix can due to coarsening but also local opening of fiber networks during drying.¹⁵

2.2 Controlling pore structure

The use of surfactant-based dispersion methods to foam cellulose fibers has strong support in literature.^{15–17,28,31,32} However, templating methods have gained traction due their ability to tune hierarchical porosity. One common approach is to use ice-templating, which involves the growth of ice crystals to generated macroscopic anisotropy in freeze-dried foams.^{13,30,33} Other ideas have explored oil,^{29,30} wax,³⁴ and polymeric particles³⁵ as removable structuring agents.

2. Background

TBA, an amphiphilic solvent, has found uses in creating foams with high specific surface areas and low thermal conductivity when dried using supercritical CO₂.^{36,37} TBA disrupts hydrogen bonding between water molecules and cellulose, and creates space between fibers due to the large non-polar methyl groups.^{38–40} Liquid phase structuring in TBA-water systems transforms depending on TBA concentration. At low TBA content, isolated TBA-rich regions are evenly dispersed within the aqueous phase, while at concentrations above 30 wt% there was evidence of the formation of a bicontinuous microemulsion.^{25,26} Therefore it was hypothesized that TBA can also act as a hierarchical templating agent to form strong porous cellulose structures.

2.3 Fiber networks

Cellulose fibers referred to in this work are wood pulp fibers of hardwood or softwood trees. The wood is typically processed via chemical pulping processes to remove bark, lignin and other impurities. Further breakdown of pulp fibers can form cellulose nanofibers (CNFs) and highly crystalline cellulose nanocrystals (CNCs).⁴¹ The three hierarchies of cellulose fibrils presented in Figure 2.1 have all been used extensively to form cellulose foams and each provides unique characteristics to the final material.

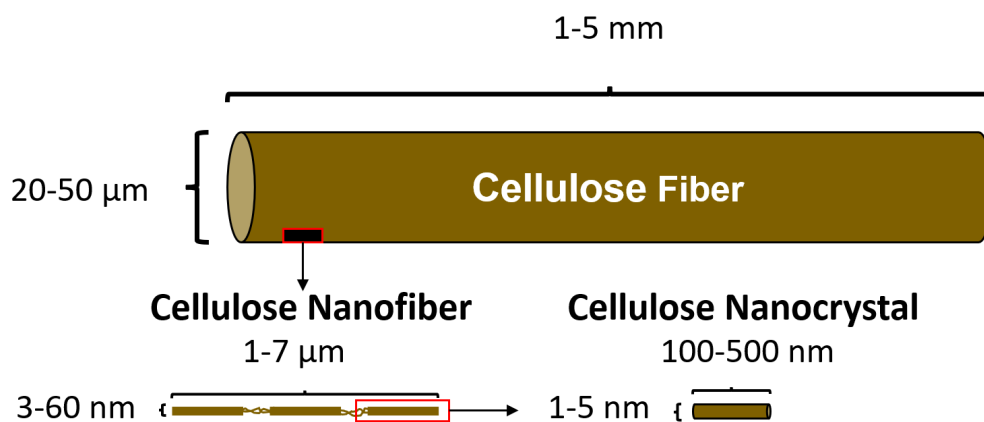


Figure 2.1: Representation of cellulose material nomenclature at different length scales. Fibrils are not drawn to scale.

The geometric structure of a foam fiber network and its properties are heavily influenced by the size, flexibility, bonding ability, and orientation of the fibers

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within the network. At all fiber length scales, inter-fiber interactions such as physical entanglements and fiber-to-fiber contacts dictate the mechanical and structural strength of the foam. At lower fiber concentrations, the number of contact points between fibers lessens as the distribution is scarcer throughout the material. Lower contact between fibers reduces the structural support a fiber can receive from neighboring fibers. In such cases, fibers may act more like individuals when load is applied as opposed to a reinforced network.^{15,19} The result of this is disparate stress variations across the foam causing uneven mechanical performance. A higher fiber density in pore walls promotes fiber-fiber contacts, which increases the compressive strength of cellulose fiber foams following a power law.^{7,19,20} With fiber materials of matching relative density, the pore morphology and packing density of fibers in cell walls was found to be the key criteria towards increased mechanical properties.^{18,19,29}

Wood pulp fibers can help link disassociated structural areas within a foam network with their length. Yet, fibers are quite coarse and tend to exacerbate the heterogeneous nature of a fiber network, creating exceedingly porous foams.²⁸ CNCs and CNFs by comparison are much smaller and bear higher aspect ratios. Their size creates favorable short-range fiber interactions which evenly distribute localized stresses. In addition, they can form pickering emulsions in wet foams, stabilizing gas bubbles to form homogenous pore morphologies.^{18,31,42,43} However as individual units, CNCs and CNFs exhibit lower structural strength than wood pulp fibers.^{19,43} Thus, fiber networks with consistently high mechanical performance and heterogeneous pore networks combined the network connectivity of CNC or CNFs with the structural reinforcement of large fibers in a foam, given that all components are well bonded in the matrix.^{15,18,19,43,44} Fibrillation of wood pulp fibers and the re-introduction of fines can achieve similar effects while requiring significantly less pre-processing.^{15,16}

An alternative method to physical cross-linking involves the formation of chemical cross-links between cellulose fibers. This removes the reliance on frictional forces to maintain the structural integrity of the fiber network. This method typically requires the introduction of other compounds, however provides significant strength to cellulose networks.

2.4 Chemical cross-linking of cellulose

Chemical cross-links are particularly interesting for cellulose as the hydroxyl groups at the C2, C3 and C6 carbons can react to form covalent bonds with numerous other molecules. Therefore in this work, phytic acid was cross-linked to cellulose to reinforce the fiber networks. The use of a multi-functional bio-based solutions such as PA promotes progress towards creating sustainable solutions to cellulose challenges in foams.

Phytic acid, a polyphosphate derived from plants, has been used to improve fire-retardancy in cellulose and fabrics by enhancing the charring of the fiber surface, creating a shield against heat and oxygen.⁴⁵⁻⁴⁷ Its ability to chelate with metal ions and form hydrogen bonds makes it useful in both inorganic and nonhalogenated flame-retardants (FRs); the non-toxic and competitive alternative to highly regulated halogenated FRs. Phytic acid is soluble in water and thus some degree of cross-linking is required to retain it on washable cellulose substrates.^{23,48} An efficient methodology to do so is to react phytic acid and fabrics with compounds containing amine groups such as melamine and diacylamide.⁴⁵⁻⁴⁷ The result is strong covalent bonds which further increase the FR properties due to the presence of nitrogen. However, this method requires the use of toxic compounds to catalyze the reaction. Others have turned to the use of catalysts such as urea⁴⁶ and enzymes⁴⁹ to promote the covalent linking between PA phosphate groups and substrate hydroxyl groups. It has also been suggested that the electrostatic potential and hydrogen bonding provides sufficient cross-linking stability when formed via layer-by-layer deposition, although washability has not been verified.^{48,50}

The approach taken by this work involves a catalyst-free method to cross-link phytic acid with cellulose fibers. It takes inspiration from traditional fabric finishing techniques where citric acid is hot-pressed or cured onto fabrics to impart strength, wrinkle resistance and laundering durability.²¹ Hot-pressing, or curing, applies heat around 120 - 180 °C to the fabric surface. This causes dehydration synthesis, a type of condensation reaction, to occur within citric acid molecules. Heat drives the removal of water from the system, causing hydroxyl groups to react and form highly reactive cyclic anhydrides. Cellulose OH groups then attack the cyclic anhydride, forming a covalent bond between citric acid and cel-

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lulose. Citric acid possesses three hydroxyl groups, allowing the condensation reaction to occur twice and synthesizing covalent linkages between cellulose fibers.⁵¹ This technique has also been applied to cellulose fiber foams, making citric acid a common bio-based cross-linker for these foams.^{52–55} Thus, the cross-linking of phytic acid to cellulose is hypothesized to also occur via condensation reactions at 160 °C. The result is the formation of both oligo-phosphates and the phosphorylation of PA on cellulose. Here, we elucidate the effect curing temperature has on the molecular structures formed between cellulose fibers and phytic acid and the resulting solid foam properties.

2.5 Mechanical behaviour in compression

As a pore or cell in a foam is compressed, it undergoes three distinct deformation behaviours i) bending linear elasticity ii) buckling plateau and iii) densification. These regions are identifiable in a stress-strain graph such as Figure 2.2. The linear elasticity region defines the modulus or stiffness of the material and is controlled by the resistance of the cell wall/fibers to bending. In closed-cell foams, the amount of material enveloping the cell and the compression of trapped air leads to higher moduli compared to open-cell foams.⁷ With less porosity or air inclusion, more fibers can contribute to the strength of the material by forming pore walls.^{19,20} In an open-cell configuration, fewer fibers are forming structural walls and compression leads to gas being ejected from the pores. The material may retain some mechanical advantage via reduced connectivity, high strain rates and slowed rate of gas evacuation through tight bottleneck pores. Interestingly, hollow fibers have been found to resist bending much better than solid struts in cell walls. For cellulose, preventing the collapse of the lumen during drying, using never-dried pulp, or chemi-thermomechanical pulp are all viable methods to attain this property.^{7,19,56}

The second region is the buckling plateau. At higher stresses, fibers begin to buckle, slip, displace and eventually break as the stress reaches critical levels. The principle mechanism of mechanical failure in fiber foams is caused by weak bonds between fibers as opposed to failure of the fibers themselves.¹⁸ Individual fibers will typically pull-out from each other and unravel to dissipate energy.⁷ Thus, the orientation of the fibers and how they interact through slipping or

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breaking dictates how the material will deform. It also was noted that dangling ends, loops or free fiber segments do not participate in the material response to mechanical stresses.^{13,19} Pöhler et al.¹⁵ postulated that shape recovery of the fiber foam depends on the recovery of fibers from buckling and not on bonding properties. Models describing foam mechanical performance as a result of individual fiber and fiber network deformation behavior has been the subject of recent study by several groups.^{15,19,20,57} Pöhler et al.¹⁵ gave a summary of these recent advances in failure mechanism modelling and also explained how the models work well until the addition of physical and chemical cross-linkers. In the final region of foam deformation, stresses cause the cell walls to completely buckle, causing the cell walls to touch. In a stress-strain graph, the slope of the line increases drastically, and densification starts to occur.

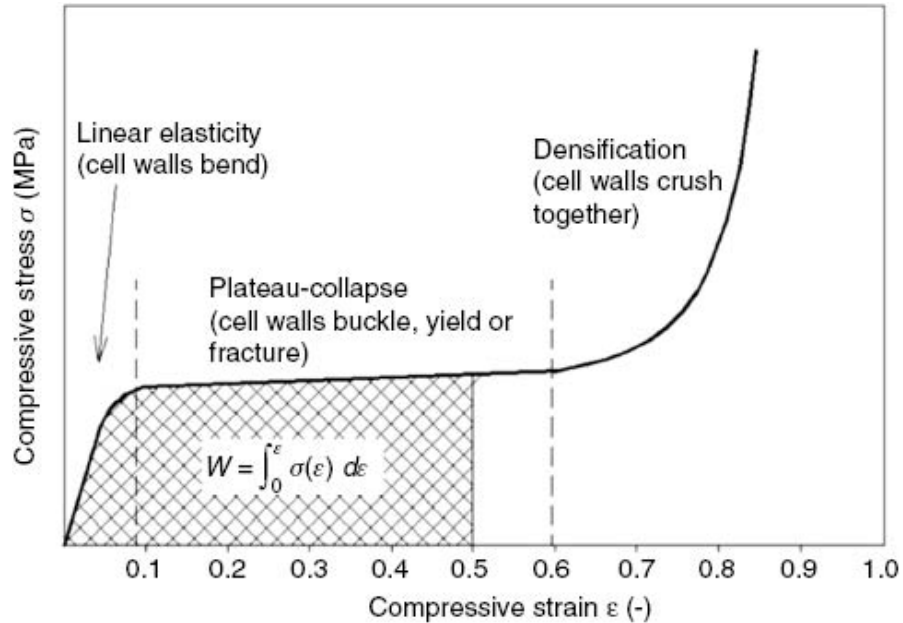


Figure 2.2: Example stress-strain graph of a solid foam mechanical compression test.* Three distinct regions of interest are i) bending linear elasticity, ii) buckling plateau, and iii) densification.

In terms of energy absorption, a foamed material can be optimized to match application-based impact criteria while minimizing density. Specifically, there exists a point where the cell walls are no longer considered elastically buckling and undergo irreversible damage. In polymeric foams, this peak stress is defined by the beginning of the region where densification occurs.⁷ The area under

*Credit: Sagar Chandra et al. <https://doi.org/10.1515/polyeng-2015-0360>

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the stress-strain curve up to this point represents the theoretical limit of energy absorption with the possibility of elastic recovery. For a material to be considered reusable in energy absorbing applications, it must be able to absorb all the kinetic energy without damaging the matrix. In a dense foam, the force may exceed the critical damaging value before enough energy has been dissipated through the buckling plateau. On the other hand, low density foams cannot withstand the applied force and will completely collapse, leading to densification before the energy has been absorbed. Thus, the ideal combination of properties would lead to a material with a plateau stress under the critical damaging value and the ability to absorb all the energy before the peak-stress point.^{7,30}

3

Experimental

3.1 Preparation of cellulose fiber substrates

3.1.1 Cellulose papers

Whatman Cytiva qualitative filter paper (Grade 5, 47 mm) was purchased from Fisher Scientific. Phytic acid solution (50 % w/w in H₂O) was purchase from Sigma-Aldrich. All reagents purchased were used without further purification. 0.013 mL 50% (w/w) phytic acid solution was diluted in 0.3 mL DI water. The diluted solution was evenly spread over Whatman Cytiva grade 5 qualitative filter paper (0.166 g) without excess, leading to a theoretical dry concentration of 5 wt% phytic acid on dried filters. Filters labelled with a W were washed after curing by adding 200 mL DI water, followed by 100 mL 95% ethanol, and once again with 200 mL DI water in a Büchner funnel. The filters were dried again at 80 °C for 1 hour.

3.1.2 Cellulose foams

Bleached hardwood and softwood kraft pulp fibers were kindly donated by Stora Enso and Pöls, respectively. Hardwood fibers were fibrillated to a Schopper-Riegler (SR) value of 25°. Fibers were dispersed in H₂O to obtain a solid consistency of approximately 15%. Sodium dodecyl sulfate (SDS), carboxymethyl cellulose (CMC) and the cross-linker were added to 3:1 softwood to hardwood fibers obtaining a dry foam composition of 5 wt% CMC, 0.7 wt% SDS and 5 wt% acid cross-linker. The wet ingredients were whipped using a hand-mixer for approximately 30 seconds to achieve a consistent air content. The wet foams were placed in a teflon mold and oven dried.

3. Experimental

3.1.3 Oven-drying and curing

Cellulose filters and foams were dried at 80 °C for 15 hours in a convection oven. Post-drying curing conditions and sample nomenclature is provided in Table 3.1. Curing time and temperature were chosen to mimic conditions used by other authors.^{21, 22, 52–55, 58, 59}

Table 3.1: Nomenclature of cellulose substrates based on curing conditions.

Post drying curing		Nomenclature*		
Temp.	Time	Control	Citric acid	Phytic acid
20	2 days	20	C20	P20
80	2 hours	80	C80	P80
120	2 hours	120	C120	P120
160	5 mins	160	C160	P160

3.2 Analysis of cellulose fiber substrates

3.2.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Solid state NMR spectroscopy was performed in a 4 mm ZrO₂ MAS rotor with a set temperature of 298K in all experiments. The following parameters were set for ¹³C and ³¹P solid state NMR:

¹³C CP at 10KHz with P3(1H)=3.0us, P15(contact time)=1.5ms, CP at 60.0 kHz ¹³C (PLW1=109W) SPW0=110W optimized ramp 45-90kHz 1H and 1H decoupling SPINAL64 at 83 kHz (PCPD2=6.0us, PLW12=96W), d1(recovery delay)=2.0s, ns=4000.

³¹P hpdec at 12.5kHz with P1(31P)=3.5us @PLW1=176W, 1H decoupling TPPM15 at 54 kHz (PCPD2=9.3us, PLW12=40W), d1(recovery delay)=10.0s, ns =64.

*Substrates which appear with a U or W label denote unwashed and washed cellulose filters respectively.

3. Experimental

3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR was performed on dried cellulose substrates using an attenuated total reflection (ATR) component. Substrates were cured as described by Table 3.1, put immediately in a desiccator, and analyzed soon after, taking the most representative line. A PerkinElmer Fronteier FT-IR spectrometer with PIKE technologies GladiATR was used to measure 32 scans of each substrate 3 times with a data interval of 1 cm^{-1} and 4 cm^{-1} resolution. The scanned wavenumbers were from $400 - 4000\text{ cm}^{-1}$. PerkinElmer Spectrum software was used to correct for background noise.

3.2.3 Elemental analysis

To determine the phosphorous content on cellulose substrates, elemental analysis was performed by MIKROLAB Mikroanalytisches Laboratorium Kolbe.

3.2.4 Thermogravimetric Analysis (TGA)

In order to understand the degradation behaviour of phosphorylated cellulose papers when exposed to heat, a Mettler Toledo TGA/DSC 3+ was utilized to sequence the following heating sequence using STARe Software: 1. Ramp from $30\text{ }^{\circ}\text{C}$ - $500\text{ }^{\circ}\text{C}$ at a rate of 10 K/min under 60 mL/min air flow, 2. Temperature hold at $500\text{ }^{\circ}\text{C}$ for 5 mins, 3. Ramp from $500\text{ }^{\circ}\text{C}$ - $700\text{ }^{\circ}\text{C}$ at a rate of 10 K/min under 60 mL/min air flow, 4. Temperature hold at $800\text{ }^{\circ}\text{C}$ for 10 mins.

Property values relevant to material flame-retardancy were taken as the average of 3 separately prepared samples. Carbonization onset was set as the point where the initial slope of the graph deviated by more than 3%. Weight loss during carbonization was calculated from this point to where the slope begins levelling out as indicated by a change in slope of 30%. Finally, residual weight was taken as the weight percent of the material remaining at $700\text{ }^{\circ}\text{C}$.

3. Experimental

3.2.5 Determination of density and porosity

The envelope density (ρ_E) of solid foams was measured using calipers and a high-precision balance. Skeletal density (ρ_S) was measured using a Micromeritics AccuPyc II gas displacement pycnometer set with helium gas. Relative density (ρ_R) was given as the ratio of the envelope density to the skeletal density (Equation 3.1). Porosity was then calculated using Equation 3.2.⁷

$$\rho_R = \frac{\rho_E}{\rho_S} \quad (3.1)$$

$$P(\%) = (1 - \rho_R) \cdot 100 \quad (3.2)$$

3.2.6 Mechanical compression testing of fiber foams

To evaluate the mechanical behaviour of the cross-linked cellulose fiber foams, quasi-static compression testing was undertaken in an Instron 5565A Mechanical tester using Bluehill 2 software. A pre-load force of 5N was applied with a 5 kN load cell. The crosshead was lowered at a rate of 5 mm/min until the material reached 60% strain.

The compressive modulus was taken as the slope of the stress-strain curve below 10% strain, while the compressive strength corresponded to the stress at 10% strain. Energy absorption was calculated using the area under the stress-strain curve until up to 50% strain. Variations in density between solid foams were accounted for by dividing all values by their relative density.

3.3 Preparation of CNC suspensions and foams

3.3.1 CNC suspensions

Suspensions were prepared from a 10 wt% CNC stock solution in MilliQ-water and stirred in an IKA EUROESTAR 60 (Germany) overhead stirrer with a four-bladed R-1342 propeller at 1200 rpm for 1 hr. The composition of ternary suspensions consisting of water, TBA, and CNC were designed using JMP Pro 16.2.0 software from SAS (USA). Figure 3.1 summarizes the tested composition range

3. Experimental

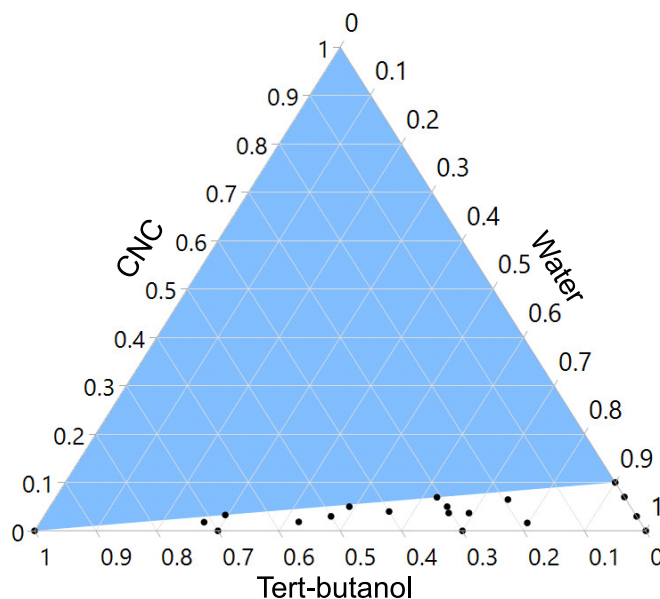


Figure 3.1: Ternary plot summarizing the combinations of suspensions containing concentrations of CNCs, water, and TBA assessed in this study (black dots).

(white region) as the actual range was limited to 10 wt% CNCs in water. The suspensions were then prepared by diluting the stock suspension in water and TBA was added in seven incremental steps to avoid heterogeneous or phase-separated suspension, with thorough shaking after each step. Finally, the suspensions were shaken overnight on a moving platform at 180 rpm.

3.3.2 Freeze-drying

To transform the suspensions into free-standing dry foams, they were first injected into molds and degassed. The molds were subsequently submerged in liquid nitrogen and placed in a ScanVac CoolSafe freeze-dryer at -105 °C for 2 days. The solid foams are believed to maintain an intact structure when subjected to rapid freezing followed by freeze-drying.⁶⁰

3.4 Analysis of CNC foams

3.4.1 Brunauer-Emmett-Teller (BET) surface area

The surface area was determined using a Micrometrics TriStar 3000 with TriStar II Plus software and N₂ gas at 0-0.98 relative pressure. For BET linearization, the relative pressure corresponding to the nitrogen monolayer coefficient in the BET equation was included and the maximum value of the Rouquerol BET graph was the last chosen point.

3.4.2 Scanning electron microscopy (SEM)

The solid foams were cut through the center and sputter-coated with 4 nm of gold. A JEOL 7800F Prime instrument was used to visualize the coated surface at an acceleration voltage of 5 kV.

3.4.3 Mechanical compression testing of CNC foams

Solid foams were conditioned at 20 °C in a desiccator for a week before mechanical testing. Compression tests were performed using a Texture Analyser (Stable Microsystems, UK) with a crosshead rate of 1 mm s⁻¹ after reaching a pre-load force of 0.5 N. The solid foams were pressed between parallel plates of 40 mm in diameter using a load cell of 50 kg.

4

Results and Discussion

In the interest of strengthening the structure of cellulose foams, approaches towards chemical cross-linking and pore structure formation were evaluated. Phosphorylation of cellulose with a polyphosphate such as phytic acid was hypothesized to form covalent bonds between cellulose fibers. This would strengthen fiber-fiber contacts and provide flame-retardancy to the cellulose foam. On the other hand, using a structuring co-solvent such as TBA was hypothesized to create a template around which cellulose can assemble. By understanding the liquid-phase structuring of TBA in water and its interactions with CNCs, control over the pore formation when developing the solid foams could be achieved. To investigate these ideas, mechanical compression testing was used to reveal changes in the modulus, strength and energy absorption of the solid foams. Then, analysis of the key underlying structures using techniques such as FTIR and NMR for molecular changes, and SEM to visualize morphological changes was performed.

4.1 Cellulose cross-linking via phytic acid

4.1.1 Dehydration synthesis condensation reactions

Hydroxyl-rich phosphates from PA come into contact with both cellulose and other PA molecules when spread on the surface of the cellulose substrates. When hot-pressing or curing is applied, a covalent cross-link between these molecules is proposed to have formed as heat drives the removal of water.⁵⁸ Figure 4.1 displays the mechanisms and products which may arise due to the dehydration synthesis between cellulose and phytic acid.⁶¹ Each mechanism depends on the environment and reactivity of nearby molecules.

4. Results and Discussion

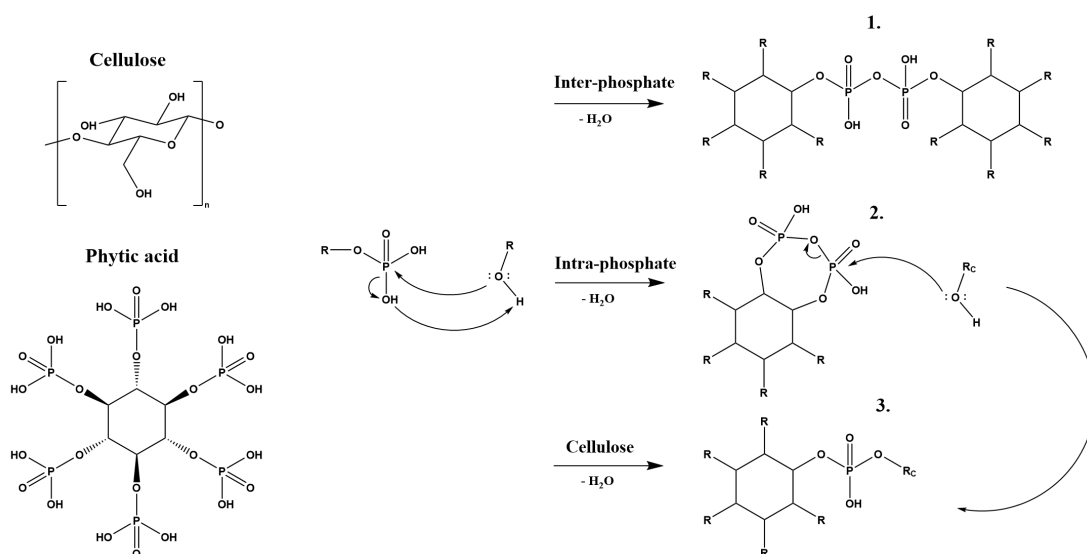


Figure 4.1: Molecular structures of cellulose and phytic acid with proposed mechanisms for dehydration synthesis condensation reactions between them. The reactants comprise of a phosphate group and either cellulose or another phytic acid molecule where R is either phosphate groups (PO₃H⁻) or C2, C3 or C6 of cellulose. R_C is defined specifically as C2, C3 or C6 of cellulose. Products 1, 2 and 3 are the proposed products of the reaction, depending on the mechanism of action described above the reaction arrow. Product 2 may react rapidly with cellulose generating product 3 as indicated by the curved arrow.

The electrophilicity of phosphorus in phosphate groups encourages nucleophilic attack by both cellulose and other phosphate groups. The hydroxyl groups of attacking phosphates are more nucleophilic than cellulose OH groups due to the lower electronegativity of the phosphorus group.^{61,62} Thus, inter-phosphorylation reactions between PA molecules are favored and generate product 1, a mechanism which is well supported in literature.^{45,48,62} This reaction may propagate, creating large oligo-phosphate chains with sufficient nearby phosphates. However, the low concentration of phytic acid distributed on the surface of the cellulose substrates in this study suggests two competing reactions. In a dilute system of phosphates, cellulose is hypothesized to undergo phosphorylation, generating product 3. An intra-phosphorylation reaction may generate a reactive cyclic anhydride shown in product 2; similar to the product made when curing citric acid. The structure would be susceptible to nucleophilic attack by cellulose, thereby creating product 3 as shown by the curved arrow.

4. Results and Discussion

When phytic acid undergoes dehydration synthesis, the phosphates change from being monoesters to diesters. We can visualize this by tracking the shift of the monoester band at 1250 cm^{-1} to lower wavenumbers ($1250\text{-}1210\text{ cm}^{-1}$) for diesters.⁶³ In our system, we see a shift in the band from 1249 cm^{-1} (P20U) to 1243 cm^{-1} (P160W) (Figure 4.2). The displacement of the band depends on the nature of the element forming the diester bond, and the excess of unreacted phosphates.

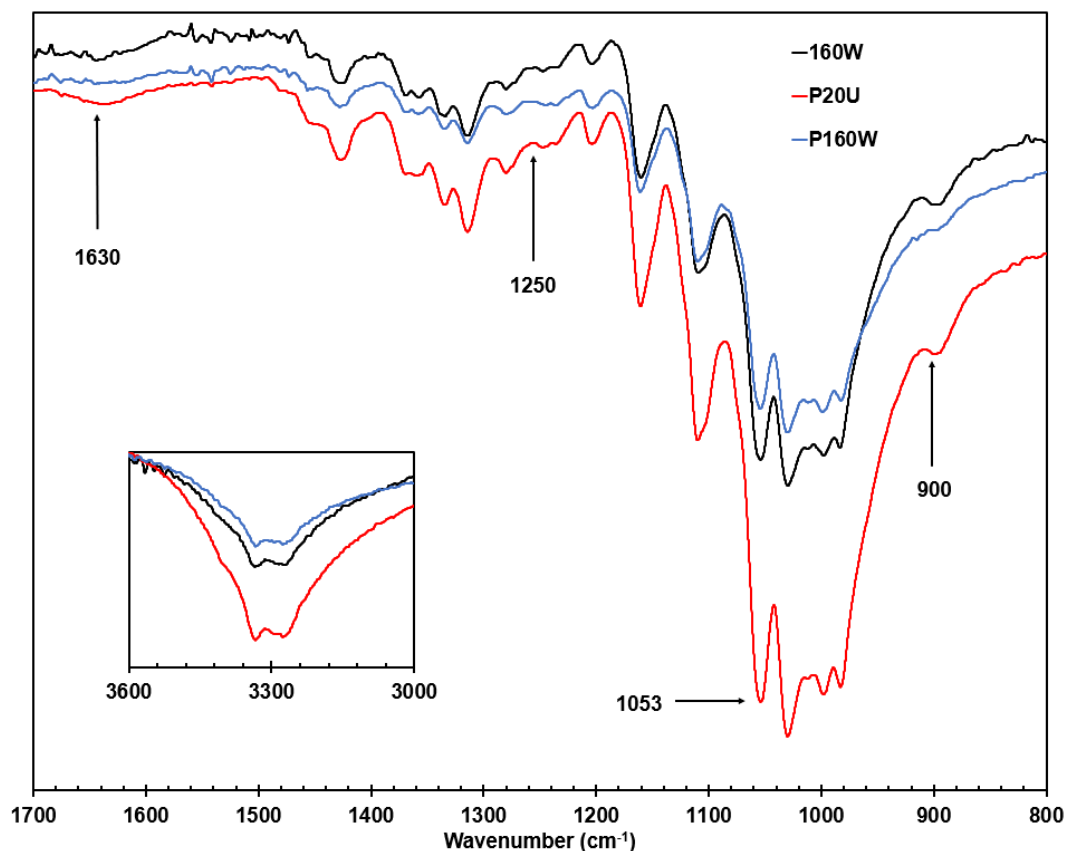


Figure 4.2: FTIR spectrum comparing a blank cellulose substrate exposed to $160\text{ }^{\circ}\text{C}$ curing and washed (160W), a substrate cured with phytic acid at $160\text{ }^{\circ}\text{C}$ and washed (P160W), and a substrate with phytic acid and dried at RT (P20U).

The successful synthesis reactions to form product 3 can be verified by evaluating the intensity of FTIR bands at 1630 and 3300 cm^{-1} . The band at 1630 cm^{-1} represents water bound to cellulose and phytic acid via hydrogen bonding while 3300 cm^{-1} describes the hydroxyl groups present on both cellulose and phytic acid. Therefore, the band intensity at 3300 cm^{-1} was expectedly highest for the cellulose substrate coated in phytic acid dried at room temper-

4. Results and Discussion

ature (P20U). This in turn also maximized the capacity for hydrogen bonding, increasing the intensity of the peak at 1630 cm^{-1} . When the substrate was cured by heating it at $160\text{ }^{\circ}\text{C}$, bound water was evaporated, reducing this peak as seen in both cellulose and cellulose with phytic acid (160W and P160W). The intensity at 3300 cm^{-1} for P160W decreases below that of the substrate without PA (160W), giving an indication that dehydration synthesis reactions with cellulose hydroxyl groups have occurred and covalent ester bonds were formed. This can be further supported by observing the increase in ratio between the peak at 1053 cm^{-1} (δ_{C-O-P}) and 900 cm^{-1} (δ_{P-O-P}) for P20U and P160W.^{58,63} As the ratio rises from 0.96 to 0.98 respectively, ester bonds to carbon are formed.

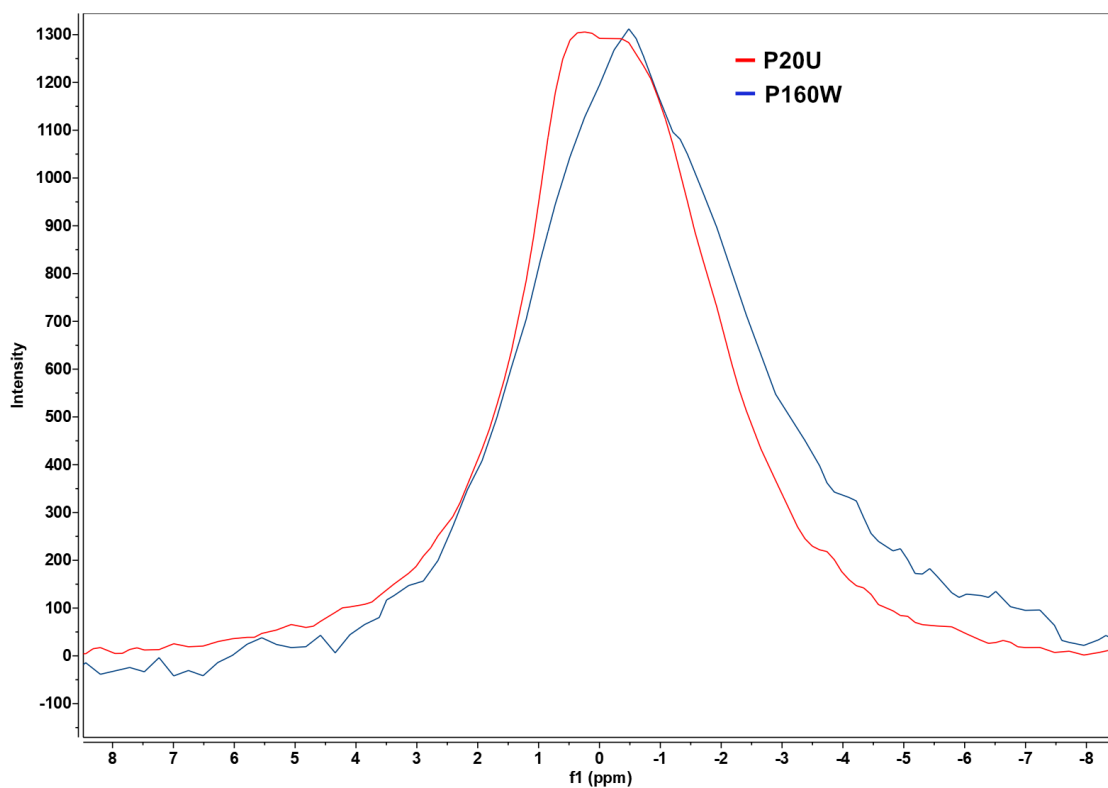


Figure 4.3: Stacked ^{31}P solid state NMR peaks depicting a peak intensity shift from -0.45 ppm (P20U) to 0.24 ppm (P160W) after curing. Peaks were re-scaled to similar intensities for comparison.

This effect can also be visualized in the solid state ^{31}P -NMR spectrum (Figure 4.3). As the OH group on the phosphate changes to a covalent ester bond with either C or another P, a shift to the right in the primary phosphorus peak is expected as the phosphorus becomes more deshielded. However, NMR results provide no indication of whether the ester linkage is to hydroxyls attached to

4. Results and Discussion

carbon or another phosphate group. Rather, it provides substantial evidence that PA phosphates change from mono to diester linkages and therefore the presence of product 1 is still likely and should not be discounted.

Separate analysis of these signals revealed a gradual increase in the phosphorus peak intensity of washed substrates cured at higher temperatures. This result was confirmed by the increased phosphorous content seen in elemental analysis (Table 4.1). The decrease in phosphorus content from the washing step was noticeably minimized on substrates treated with progressively high curing temperatures. Notably, P20W substrates retained very little phosphorus, indicating that hydrogen bonding between phosphate and cellulosic hydroxyl groups was insufficient to retain PA on the fiber surfaces. Therefore, phosphorylation likely created covalently bound PA molecules which were increasingly difficult to remove from the cellulose matrix when cured at higher temperatures. While covalent bonds to cellulose are proposed as the primary product of this reaction, the formation of inter-phosphorylated PA chains may create large structures which have reduced solubility in water and ethanol, and are physical restrained within the cellulose network due to entanglements and frictional forces. This would also potentially allow phosphorus to be retained in the cellulose substrates without covalently binding it to cellulose molecules.

Table 4.1: Phosphorus content (weight %) on cellulose substrates treated with PA detected via elemental analysis.

<i>Substrate</i>	Unwashed	Washed
P20	1.78	0.05
P80	1.66	0.08
P120	1.65	0.27
P160	1.42	0.70

4.1.2 Substrate properties

The addition of phytic acid to cellulose fibres caused changes in crystallinity. Crystalline domains of cellulose at C4 and C6 are indicated by broad peaks at 63 and 84 ppm in solid state ^{13}C -NMR (Figure 4.4).⁶⁴ The addition of PA to the cellulose substrates caused both of these peaks to decrease in intensity, with curing at 160 °C decreasing intensity even further. The degradation of PA to gaseous phosphoric acids at 160 °C likely degraded the crystalline moieties further.⁶⁵ Reduction in cellulose crystallinity would cause a weakening of the cellulose fibre structure, creating a network with worse mechanical performance. However, successful phosphorylation of cellulose would indicate that covalent cross-links between fibers is possible, which would lead to improved mechanical strength. Therefore, competition between these effects was expected to cause visible changes on the mechanical properties of the cellulose fiber foams.

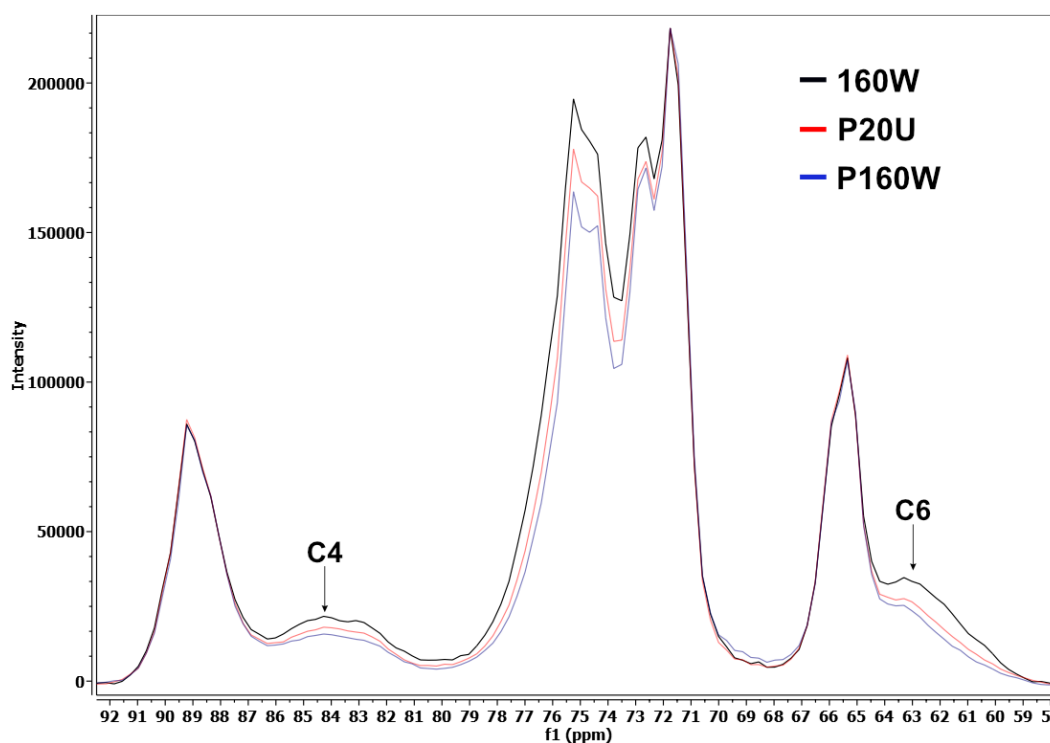


Figure 4.4: Solid state ^{13}C -NMR of cellulose substrates comparing the effect of PA and curing on cellulose surface C4 and C6 moieties. Cured blank cellulose substrate (160W), PA on cellulose substrate (P20U), and a cellulose substrate cured with PA (P160W) were auto-scaled to match interior moieties of C4 and C6 at 66 and 89 ppm.

4. Results and Discussion

To verify how phytic acid affected the fiber network, compression testing of cellulose fiber foams cured at different temperatures was performed. The results were compared against foams similarly cured with citric acid and foams without any cross-linker added. The cellulose substrates displayed a progressive visual darkening at each higher curing temperature as shown in Figure 4.5i. In terms of mechanical performance, P80 had significantly lower properties when compared to the control foam (80) (Figure 4.5ii,iii,iv). At this curing temperature, it was thus concluded that degradation of crystalline cellulose domains is the dominant mechanism governing performance. P120 had improved mechanical properties when compared to P80, yet did not outperform the control. However, P160 demonstrated a significant improvement in both modulus and strength. In terms of modulus P160 even outperformed C160, the citric acid cross-linking, matched it in strength. Where P160 suffered however was in energy absorption, likely due to the observably brittle structure. Phosphorylation of cellulose using phytic acid therefore successfully forms covalent bonds between fibers, creating mechanically strong fiber networks.

The flame-retardancy mechanism of organophosphates and phytic acid is well understood. In general, the thermal stability of phytic acid is low in comparison to cellulose and other materials due to the hygroscopicity of the multiple phosphate groups. As temperature increases, the molecule begins to decompose, forming phosphoric acids. These acids catalyse the dehydration of cellulose, causing the onset of carbonization. As the accelerated carbonization of cellulose occurs, a char layer is formed on the surface of the fibers. This char creates a physical barrier against heat and oxygen, which prevents further degradation of the fibers.²³

According to a study by Daneluti and Matos,⁶⁵ the onset of phytic acid carbonization was determined to be around 160 °C for pure phytic acid when analysed via thermogravimetric analysis (TGA). They also noted a visual darkening of the solution when the solution was treated at 150 °C, which they ascribed to carbonization of the phytic acid. We suggest that this carbonization reaction occurs gradually with temperature increase as the cellulose substrates displayed a progressive visual darkening at each higher curing temperature (Figure 4.5i) and TGA curves changed significantly (Figure 4.6a). Unwashed substrates with PA gradually rose in carbonization onset with increasing curing temperature as

4. Results and Discussion

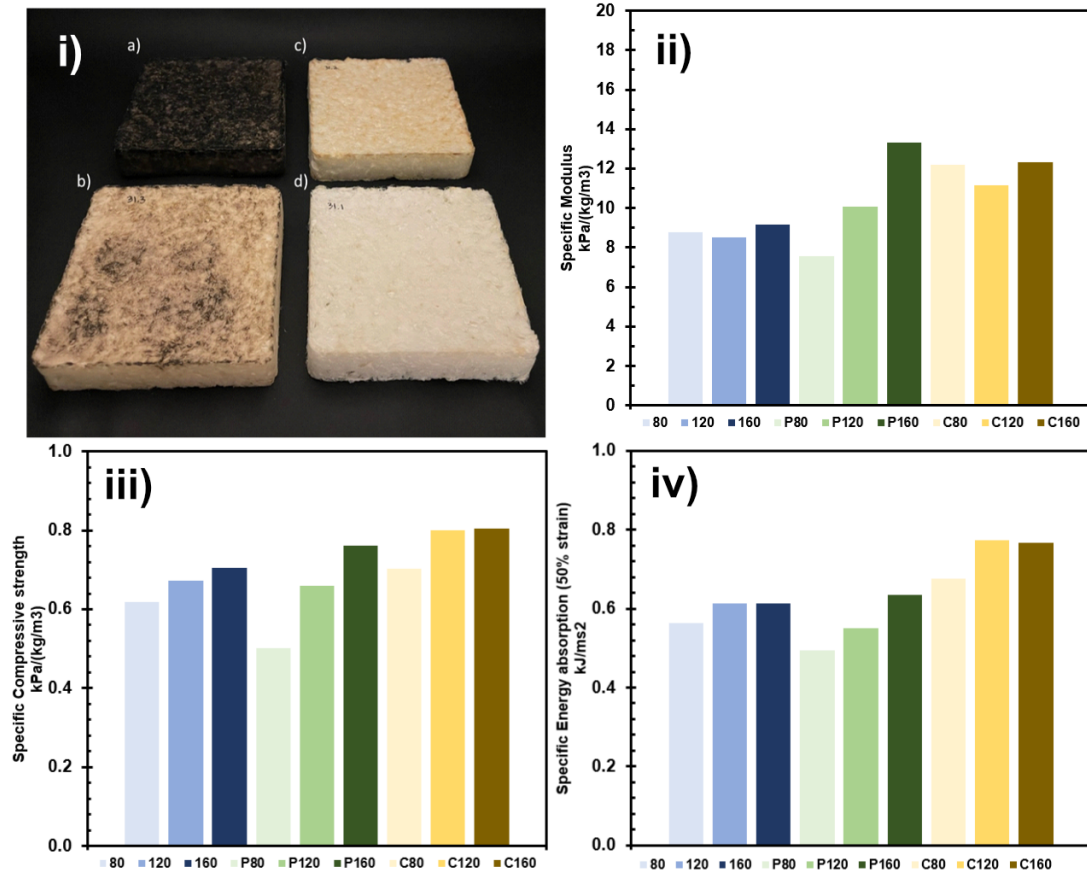


Figure 4.5: Cellulose fiber foams showing i) visual darkening with higher curing temperatures for a) P160, b) P80, c) C160 and d) 160, and bar graphs of specific compressive properties ii) modulus, iii) strength, and iv) energy absorption. The bar graph legend describes the crosslinker used (P = PA, C = CA) and the temperature at which the foam was cured.

shown in Figure 4.6b. This indicates a reduction in the initial ability of the material to cause carbonization, which correlates well with the phosphorus content found in elemental analysis. However, the interesting finding was the material properties after washing. As curing temperature increased, the change in property values from unwashed substrates was incrementally minimized (Figure 4.6). P160W in particular changed by less than 5% in all evaluations. However this result lacks consistency when compared to the reduction of nearly 50% in phosphorus content found by elemental analysis in Table 4.1.

4. Results and Discussion

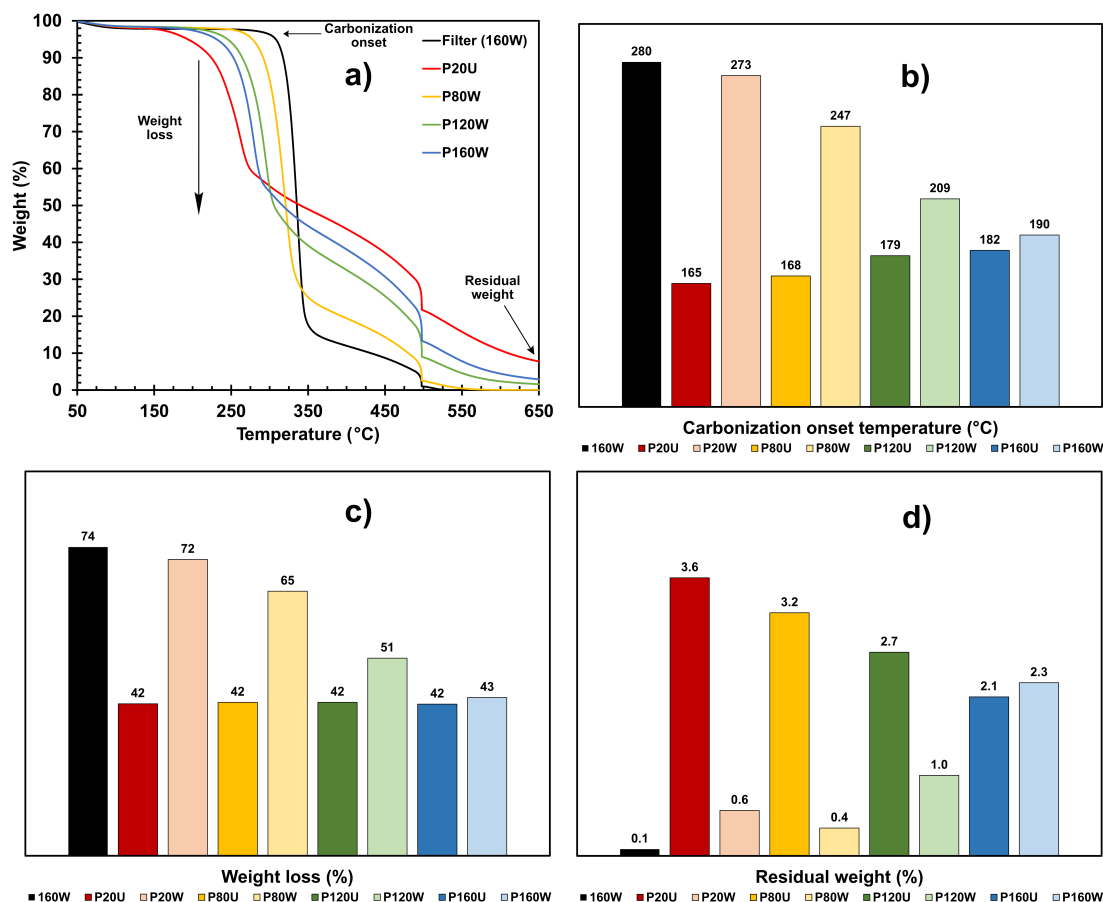


Figure 4.6: TGA analysis of cellulose filters with phytic acid showing a) the full TGA graph with points of analysis, b) carbonization onset temperature, c) weight loss in percent due to carbonization and d) residual weight in percent at 800°C. The number following P is the curing temperature while U and W are unwashed and washed substrates respectively.

4.2 Hierarchical structuring via TBA templating

To evaluate the effect a structuring agent such as TBA has on a cellulose network, CNCs were instantly frozen in liquid nitrogen and freeze-dried to maintain the structuring present in the liquid-phase. Foams from CNC-water suspensions displayed layered sheet-like lamellar macro-structures (Figure 4.7a). Upon closer inspection, the sheet micro-structure reveals homogenous surfaces, indicating a highly densified packed structure of CNCs. This showcases how CNCs form networks which have high short-range interactions between crystals yet poor macro-connectivity throughout the foam. The disparate nature of the structures

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caused these foams to display poor mechanical performance in comparison to other tested foams. Increasing the concentration of CNCs reinforced the sheets, improving mechanical properties at the cost of reduced porosity (Table 4.2). Interestingly, the surface area of foams above 4 wt% CNCs was consistently below 5 m²/g, and increased drastically to 15 m²/g at 3 wt% CNC concentration.

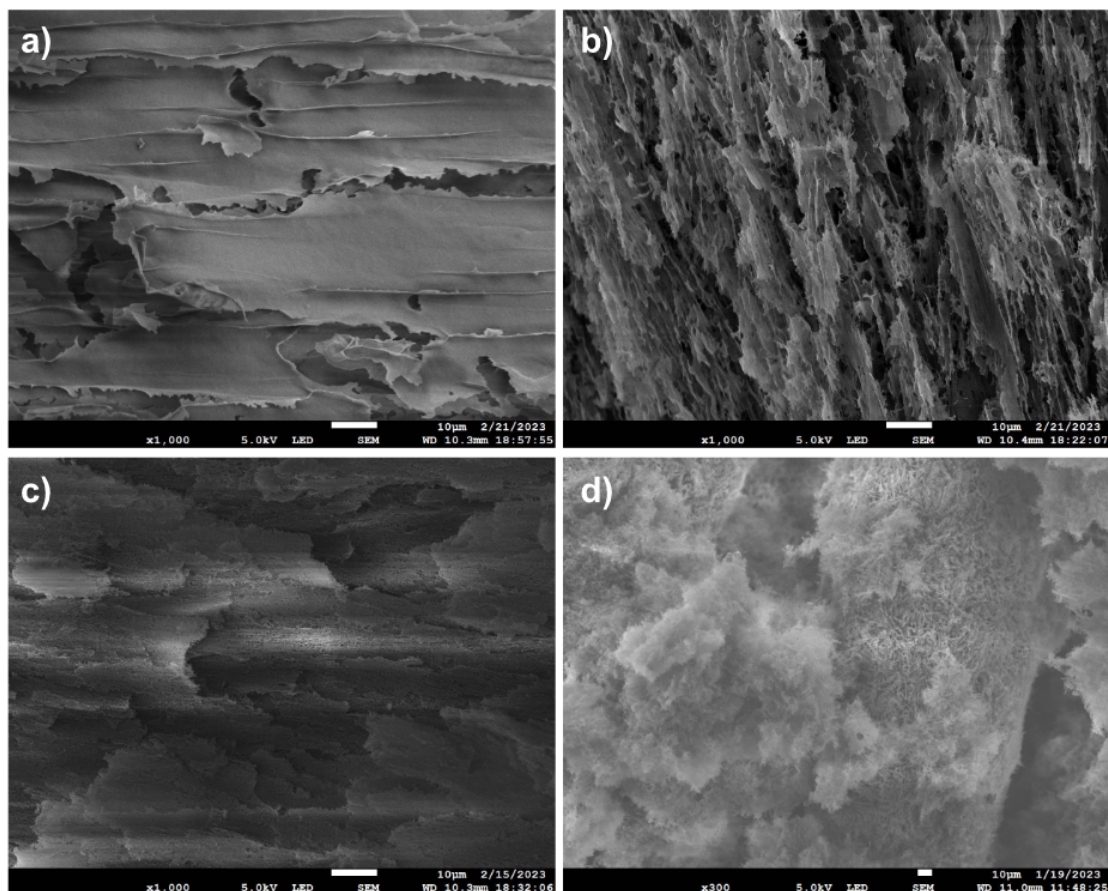


Figure 4.7: SEM images of representative structures found in CNC foams at 1000x magnification. The TBA content and morphology description are given as a) 0 wt% TBA (lamellar, paper), b) 30-50 wt% TBA (tubular, algae), c) <30 wt% TBA (porous lamellar), and d) >60 wt% TBA (fibrillated, mossy).

To improve the hierarchical network of the CNC foams, TBA was introduced as a templating agent. At similar concentrations of CNCs, the addition of any TBA immediately strengthened the foam structure and created high surface areas. The trend in property values indicated that using TBA could compensate mechanically for lower CNC concentrations. For example, the specific moduli of 7 wt% and 10 wt% CNC foams without TBA were 22 and 40 MPa respectively; whereas that of 4 wt% CNC with addition of 40% TBA exhibited a modulus of

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36 MPa (Table 4.2). Solid foams with 7 wt% CNCs demonstrated clearly how the presence of TBA altered the morphology of the CNC network. The lamellar sheets of 7CNC0T (Figure 4.7a) were transformed into algae-like structures with a more macro-structurally homogeneous texture in 7CNC30T (Figure 4.7b). The formation of disrupted tube-like structures seemed to ameliorate connectivity throughout the 7CNC30T foam. As a result of this changed morphology, the strength and stiffness of 7CNC30T increased by 180%, energy absorption by 120%, and surface area rose from 5 m²/g to 52 m²/g compared to 7CNC0T (Table 4.2). The bicontinuous nature of the suspension at this TBA concentration was concluded to have altered the assembly of CNC structures to shape around TBA-rich regions.²⁵

Table 4.2: Experimental values for surface area, specific modulus, specific energy absorption, and specific compressive strength of solid foams obtained from the suspensions denoted in the first column. Foams are labelled xCNCyT where x and y represent the wt% of CNCs and TBA respectively in the suspensions.

	Surface Area (m ² /g)	Modulus (MPa)	Energy Abs. (MJ/m ³)	Strength (MPa)
4CNC30T	71	9.0	0.83	1.1
4CNC40T	56	36	2.45	1.5
6CNC19T	80	21	1.67	1.7
7CNC0T	4.9	22	1.58	1.4
7CNC30T	52	64	4.32	3.0
10CNC0T	4.0	40	3.15	1.7

This result could be confirmed by observing the morphology of a foam formed from 6 wt% CNCs and 19 wt% TBA in Figure 4.7c. The formation of small micropores within the lamellar sheets indicated that CNCs had assembled around small TBA-rich regions, generating the peak surface area of all the solid foams. High (>60 wt%) TBA concentrations displayed similar surface areas yet had vastly different morphologies. Figure 4.7d shows the formation of large aggregated porous structures with dispersed "mossy" formations on their surface. Large TBA-rich regions formed disparate structures, which had poor compressive mechanical performance and phase separated as suspensions.

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An indirect relationship between mechanical properties and surface area was apparent for systems containing TBA as a co-dispersant (Figure 4.8). At low (<30 wt%) and high (>60 wt%) concentrations of TBA, surface area was maximized yet mechanical properties were mostly unchanged compared to solid foams with 0% TBA. On the other hand, incorporation of 30-50 wt% TBA in CNC suspensions resulted in outstanding compressive mechanical performance. Therefore, solid foams in this range can be tailored towards applications requiring high specific mechanical performance while maintaining a greater surface area than foams devoid of TBA.

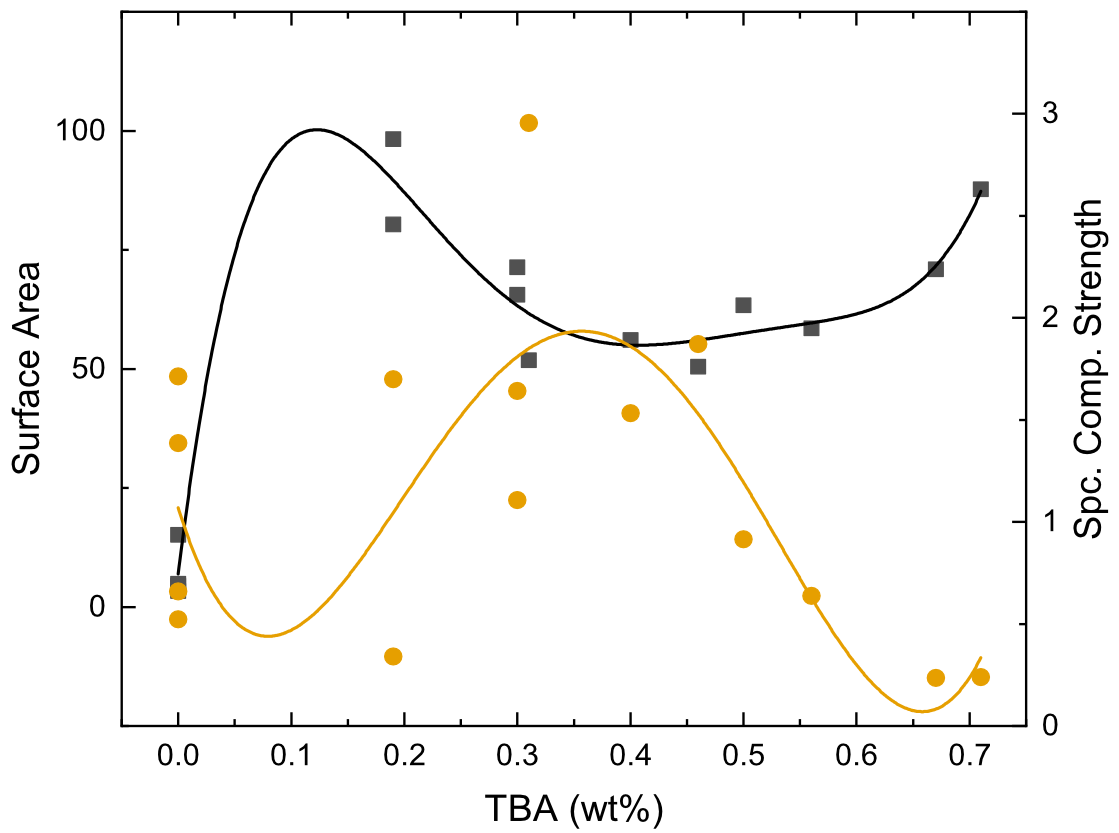


Figure 4.8: The inverse correlation between surface area and specific compressive strength in CNC foams with changing TBA wt%. Surface area is shown in black and compressive strength in yellow.

5

Conclusions

By drawing inspiration from the hierarchical structures in nature, the goal of this thesis work was to present solutions to a challenge faced when working with cellulose substrates: strengthening of cellulose fiber foams. Phytic acid (PA) is a multifunctional bio-based component which enables solutions towards forming mechanically performant cellulose fiber foams that are fire-retardant. In systems with dilute concentrations of PA, the proposed dehydration synthesis reaction initiated via curing with heat was confirmed, indicating the successful phosphorylation of cellulose. This provides a catalyst-free methodology to cross-link PA with cellulose. Knowledge of the reaction mechanisms and conditions allows this phosphate cross-linking technology to be applied in strengthening cellulose fiber materials such as foams. The concept can also be adapted toward other hydroxyl containing substrates.

To structure pore formation in cellulose foams a tertiary alcohol, TBA, was employed as a co-solvent in aqueous cellulose systems and was shown to direct the assembly of CNCs. TBA inhibited CNC packing into highly densified lamellar sheets, instead forming hierarchical cellular structures in the dried foams. Control over the TBA concentration changed the assembly, allowed modulation of the mechanical performance and surface area. This templating method demonstrates how co-solvents may be used in cellulose systems to create foams with tuned pore structures.

6

Outlook

Overcoming obstacles is rooted in the human ability to survive. In the face of the mounting climate crisis, it is time for our generation to turn to solutions which can reduce our energy consumption and production of greenhouse gasses. To that end, this work showcases cellulose substrates and lightweight construction as two facets which represent major players in the materials industry. In an effort to guide and inspire future works, important considerations and solutions to fundamental issues are outlined in the use of cellulose for lightweight materials.

The successful phosphorylation of cellulose using curing technologies marks an important transition to using non-toxic bio-based compounds for flame retardant materials. Phytic acid cross-linking provides solutions to two major issues which plagues the development of cellulose: strength of fiber networks and fire-resistance. This bio-based molecule also provides multifunctionality, a trait which is becoming increasingly valuable in the materials world. The established concept can now be considered for applications in materials manufacturing and what limitations regarding the materials performance remain.

The porous network structure necessary for lightweight materials also governs an important part of material behavior. Finding adaptable solutions to control the formation of this structure, such as use of co-solvents, is therefore crucial when designing the material for specific functions. Strengthening by combination of chemical and physical means is going to be a necessary part of the solution. The concepts provided in this work are not necessarily limited to cellulose, and should be used to inspire the advancement of bio-based lightweight materials as promising alternatives for structural materials.

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Appended Papers

Paper I

Tert-butanol as a structuring agent for cellulose nanocrystal water suspensions

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Manuscript

Tert-butanol as a structuring agent for cellulose nanocrystal water suspensions

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Abstract

Alcohol-water mixtures exhibit conformations which offer a platform for chemical synthesis and the physical organization of nanomaterials. The structuring of nanocelluloses in alcohol-water systems has been demonstrated to alter the rheological response of suspensions and the surface area of resulting solid foams. However, the relationship between structural formations and substrate properties remains unclear. This study elucidates how tert-butanol (TBA) influences the packing of rod-like cellulose nanocrystals (CNCs) in suspensions, effectuating control over the macrostructural stability of

solid foams. Understanding the hierarchical assembly of CNCs via X-ray scattering and scanning electron microscopy (SEM) leads to the reliable modulation of substrate properties. As a co-dispersant, TBA inhibited CNC packing into highly densified lamellar structures. The modified structuring achieved controllable gelation in CNC suspensions. Freeze-dried foams attained superior surface area and mechanical properties to those formed without TBA. This promotes the use of alcohols as structuring agents to control properties of suspensions and solid foams without the use of materials such as salts or surfactants, which can be challenging to remove from materials.

Introduction

Alcohol-water mixtures are convenient to use as reaction media and for studying amphiphilic and hydrophobic interactions. Tert-butanol (TBA) is particularly interesting as the largest monohydric alcohol which is still miscible in water. The addition of TBA to water changes local density and hydrophobic effects dominate water structuring by direct alcohol-alcohol contacts.¹ Thus, TBA disrupts hydrogen bonding between water molecules.^{2,3} Liquid phase structuring in TBA-water systems forms dynamic TBA-rich and water-rich regions.⁴⁻⁶ The structuring of the alcohol-water system has then been combined with nanotechnology in, for example, synthesis of silica particles where the alcohol to water ratio was observed to facilitate the tuning of porosity.⁷

Cellulose is a critical component for materials science and engineering due to it being abundantly available from plants. The discovery of cellulose nanomaterials opened the world of nanotechnology for cellulosic materials.⁸ Cellulose nanocrystals (CNCs) are nanoparticles which form colloidally stable viscous suspensions or gels in water, and can be dried into porous solid foams. The addition of salts, surfactants, or co-solvents to a nanocellulose suspension, comprised of CNCs or cellulose nanofibers (CNFs),^{9,10} can alter the electrostatic interactions between those nanocelluloses through charge screening. This, in turn, changes the colloidal stability, rheology, and optical properties of the suspensions. In a dilute suspen-

sion, CNCs form a dispersed isotropic phase where they are free to rotate without interacting with each other. However, as the concentration of CNCs increases, they begin to pack together.¹¹ Moreover, above a critical concentration, they spontaneously self-assemble into a chiral nematic liquid crystalline phase.^{12–15} Structuring can also be observed by increasing the ionic strength of the CNC suspension, leading to partial aggregation, gelation, and altering of orientation in a flowing liquid crystal phase.^{16–18} Partial aggregation and increased suspension viscosity can also result upon addition of co-solvents such as glycerol and specific molecular weight alcohols.^{19,20}

TBA was found to direct the assembly and aggregation of silica nanoparticles (0.2-0.5 nm radius) in relation to the solvent composition.⁷ Silica nano-particles did not form structures around water or TBA-rich domains, but instead influenced the resulting morphology of those domains. TBA has been used to help direct the hierarchical assembly of nanocelluloses in nanopapers, aerogels, and cryogels, creating structures with high surface area and porosity.^{21–24} TBA is thought to prevent inter-fibril hydrogen bonding while its three bulky methyl groups add steric hindrance, increasing the fiber-fiber distance. As a result of impaired self-assembly, the specific surface area increases while thermal conductivity decreases.^{21,25–27}

In this study, the ability of TBA to disrupt the hydrogen bond network between water molecules was expected to impact nano- to macro-scale structuring of CNC suspensions and the resulting freeze-dried foam. The formation of the structures was elucidated by combining scattering and rheological characterization, and the properties of the foams were evaluated by their strength in relation to the pore structure. Understanding the interactions which govern nanoparticle behavior in alcohol-water systems provides a simple route toward the formation of materials with controllable properties

Experimental

Materials

CNCs were purchased from Celluforce (Canada). TBA and HCl were purchased from Sigma-Aldrich (Sweden). MilliQ-water (resistivity $18.2 \Omega^{-1} \text{ cm}^{-1}$ at 25°C) was from the Millipore water purification system.

Methods

Design of experiments

The experiments were designed using JMP Pro 16.2.0 software from SAS (USA), which defined the composition of ternary suspensions with respect to water, TBA, and CNC. The systems that were investigated are shown in white in Figure 1. The accessible range was limited by the 10 wt% CNCs stock suspension concentration in water. The following naming convention was applied: xCNCyT, where x is the concentration of CNC in wt%, and y is the concentration of TBA in wt%.

Preparation of CNC suspensions

The suspensions used a 10 wt% CNC stock solution that was prepared in MilliQ-water and stirred in an IKA EUROESTAR 60 (Germany) overhead stirrer with a four-bladed R 1342 propeller at 1200 rpm for 1 h. According to Fig. 1, the suspensions were then prepared by diluting the stock suspension in water to the selected concentration. TBA was added in seven incremental steps to avoid heterogeneous or phase-separated suspension, with thorough shaking after each step. Finally, the suspensions were shaken overnight on a moving platform at 180 rpm.

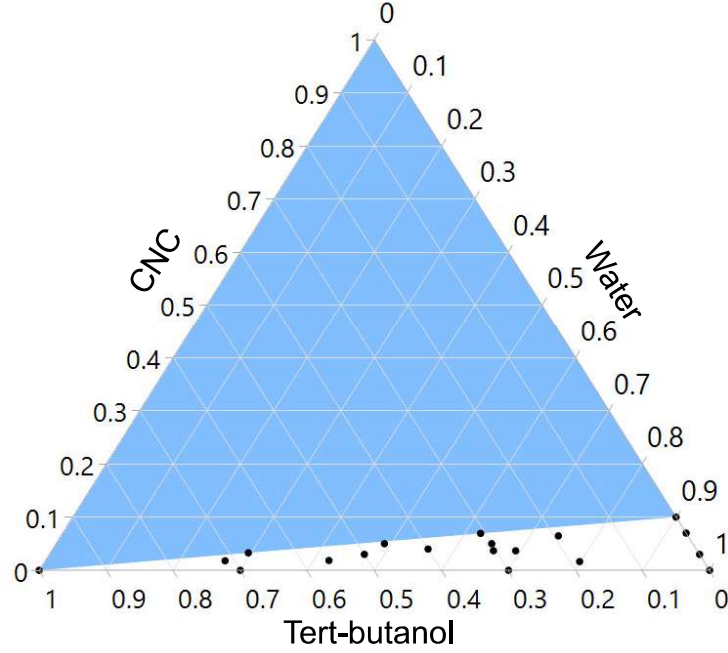


Figure 1: Ternary plot summarizing the combinations of suspensions containing selected mass concentrations of CNCs, water, and TBA assessed in this study (black dots).

Small angle and wide-angle X-ray scattering

SAXS and wide-angle X-ray scattering (WAXS) were measured in a SAXSLAB Mat: Nordic (Denmark) benchscale instrument, with $\text{CuK}\alpha$ radiation and a Q (scattering vector) range of $0.003\text{--}2.7\text{ \AA}^{-1}$. The sample-to-detector distance was 1530 mm for SAXS and 130 mm for WAXS. The beam size for the SAXS configuration was 0.2 mm. Q -calibration was performed using LaB_6 powder. Suspensions were assayed at room temperature in glass capillaries of 2 mm in diameter (WJM-Glas, Germany) and 0.01 mm wall thickness. Transmission correction was applied to express intensity as absolute units $\times$ thickness. Masking of the beamstop area and gaps between the detector elements was done by SAXSGUI software (version 2.27.03), scattering from an empty capillary was subtracted in MATLAB, and model fitting was performed in SasView software (version 5.0.5).

Rheological characterization

The rheological properties of the suspensions were determined using a TA Discovery HR-3 rheometer (TA instruments, USA). A 40 mm diameter sandblasted plate with a measuring gap of 1 mm was used for suspensions containing CNCs. For systems consisting of only water and TBA, a 40 mm cone with a truncation angle of 1° and a pre-set measuring gap of 26 μm was used. A Peltier lower plate was used to maintain a constant measuring temperature of 20 °C. After placing the solutions or suspensions in the assay position, they were allowed to equilibrate for 300 s before performing the measurements. Shear viscosity was assayed at shear rates 10-1000 s^{-1} (solutions without CNCs) and 0.03-1000 s^{-1} (suspensions containing CNCs). Shear strain sweep measurements were conducted at 1 Hz and strain amplitude of 0.01%-800%. Data were analyzed in TRIOS software.

Freeze-drying of the suspensions

To transform the suspensions into free-standing dry foams (cryogels), they were first injected into molds and degassed. The molds were subsequently submerged in liquid nitrogen and placed in a ScanVac CoolSafe freeze-dryer at -105 °C for 2 days. The suspensions maintain an intact structure when subjected to rapid freezing followed by freeze-drying.²⁸

Density and porosity

The envelope density (ρ_E) of solid foams was measured using calipers and a high-precision balance. Skeletal density (ρ_S) was measured using He gas in a Micromeritics AccuPyc II gas displacement pycnometer. Relative density, ρ_R , was given as the ratio of the envelope to skeletal density (Eq. 1). Porosity was then be calculated using Eq. 2 according to Gibson.²⁹

$$\rho_R = \frac{\rho_E}{\rho_S} \quad (1)$$

$$P(\%) = (1 - \rho_R) \cdot 100 \quad (2)$$

Determination of surface area

The Brunauer-Emmett-Teller (BET) surface area was determined using a Micrometrics TriStar 3000 with TriStar II Plus software and N₂ gas at 0-0.98 relative pressure. For BET linearization, the relative pressure corresponding to the nitrogen monolayer coefficient in the BET equation was included and the maximum value of the Rouquerol BET graph was the last chosen point.

SEM imaging of solid foams

The solid foams were cut through the center and sputter-coated with 4 nm of gold. They were then visualized on a JEOL 7800F Prime instrument at an acceleration voltage of 5 kV.

Mechanical testing of solid foams

Solid foams were conditioned at 20 °C in a desiccator for a week before mechanical testing. Compression tests were performed using the Texture Analyser (Stable Microsystems, UK) at a rate of 1 mm s⁻¹ after reaching a pre-load force of 0.5 N. The solid foams were pressed between parallel plates of 40 mm in diameter using a load cell of 50 kg. The compressive modulus was taken as the slope of the stress-strain curve below 10% strain, while the compressive strength corresponded to the stress at 10% strain. Energy absorption was calculated using the area under the stress-strain curve until up to 50% strain. Variations in density between solid foams were accounted for by dividing all values by their relative density.

Fitting of ternary plot models

Model fitting and data visualization were performed using JMP software. Experimental values were fitted using a Schiffe cubic macro and a second degree polynomial. Stepwise

fitting was used to find the model with the most significant effects. A Box-Cox transformation was applied to the data. The fitted models provided an easier visualization of the trends in the ternary plots; to this end, they had an adjusted R-squared value of at least 0.9.

Results and discussion

Submicron scale ordering in CNC suspensions

WAXS diffractograms of TBA in water systems are shown in Fig. 2a. The peak at $2 \text{ \AA}^{-1}$ corresponds to water O-O distances, while subsequent peaks at lower Q originate either from hydrophobic TBA aliphatic chain interactions which cluster together ($1.5 \text{ \AA}^{-1}$) or hydrophilic hydroxyl groups of TBA molecules which interact with water molecules ($0.5 \text{ \AA}^{-1}$).⁴ The presence of CNCs (Fig. 2b) leads to the appearance of the 200 diffraction peak of cellulose I_β around $q = 1.6 \text{ \AA}^{-1}$ and the 1-10 and 110 peaks between $q = 1.0$ and $1.2 \text{ \AA}^{-1}$. However, the last two peaks are difficult to distinguish from TBA structure scattering in 5CNC30T and 5CNC46T. All of the mentioned observable structures were present and unperturbed even after addition of CNCs. The appearance of an upturn below $0.5 \text{ \AA}^{-1}$ corresponds to the start of mesostructure scattering in the SAXS range in 5CNC30T and 0CNC30T (Fig. 2).⁴

Following the approach of Munier et al.³⁰, the SAXS intensities originating from the CNCs were fitted using a parallelepiped form factor and hard-sphere structure factor. The most diluted CNC water suspension containing 3 wt% CNCs (3CNC0T) fitted results corresponding to parallelepipeds with thickness of $3.78 \pm 1.34 \text{ nm}$ and width of $20.10 \pm 1.74 \text{ nm}$, packed with an effective radius of $24.55 \pm 0.67 \text{ nm}$ (Fig. 3a). The length was fixed at 183 nm , taken from atomic force microscopy (AFM)³¹, as a result of low fitting sensitivity in the measured Q range. AFM measurements confirmed the expected CNC diameter of $4 \pm 1 \text{ nm}$.³² The parallelepiped form factor, therefore, indicated the lateral packing of several CNC rods or crystals in the width direction in systems containing only CNCs and water.^{33,34}

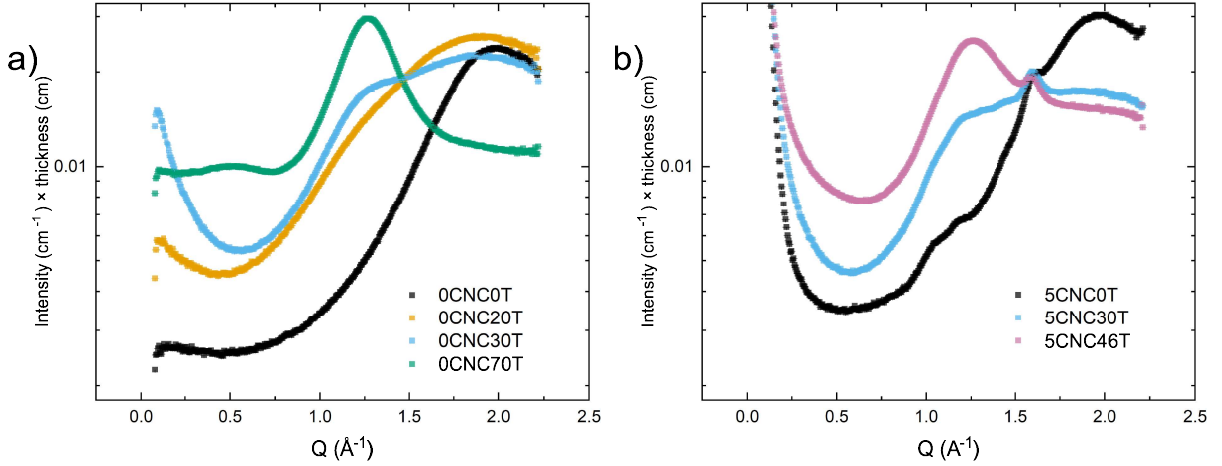


Figure 2: 1D WAXS intensities of a) water with 0, 20, 30, and 70 wt% TBA as a co-dispersant and b) 5 wt% CNCs in water with 0, 30, and 46 wt% TBA as a co-dispersant.

CNC-water suspensions exhibited a peak around $0.01\text{-}0.02\text{ \AA}^{-1}$ and a shoulder around $0.02\text{-}0.05\text{ \AA}^{-1}$ in 1D SAXS intensities (Fig. 3a), which became more pronounced when plotted in Lorentz corrected plots (Fig. 3b). Both peaks were shifted to higher Q values with increasing CNC concentration. However, the shoulder remained at a constant Q -ratio of 2:1 to the peak. The peak at $0.01\text{-}0.02\text{ \AA}^{-1}$ was assumed to represent the CNC packing distance,^{15,35} whereas the 2:1 Q -ratio indicated that the shoulder at $0.02\text{-}0.05\text{ \AA}^{-1}$ corresponded to a second-order scattering peak derived from the same, presumably lamellar periodic structure.^{35,36} The shift of both peaks towards higher Q was interpreted as shorter CNC packing distance with increasing concentration.¹⁵ Furthermore, 2D SAXS intensity patterns (Supporting Information Fig. S1) revealed increasing anisotropy at 5 wt% CNC and above, indicating an alignment of structures in domains at the μm scale (comparable to or larger than the X-ray beam size of 0.2 mm).³⁵ Hence, in the absence of co-dispersants, CNC structures in water became more densely packed and anisotropic at increasing CNC concentrations, complying to reports in literature.^{30,35}

At 30 wt% TBA or below, no significant changes in the shape of the SAXS intensity curve were observed compared to CNC-water suspensions without TBA (3CNC0T in Fig. 3a vs 6CNC19T in Fig. 3d). In addition, the two peaks at $0.01\text{-}0.02$ and $0.02\text{-}0.05\text{ \AA}^{-1}$

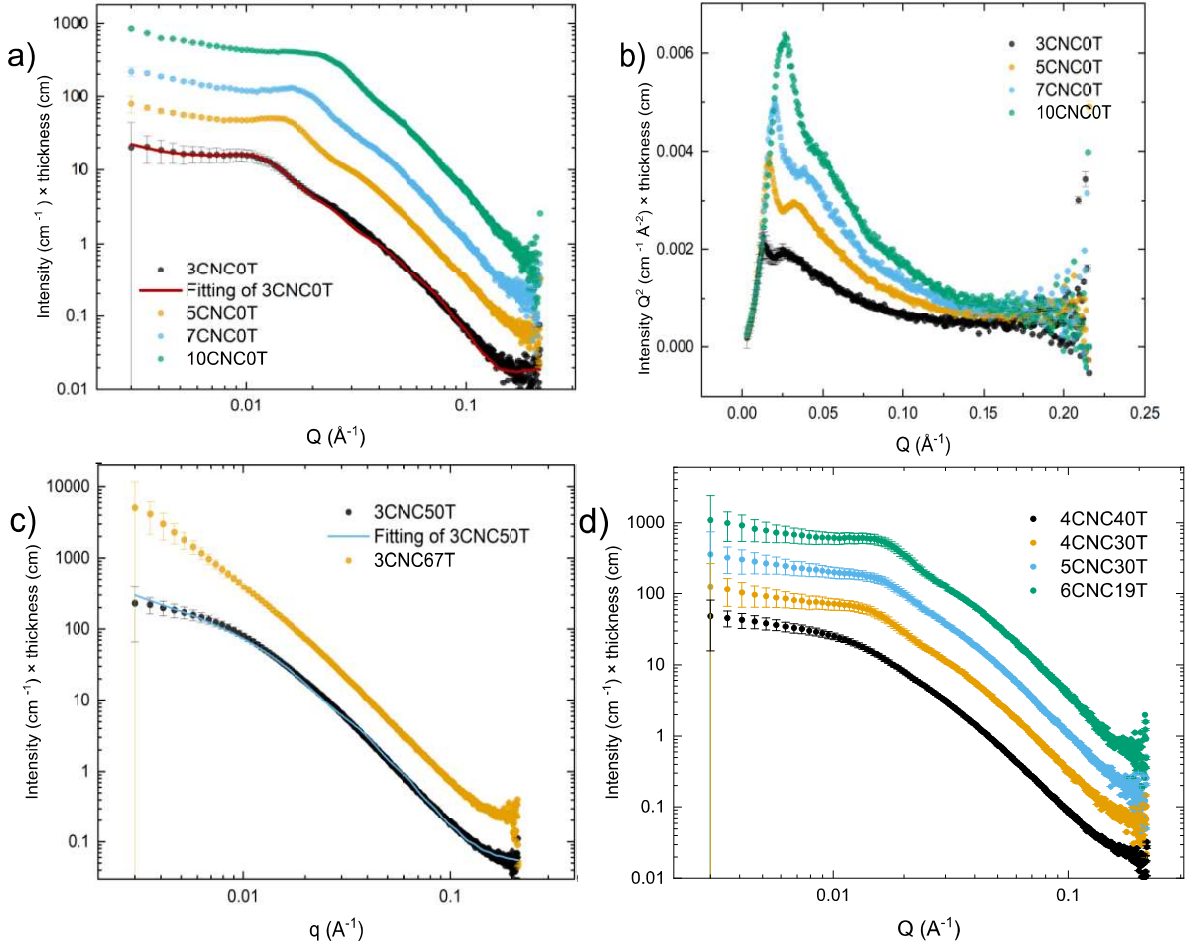


Figure 3: a) 1D SAXS intensities for CNC-water suspensions differing by CNC concentrations (3, 5, 7, 10 wt%) (3CNC0T, 5CNC0T, 7CNC0T, 10CNC0T),. The red line signifies a fit to a parallelepiped form factor with hard-sphere structure factor, b) Lorentz corrected plot ($Q^2 I(Q)$ vs. Q) for the aforementioned suspensions, c) 1D SAXS intensities for 3 wt% CNC suspensions with TBA concentrations of 50 and 67 wt% (3CNC50T and 3CNC67T). The green line signifies a fit to a parallelepiped form factor without hard-sphere structure factor, and d) 1D SAXS intensities for suspensions with 6 wt% CNC with 19 wt% TBA, 5 wt% CNC with 30 wt% TBA, and 4 wt% CNC with 30 and 40 wt% TBA (6CNC19T, 5CNC30T, 4CNC30T, and 4CNC40T). Note that 1D SAXS intensities were shifted vertically for easy viewing.

originating from CNC packing were still pronounced, indicating that the packing of the CNCs (structure factor) remained rather unchanged. However, suspensions 4CNC30T and 5CNC30T displayed anisotropic 2D scattering patterns compared to 5CNC0T (Supporting Information Fig. S1). The increased anisotropy could indicate that 30 wt% TBA leads to an

increased alignment in structures with CNC concentrations above 4 wt%. At 40 wt% TBA, both peaks decreased in intensity (Fig. 3d) yet maintained a consistent low Q decay slope below $0.6 \text{ \AA}/\text{cm}^{-1}$ (Supporting Information Fig. S2). At 50 wt% TBA, CNC packing peaks disappeared completely and a low Q decay ($<0.009 \text{ \AA}^{-1}$) of Q^{-1} , typical of rod-like shapes, was obtained (Fig. 3c). The suspension could be modeled as polydisperse parallelepipeds without a hard-sphere structure factor. The fitting corresponds to parallelepipeds with thickness of $3.18 \pm 0.35 \text{ nm}$, lognormally distributed with a PD-ratio of 0.55, and a width of $26.79 \pm 3.74 \text{ nm}$. The length was again, fixed at 183 nm. This suggests that CNCs existed in 50 wt% suspension without periodic structuring. Increasing the concentration of TBA to 67 wt% resulted in a similar trend to 50 wt% at high and medium Q , but with a steeper $Q^{-2.2}$ decay at low Q (Fig. 3c). This could indicate an irregular aggregated structure, such as a network of smaller structural subunits. In the 2D scattering pattern, no anisotropy could be observed at 40 wt% TBA and above, leading to the disappearance of structural alignment introduced by low concentrations of TBA. The observed changes in CNC interaction were consistent at all CNC concentrations.

Effect of structuring on suspension rheology

The addition of TBA to water resulted in a system with an evolving microscopic structure, as revealed by SAXS and reported in literature.^{4,37–39} Water, TBA, and their blends expressed Newtonian behavior (Fig. 4a). The shear viscosity of the TBA-water blends increased with the addition of TBA, reaching a maximum at 70 wt% TBA. The viscosity values of the TBA-water blends were close to that reported by Furukawa et al.³⁷

All CNC-water suspensions exhibited typical shear-thinning behavior (Fig. 4b).^{40,41} In particular, those containing 3 and 5 wt% CNCs showed an isotropic suspension behavior. Their viscosity functions presented a zero-shear Newtonian plateau in the limit of low shear rates, followed by a shear thinning region with an increasing shear rate. In comparison, suspensions with 7 and 10 wt% CNCs displayed a constant shear-thinning slope.

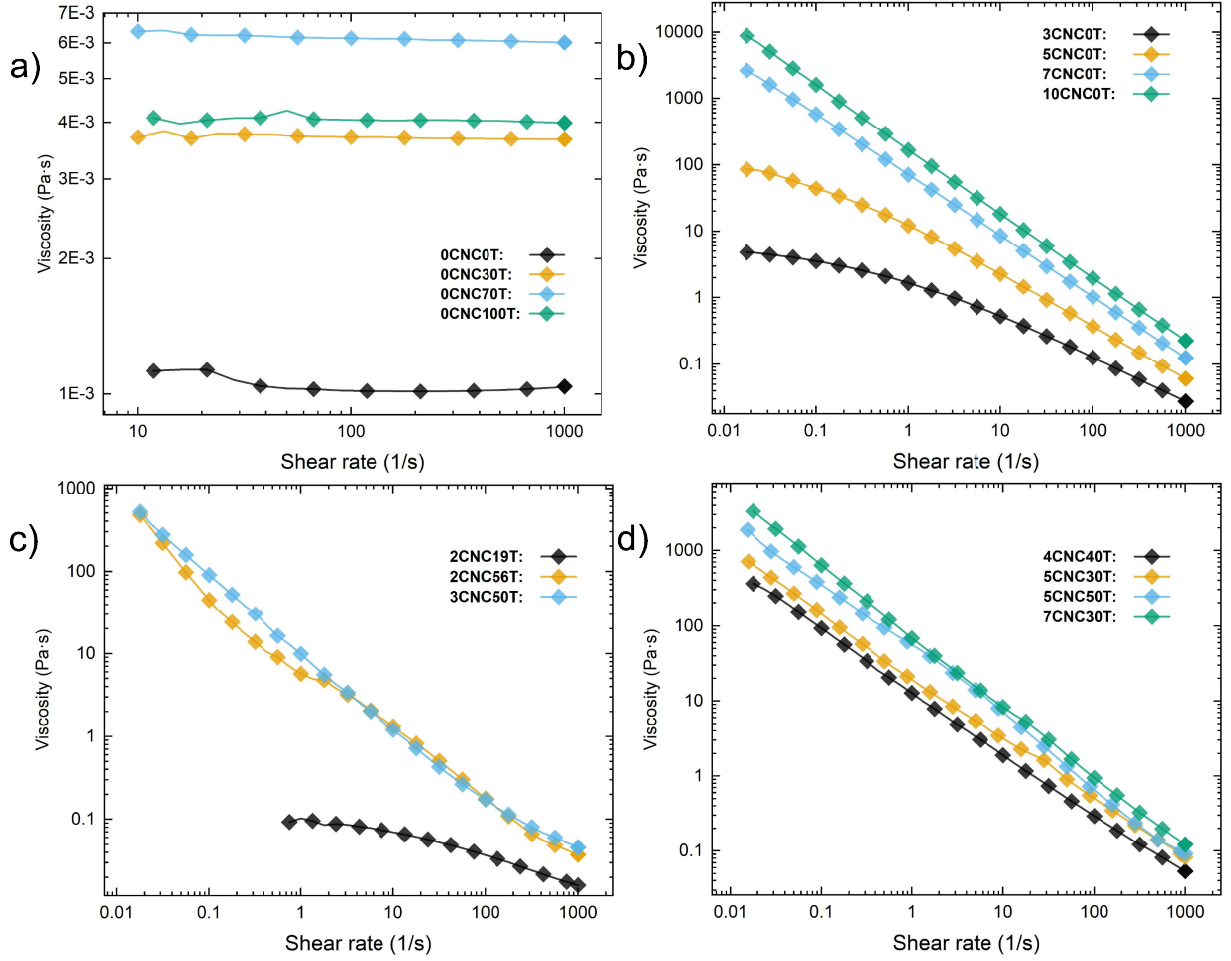


Figure 4: Shear viscosity measurements for various suspensions and blends: a) TBA-water blends with TBA concentrations of 0, 30, and 100 wt% (0CNC0TBA, 0CNC30TBA, 0CNC70TBA, 0CNC100TBA), b) CNC-water suspensions with CNC concentrations of 3, 5, 7, and 10 wt% (3CNC0TBA, 5CNC0TBA, 7CNC0TBA, and 10CNC0TBA), c) CNC-water-TBA co-solvent suspensions with CNC concentrations of 2 wt% and TBA concentrations of 19 and 56 wt%, and 3 wt% CNC with 50 wt% TBA (2CNC19TBA, 2CNC56TBA, and 3CNC50TBA), and d) CNC-water-TBA co-solvent suspensions with CNC concentrations of 4 wt% and TBA concentration of 40 wt%, 5 wt% CNC with TBA concentrations of 30 and 50 wt%, and 7 wt% CNC with 30 wt% TBA (4CNC40TBA, 5CNC30TBA, 5CNC40TBA, and 7CNC30TBA). Shear rates ranged from 0.015 to 1000 s^{-1} for CNC suspensions and from 10 to 1000 s^{-1} for blends without CNCs.

Suspensions containing only 2 and 3 wt% CNCs showed shear-thinning behavior even upon addition of TBA (Fig. 4c). At 19 wt% TBA, the suspension retained an isotropic behavior. However, at 50–60 wt% TBA (i.e., 2CNC56T and 3CNC50T) the viscosity was higher than that of the 3 wt% CNC-water suspension (3CNC0T). In suspensions with the highest TBA content, specifically, 2CNC71T and 3CNC67T, phase separation was visually observed 48 h after the suspensions were left to rest and, therefore, are not included here.

In the linear region of the oscillatory sweep, a comparison of suspensions containing 2 and 3 wt% CNCs revealed that the storage modulus (G'), which is an indicator of the strength of interactions in the network, increased dramatically following the addition of low to medium amounts of TBA (Table 1 and Supporting Information S3b¹). At approximately 50 wt% TBA (i.e., 2CNC56T and 3CNC50T), G' was higher while $\tan(\delta)$ (loss modulus (G'') and $\tan(\delta) = G''/G'$) was lower than 3CNC0T. At 71 wt% TBA (i.e., 2CNC71T and 3CNC67T), $\tan(\delta)$ was higher, suggesting lower elasticity compared to suspensions with medium (50–60 wt%) TBA concentrations. The cross-over point for curves of G' and G'' was at higher strain values in suspensions containing medium amounts of TBA rather than high TBA amounts. This suggested that addition of 50–60 wt% TBA strengthened network stability. The beneficial effect of TBA on G' was analogous to that achieved by augmenting the concentration of CNCs (Supporting Information Fig. S3), or by the hydrophobization of CNCs.⁴² At 4 to 7 wt% CNC (Fig. 4d), an increase in TBA content was accompanied by an increase in viscosity, with 30 wt% TBA (7CNC30T) attaining the highest value. These suspensions showed a shear-thinning viscosity function, typical of a CNC gel (Fig. 4d).

To better understand these results, the viscosity at a shear rate of 1 s^{-1} (Fig. 4) and G' obtained from the linear viscoelastic region of the strain sweep curve (Supporting Information Fig. S3) for each measurement were plotted in Fig. 5 and Fig. 6, respectively. For easier visualization of the trends, the values were fitted to a model in JMP and then plotted in the corresponding ternary presentations. TBA concentrations between 30 wt% and 50 wt%

¹The oscillatory sweeps for the remaining blends and suspensions can be found in the Supporting Information Fig. S3.

Table 1: Selected rheological parameters from linear viscoelastic frequency sweeps of suspensions containing 2 and 3 wt% CNC: G' , $\tan(\delta)$, and strain at $G'' = G'$.

CNC (wt%)	TBA (wt%)	G' (Pa)	$\tan(\delta)$	Strain at $G'' = G'$ (%)
2	19	0.3	1.71	-
2	56	139.3	0.20	43.25
2	71	99.0	0.19	15.43
3	0	4.1	1.15	-
3	50	66.3	0.13	93.38
3	67	319.7	0.22	15.66

strengthened the suspensions, but higher concentrations had the opposite effect. Despite having a higher CNC concentration, the 7CNC30T suspension had a lower experimental G' than the 5CNC50T suspension.

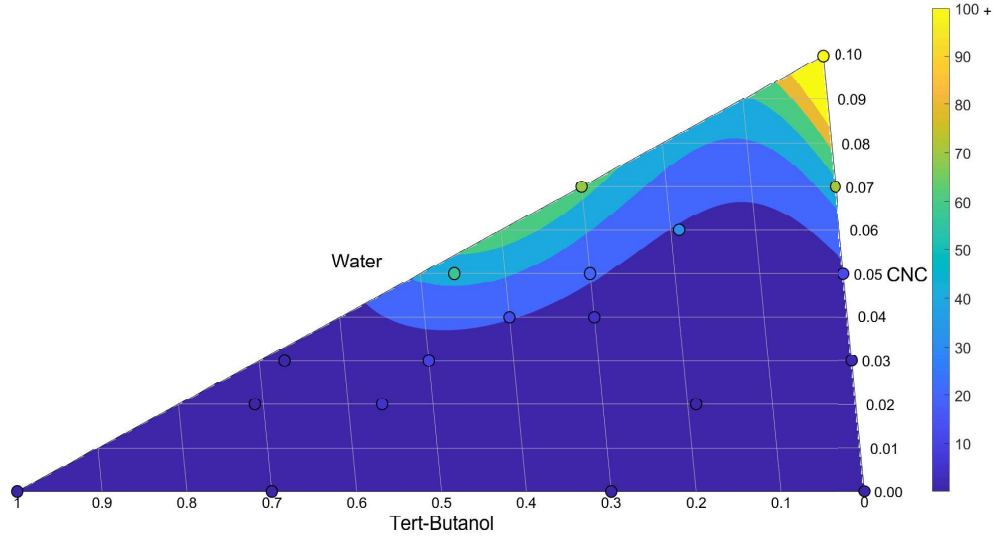


Figure 5: Ternary contour plot with selected suspensions and blends of CNC, water, and TBA. The color scale denotes steady state shear viscosity (Pa·s) at 1 s^{-1} shear rate. The contour areas were obtained in JMP by a fitted model, with yellow corresponding to higher values and blue to lower values.

Rheology measurements of viscosity, shear-thinning behavior, and elasticity revealed how TBA changed the macroscopic structure of the suspensions. Song et al.⁴³ reported an increase in G' and G'' of two and one orders of magnitude respectively in cellulose nanofibril suspensions. The strengthening effect of TBA on the network is thought to arise from re-

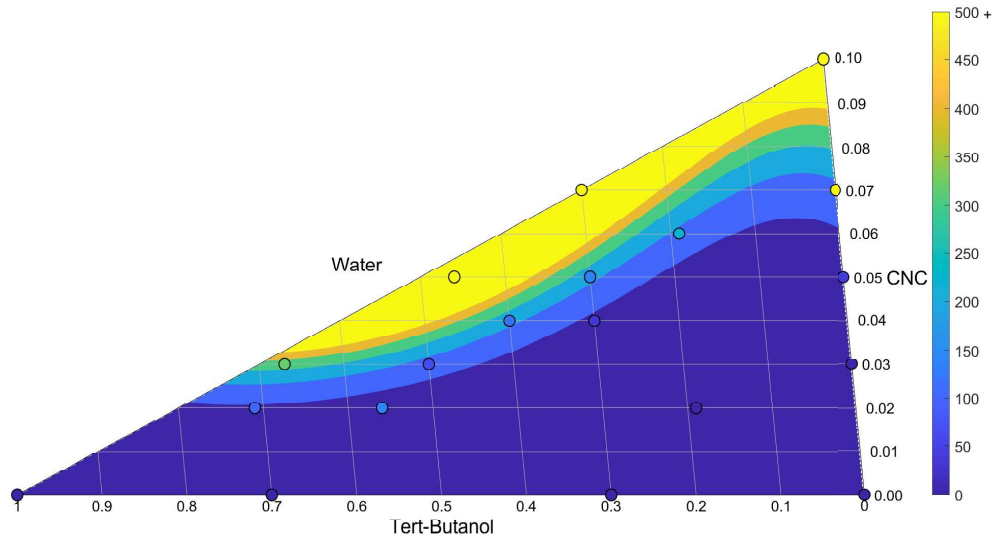


Figure 6: Ternary plot with selected suspensions and blends of CNC, water, and TBA. The color scale denotes the value of G' (Pa) in the linear region during oscillatory sweep measurement. The contour areas were obtained in JMP by a fitted model, with yellow corresponding to higher values and blue to lower values.

duced repulsion between CNCs. While this yielded highly interconnected networks, beyond a certain concentration of TBA the system became unstable, as TBA is thought to no longer mix well with water and, instead, begins to aggregate and weaken the gel structure.

Structure and properties of CNC solid foams

Solid foams prepared from CNC-water suspensions formed large lamellar sheet structures with a paper-like morphology (Fig. 7a²). The CNCs aggregated into densified sheets, forming a poorly interconnected network throughout the bulk of the solid foam. These thin lamellar structures promote crack propagation causing foams to become brittle and fracture easily.²⁹ Unsurprisingly, they displayed poor mechanical performance in comparison to the other prepared porous materials. Moreover, these solid foams exhibited the lowest compressive performance and surface area when compared to foams made with more TBA and a similar

²More SEM images of solid foams from CNC-water suspensions with varying CNC concentrations are shown in Supporting Information Fig. S4)

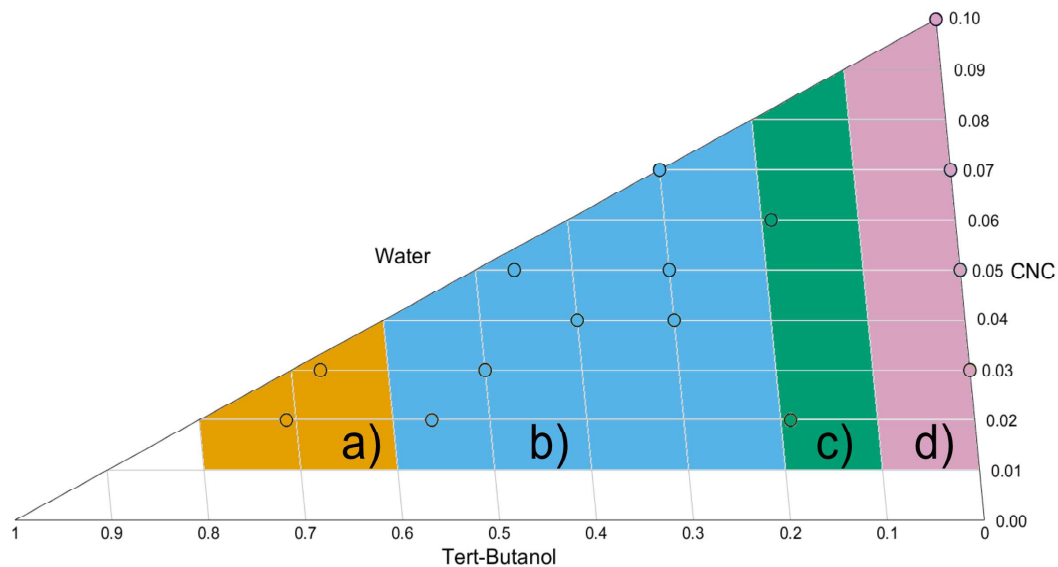
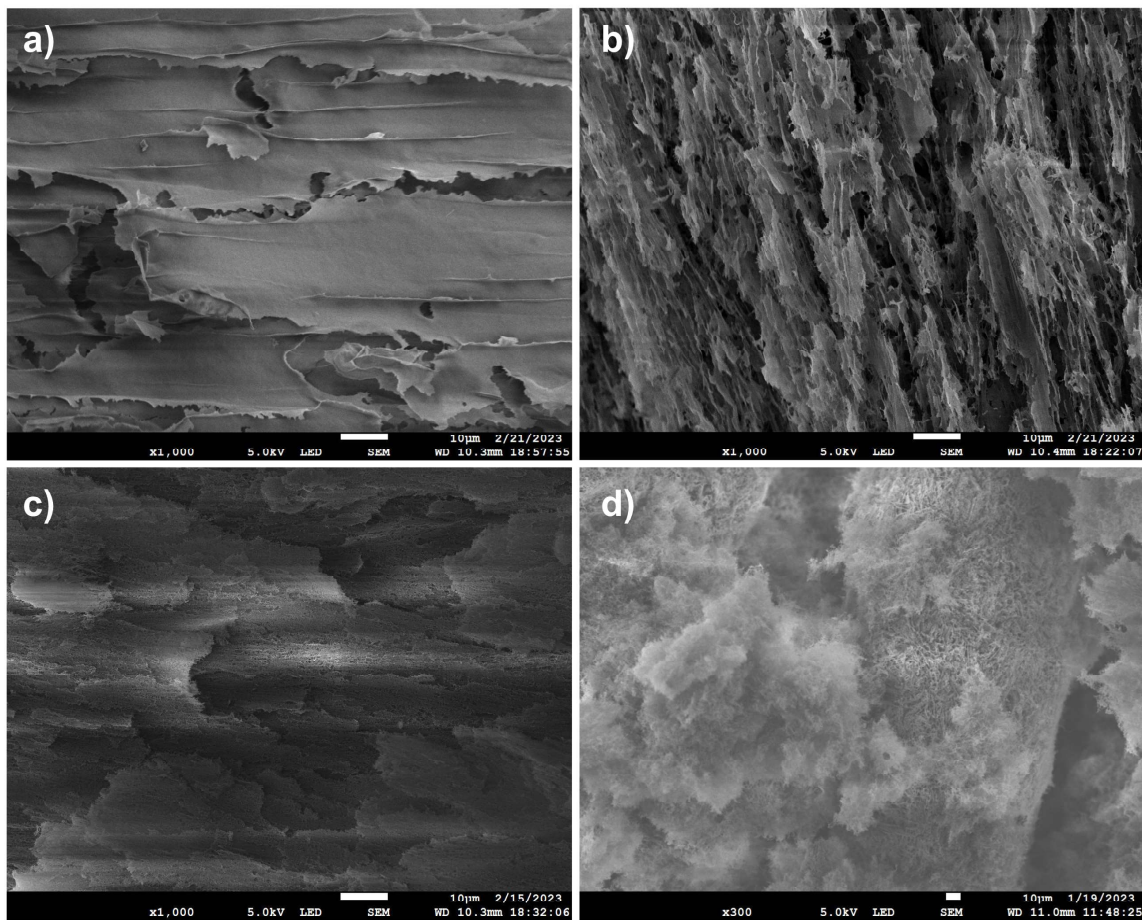


Figure 7: Characterization of CNC solid foams with SEM images of representative structures at 1000x magnification for a) 0 wt% TBA (lamellar/paper morphology), b) 30-50 wt% TBA (tubular, algae), c) <30 wt% TBA (porous lamellar), and d) >60 wt% TBA (fibrillated, mossy). The ternary diagram shows morphological regions in substrates as TBA increases.

CNC concentration (Fig. 8a). At higher CNC concentrations, the compressive properties expectedly increased as additional CNCs reinforced the sheets while lowering porosity (Fig. 8b and Supporting Information Fig. S5). The surface area of solid foams made using CNC-water suspensions with more than 4 wt% CNCs was below 5 m²/g, while 3 wt% CNC (3CNC0T) increased to 15 m²/g (Fig. 8a).

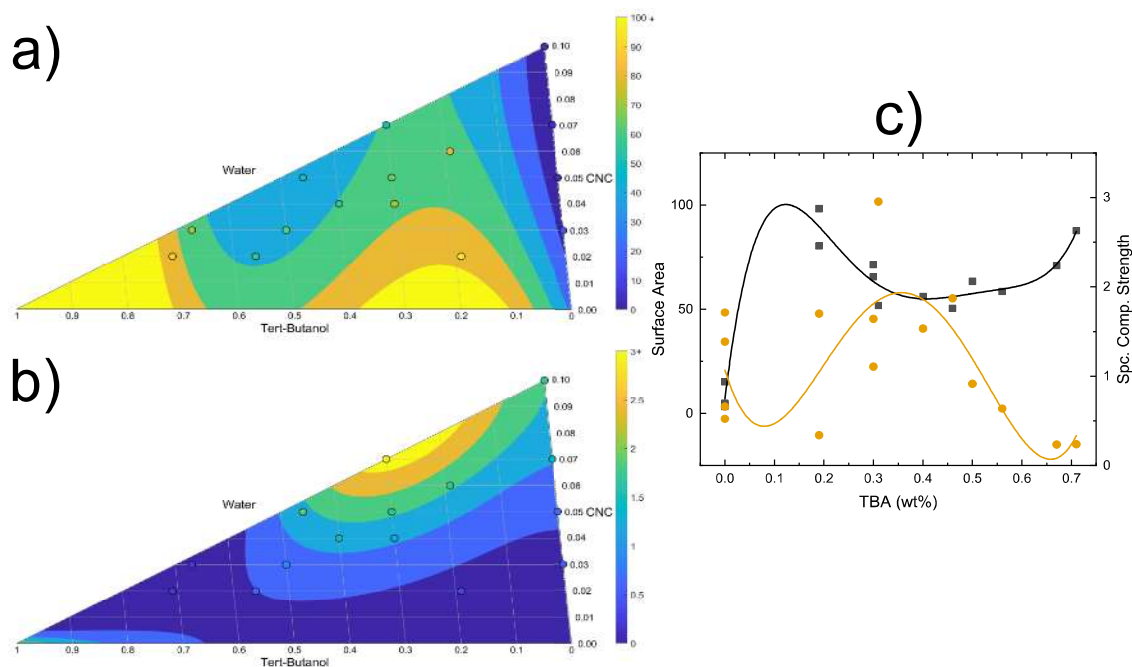


Figure 8: Solid foam properties depicted in ternary contour plots depicting a) surface area (m²/g) and b) specific compressive strength (MPa) of solid foams consisting of CNC, water, and TBA. The contour areas were obtained in JMP using a fitted model, with yellow corresponding to higher values and blue to lower values. A graph showing the inverse correlation between surface area and specific compressive strength with TBA wt% is given in c) where surface area (m²/g) is shown in black and compressive strength (MPa) in yellow.

The inclusion of TBA changed the hierarchical structuring of CNC solid foams significantly. While adding more CNCs improved the compressive properties of solid foams, similar or even improved performance could be obtained by adding TBA. For example, the specific moduli of 7CNC0T was 22 MPa; whereas those of 4CNC40T and 10CNC0T were 36 and 40 MPa, respectively (Supporting Information Table S1). This trend is also expressed by the diagonal slope of contour lines in the specific compressive strength ternary diagram. The

lines show how increasing TBA concentration compensates mechanically when using less CNCs (Fig. 8b). Solid foams with 7 wt% CNCs demonstrated clearly how the presence of TBA altered the morphology of the CNC network. The lamellar sheets of 7CNC0T (Fig. 7a) were transformed into algae-like structures with a homogeneous rough texture in 7CNC30T (Fig. 7b). Macroscopic structural features in 7CNC30T were less pronounced, and pore sizes were evenly distributed. CNCs formed disrupted tube-like structures, which ameliorated interconnectivity throughout the network. The strength and stiffness of 7CNC30T increased by 180%, energy absorption by 120%, and surface area from 5 m²/g to 52 m²/g compared to 7CNC0T (Supporting Information Table S1).

Addition of any amount of TBA to the suspensions resulted in solid foams with increased surface area compared to those made without TBA. The surface area peaked at low (<30 wt%) and high (>60 wt%) concentrations of TBA (Fig. 8c). At low concentrations of TBA, the clean lamellar sheets were partially disrupted, and sub-micron pores were observed throughout the network (Fig. 7c). On the other hand, (>60 wt%) TBA concentrations developed large aggregated porous structures with dispersed "mossy" formations on their surface (Fig. 7d). Such a heterogeneous network correlates well with the observed phase separation in these suspensions.

An indirect relationship between mechanical properties and surface area was apparent for systems containing TBA as a co-dispersant (Fig. 8c). At low (<30 wt%) and high (>60 wt%) concentrations of TBA, surface area reached an apex yet mechanical properties were unchanged compared to solid foams with 0% TBA. Morphologically, low TBA concentrations still displayed lamellar structures while at high concentrations, the TBA created disparate aggregated structures; all of which result in structurally poor networks. Incorporation of 30-50 wt% TBA in CNC suspensions however, resulted in outstanding compressive mechanical performance. Buchecker et al.⁴ reported the formation of bicontinuous microemulsions in TBA-water blends with the addition of 30-50 wt% TBA. The distributed tube-like structures shown in Fig. 7b match the description and range perfectly, confirming that liquid-phase

structuring between TBA and water has a dominant templating effect on CNC assembly. Solid foams in this range can be tailored towards applications requiring high specific mechanical performance while maintaining a greater surface area than foams devoid of TBA.

Conclusions

This study showcases the potential of using TBA to tailor the properties of nanocellulosic solid foams, such as surface area and compressive strength, by controlling nano- to macro-scale suspension structuring. The addition of TBA to water leads to the formation of liquid structures, which provide a template for CNC assembly.

Below 30 wt% addition of TBA, there was no significant impact on SAXS intensity curves, suspension viscosity, and compressive strength. Solid foams developed macro-porous semi-lamellar structures with the highest surface areas up to 98 m²/g. Addition of 30 wt% TBA gave rise to anisotropic CNC suspensions; whereas 40–50 wt% TBA formed bicontinuous phases, which yielded isotropic interconnected networks of CNCs with no periodic structuring. These suspensions displayed higher G' and viscosity compared to CNC-water suspensions. The resulting solid foams achieved high specific compressive strengths up to 63 MPa, and maintain high surface areas. Above 60 wt% TBA, CNC packing was lost, suspension stability decreased, and irregular aggregated isotropic structures were formed. The compressive strength of the ensuing solid foams was lower, but they retained a higher surface area compared to CNC-water suspensions.

Contour plots illustrated how increasing TBA concentration compensated mechanically when using less CNCs. The addition of a co-solvent structuring agent such as TBA presents a simple method to form structurally stable porous nanomaterials with controllable surface area and mechanical strength. This technology opens new doors to tailor particle systems in applications such as catalysis, biomedical engineering, and filtration.

Acknowledgement

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Author contribution

SLN, EO, TN: Conceptualization. SLN: Writing the first draft. SLN, EO, RJ: Experimenting. SLN, EO, RJ, PP: Data handling. AS, TN: Supervision. SLN, EO, RJ, PP, RK, AS, TN: Writing, reviewing editing.

Supporting Information Available

- Filename: SI.docx

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Supporting Information for

Tert-butanol as a structuring agent for cellulose nanocrystal water suspensions

By

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SAXS

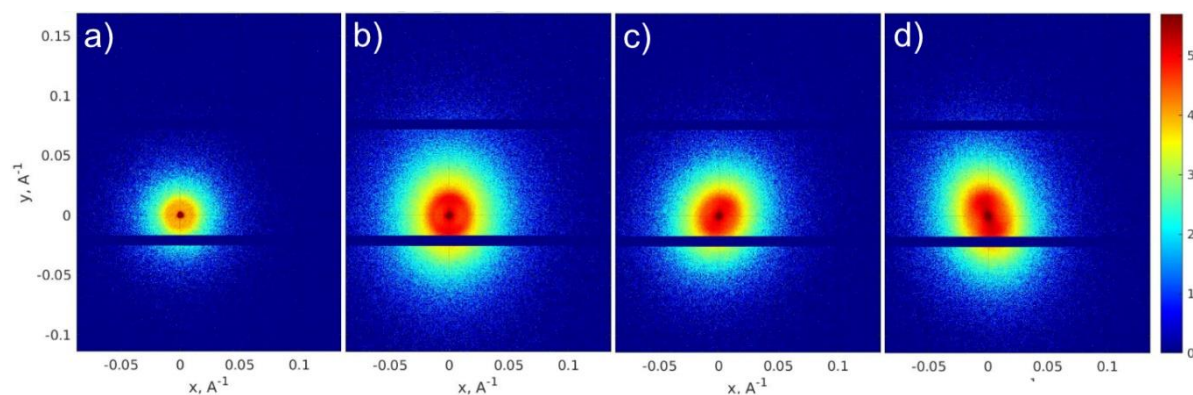


Figure S1: 2D scattering pattern of a) 3CNCOT sample, b) 5CNCOT, c) 4CNC30T, and d) 5CNC30T suspensions. Scattering intensity is isotropic despite the clear CNC tactoid peaks observed in 1D spectra.

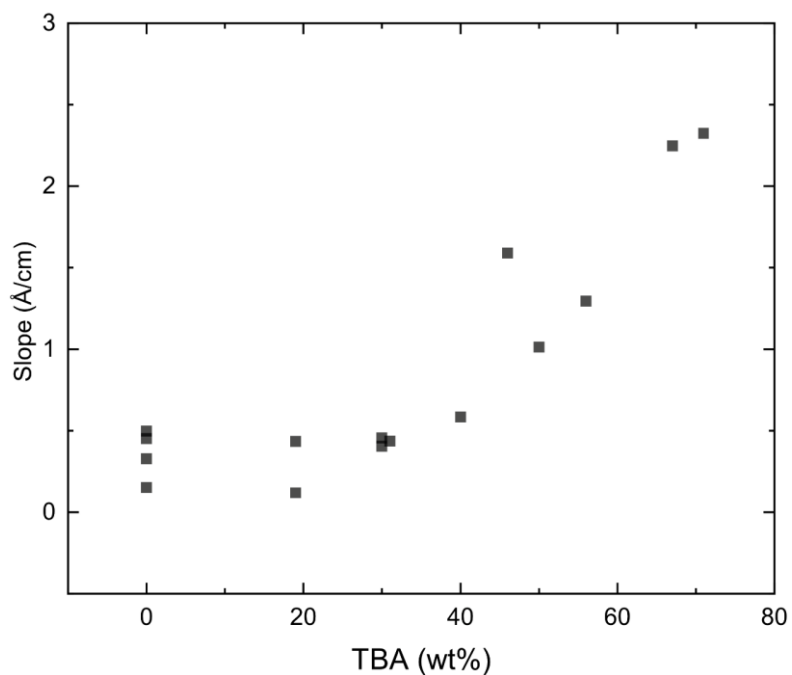


Figure S2: Plot of the decay obtained after fitting the low Q region (0.0041 to $0.01 \text{ \AA}^{-1}$) of SAXS measurements as a function of TBA content using a power law. The plot shows the variation in structure with increasing TBA concentration.

Rheology

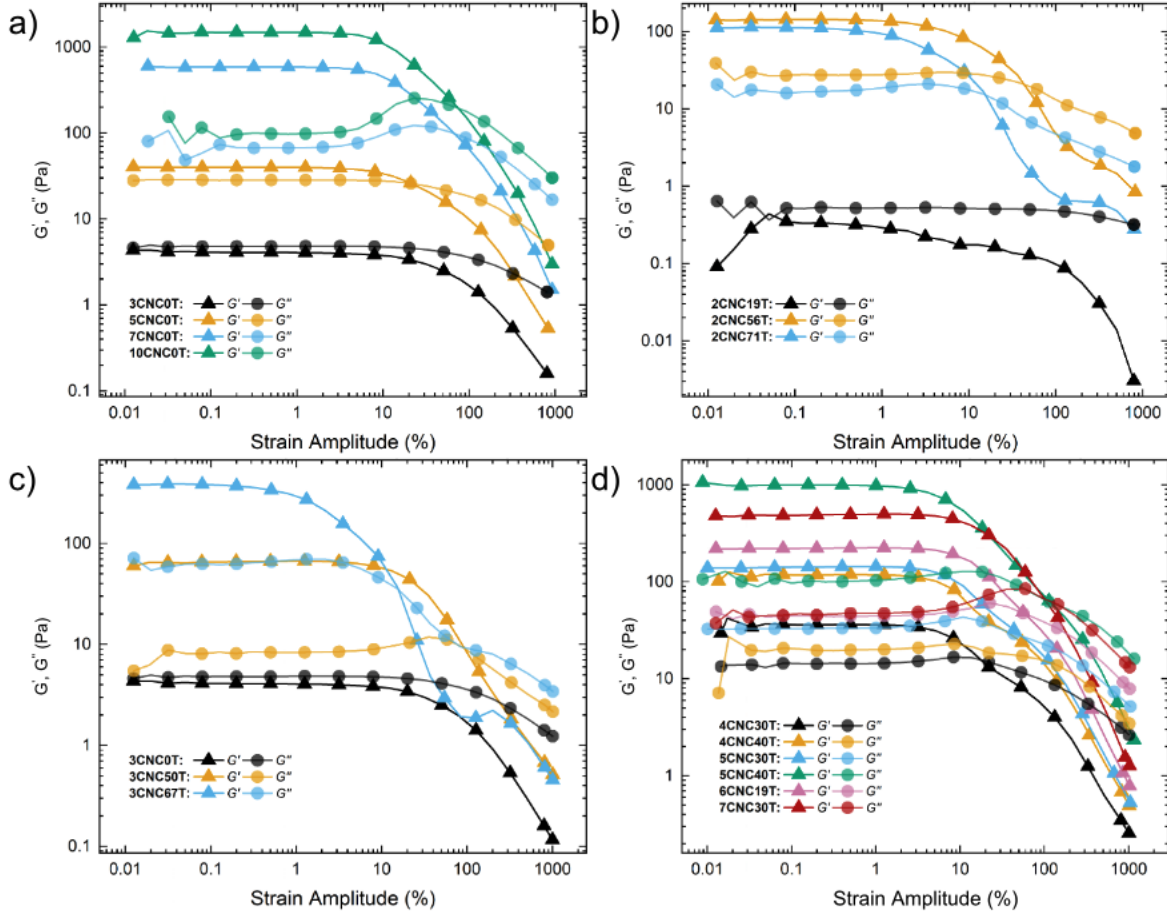


Figure S3: Shear strain sweep measurements of CNC-TBA-water suspensions of a) 3CNC0T, 5CNC0T, 7CNC0T, and 10CNC0T, b) 2CNC19T, 2CNC56T, and 2CNC71T, c) 3CNC0T, 3CNC50T, and 3CNC67T, and d) 4CNC30T, 4CNC40T, 5CNC30T, 5CNC50T, 6CNC19T, and 7CNC30T. Triangles correspond to G' , and circles to G'' . Shear strain sweep measurements were conducted at a frequency of 1 Hz and strain of 0.01 - 800% strain.

SEM

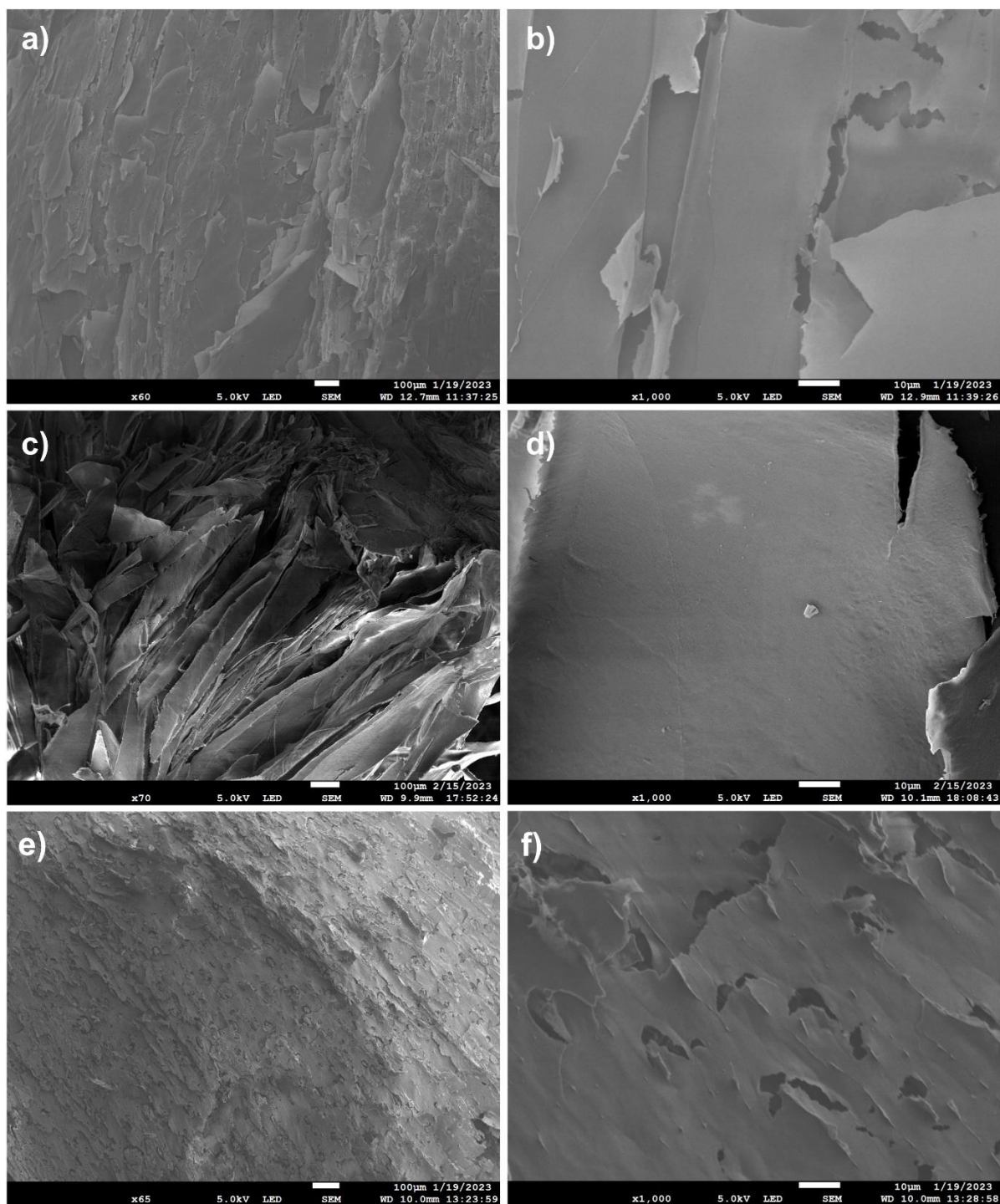


Figure S4: SEM images of solid foams made without the addition of TBA: a) 3CNCOT, 60x magnification, b) 3CNCOT, 1000x magnification, c) 5CNCOT, 60x magnification, d) 5CNCOT, 1000x magnification, e) 11CNCOT, 60x magnification, f) 11CNCOT, 1000x magnification

Foam properties

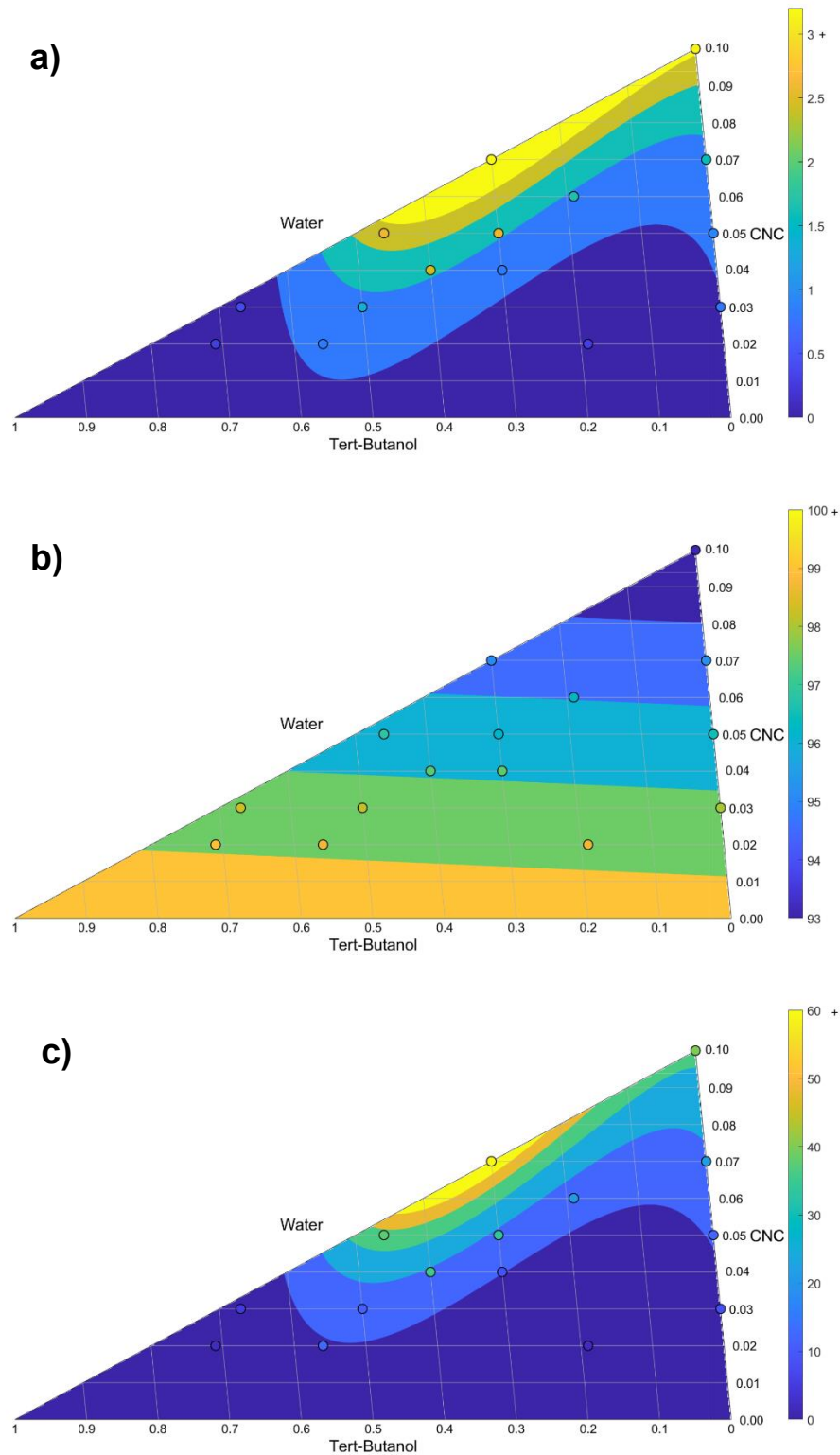


Figure S5: Ternary contour plots of freeze-dried suspensions of CNC, water, and TBA colored according to the value of the a) specific energy absorbed (MJ/m^3), b) porosity (%), and c) specific compressive modulus (MPa). The contour areas were obtained in JMP by a fitted model, with yellow corresponding to higher values and blue to lower values.

Table S1: Experimental values for surface area, specific modulus, specific energy absorption, and specific compressive strength of solid foams obtained from the suspensions denoted in the first column.

	Surface Area (m ² /g)	Spc. Modulus (MPa)	Spc. Energy Abs. (MJ/m ³)	Spc. Comp. Strength (MPa)
4CNC30T	71.3	9.0	0.83	1.1
4CNC40T	56.1	36.0	2.45	1.5
6CNC19T	80.3	21.0	1.67	1.7
7CNC0T	4.9	22.0	1.58	1.4
7CNC30T	51.8	63.4	4.32	3.0
10CNC0T	4.4	40.0	3.15	1.7

Paper II

Catalyst-free phosphorylation of cellulose for bio-based fire-retardant materials

Eliott Orzan, Stefan Spirk, Aitor Barrio and Tiina Nypelö.

Manuscript

Catalyst-free phosphorylation of cellulose for bio-based fire-retardant materials

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The transition to using non-toxic bio-based compounds in the field of materials chemistry has inspired the use of phytic acid, a multifunctional polyphosphate, for the development of novel flame-retardant materials. Covalent cross-linking of phytic acid to fabrics and cellulose has typically required catalysts and additional processing steps. A simpler alternative involves a single curing step with heat after impregnation of the substrate; however control of the product and understanding of the mechanisms has been so far neglected. Here, we elucidate the effect curing temperature has on the resulting cross-linked molecular structures formed between phytic acid and cellulose fibers. Solid-state nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infra-red (FTIR) spectroscopy analysis indicated the successful phosphorylation of phytic acid on cellulose substrates using dilute systems. In fact, the dilute condition favors inter rather than intra cross-linking providing a controllable for steering the reaction. The cross-linking mechanism was also found to enable the retention of flame-retardant properties even on washed substrates. Dehydration condensation reactions at 160 °C was found to significantly promote the cross-linking degree yet also cause degradation of the native phytate structure. This work provides the fundamental knowledge necessary to apply the simple curing to cross-link phytic acid or other phosphate compounds to OH group containing substrates.

Introduction

The transition to using non-toxic renewable resources will continue to be an exciting and technical challenge for the world of chemistry. Among those resources, phytic acid (PA) has seen a rise in popularity credit to its unique structure and bioavailability as shown by the increasing trend of phytic acid related publications (Figure 1). Also known as myo-inositol hexakisphosphate or IP6, phytic acid is extracted from the plant tissues of bran, seeds, and legumes, and has found uses in the agricultural, food science and materials chemistry. The polyphosphorylated structure allows PA to form a multitude of bonds, and as such has been used to chelate metals in the green formation of metal-organic framework catalysts,^{1, 2} and has become the newest bio-based compound of interest for the creation of flame-retardant materials.³⁻⁷

Halogenated compounds containing chlorine and bromine were traditionally used to promote flame retardancy in fabrics and cellulose.⁸ While they were highly effective, they were found to be toxic to human health and the environment, causing governmental organisations to enforce regulations regarding their use.⁹ Since then, the development of nonhalogenated and inorganic flame-retardants (FR) has taken off. Inorganic or metal-organic flame retardants are typically metal hydrates or carbonates of aluminium, boron,

antimony and magnesium. They are prized for their suppression of smoke and gas release during combustion as well as their resistance to heat. However, these compounds face challenges due to their non-renewability, use of organic solvents during processing, and cost of manufacturing.¹⁰ Of these options, non-halogenated FRs are viewed as the greenest alternative to producing flame-retardant materials. These compounds contain nitrogen, phosphorus and silicon groups, and have structures which are both diverse and complex as they are usually derived from bio-based or waste sources.¹¹ The role of the structure and the processing steps needed to integrate these compounds into materials is a continuously evolving subject which provides many opportunities to contribute towards the transition to sustainable flame-retardant technologies.

The polyphosphorylated structure of PA allows it to chelate strongly with metal ions and forms hydrogen bonds, making it useful in both inorganic and nonhalogenated FRs. The OH groups within phosphates imparts significant hygroscopicity, causing it to rapidly decompose when exposed to fire. However, this also makes the molecule highly soluble in water and thus requires some degree of cross-linking to remain on washable fabrics.^{3, 5} A highly efficient methodology is to react phytic acid and fabrics with compounds containing amine groups such as melamine and dicyanamide. The result is strong covalent bonding which further increase the FR properties due to the presence of nitrogen; yet requires the use of additional solvents and toxic compounds. Others have turned to the use of catalysts such as urea⁷ and enzymes⁶ to promote the covalent linking between PA phosphate groups and substrate hydroxyl groups. It has also been suggested that the electrostatic potential and hydrogen bonding provides sufficient cross-linking stability when formed via layer-by-layer deposition, although washability has not been verified.^{3, 12} Here, we promote the simple method of using heat to form covalent ester bonds between phosphates and cellulose. This

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methodology is commonly used for fabrics, where citric acid (CA) and 1,2,3,4-butanetetracarboxylic acid (BTCA) are hot pressed onto fabrics, leading to the formation of reactive cyclic anhydride groups.^{13, 14} Studies have verified the success of this method for PA at 140 and 160 °C the underlying mechanisms and resulting structures are not fully understood so far.^{4, 5, 15}

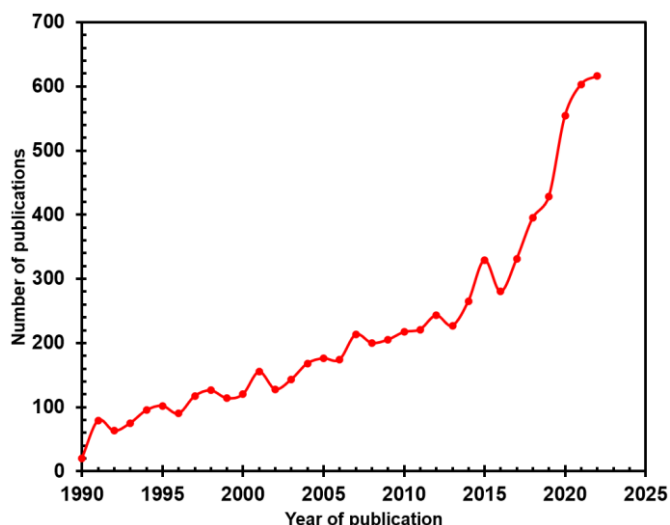


Figure 1. Web of Science search results for “phytic acid” related publications in the last 30 years. Retrieved May, 2023.

The cross-linking of phytic acid on cellulose at curing temperatures below 200 °C is hypothesized to occur via dehydration condensation reactions, promoting phosphorylation of PA and cellulose in dilute systems. The result is the formation of oligo-phosphates and cellulose-phosphate ester cross-linkages. The temperature of curing is thought to change the degree of cross-linking and the resulting flame-retardant properties. Here, we provide a fundamental understanding of the key reactions and products formed by this non-toxic methodology, which does not rely on the use of catalysts or solvents to form covalent bonds with cellulose. This will allow the progression of phosphate-based curing and hot-pressing technologies towards imparting flame-retardant properties to washable substrates.

Experimental

Materials

Whatman Cytiva qualitative filter paper (Grade 5, 47 mm) were purchased from Fisher scientific. Phytic acid solution (50 % w/w in H₂O) was purchase from Sigma-Aldrich. All reagents purchased were used without further purification.

Substrate preparation

0.013 mL of 50% (w/w) phytic acid solution was diluted in 0.3 mL of water. The diluted solution was evenly spread over Whatman Cytiva grade 5 qualitative filter paper (~0.166 g) without excess, leading to a theoretical dry concentration of 5 wt% phytic acid on dried filters. Filters labelled with a W were washed after curing by adding 200 mL DI water, followed by 100 mL 95% ethanol, and once again with 200 mL DI water in a Büchner funnel. The filters were dried again at 80 °C for 1 hour.

Drying and curing

Filters were dried at 80 °C for 15 hours in a convection oven. Post-drying curing conditions and sample nomenclature provided in Table 1. Filters dried at 20 °C were allowed to dry at room temperature for 2 days. Curing time and temperature were chosen to mimic conditions used in experiments by other authors.^{4, 13, 14, 16-20}

Table 1. Conditions used and nomenclature of substrates in this study.

Post-drying curing		Nomenclature*	
Temperature	Time	No acid	Phytic acid
20°C	-	20	P20
80°C	2 hrs	80	P80
120°C	2 hrs	120	P120
160°C	5 mins	160	P160

*Substrates with a U or W label denote unwashed and washed samples respectively.

Nuclear Magnetic Resonance (NMR) spectroscopy

Solid state NMR was performed in a 4 mm ZrO₂ MAS rotor with a set temperature of 298K in all experiments. The following parameters were set for ¹³C and ³¹P solid state NMR:

¹³C CP at 10KHz with P3(1H)=3.0us, P15(contact time)=1.5ms, CP at 60.0 kHz ¹³C (PLW1=109W) SPW0=110W optimized ramp 45-90kHz 1H and 1H decoupling SPINAL64 at 83 kHz (PCPD2=6.0us, PLW12=96W), d1(recovery delay)=2.0s, ns=4000.

³¹P hpdec at 12.5kHz with P1(31P)=3.5us @PLW1=176W, 1H decoupling TPPM15 at 54 kHz (PCPD2=9.3us, PLW12=40W), d1(recovery delay)=10.0s, ns =64.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was performed on dried cellulose substrates using an attenuated total reflection (ATR) component. Substrates were cured as described by Table 1, immediately put in a desiccator, and analyzed soon after taking the most representative line. A PerkinElmer Fronteier FT-IR spectrometer with PIKE technologies GladiATR measured 32 scans of each substrate 3 times with a data interval of 1 cm⁻¹ and 4 cm⁻¹ resolution. PerkinElmer Spectrum software was used to correct for background noise.

Thermogravimetric Analysis (TGA)

A Mettler Toledo TGA/DSC 3+ was utilized to sequence the following heating sequence using STARE Software: 1. Ramp from 30 °C - 500 °C at a rate of 10 K/min under 60 mL/min air flow, 2. Temperature hold at 500 °C for 5 mins, 3. Ramp from 500 °C - 700 °C at a rate of 10 K/min under 60 mL/min air flow, 4. Temperature hold at 800 °C for 10 mins. Properties were taken as the average of 3 separately prepared samples. Carbonization onset was set as the point where the slope of the graph deviated by more than 3%. Weight loss during carbonization was calculated from this point to where the slope begins levelling out as indicated by a change in slope of 30%. Residual weight was taken as the weight percent of the material at 700 °C.

Elemental analysis

Elemental analysis was performed by MIKROLAB Mikroanalytisches Laboratorium Kolbe.

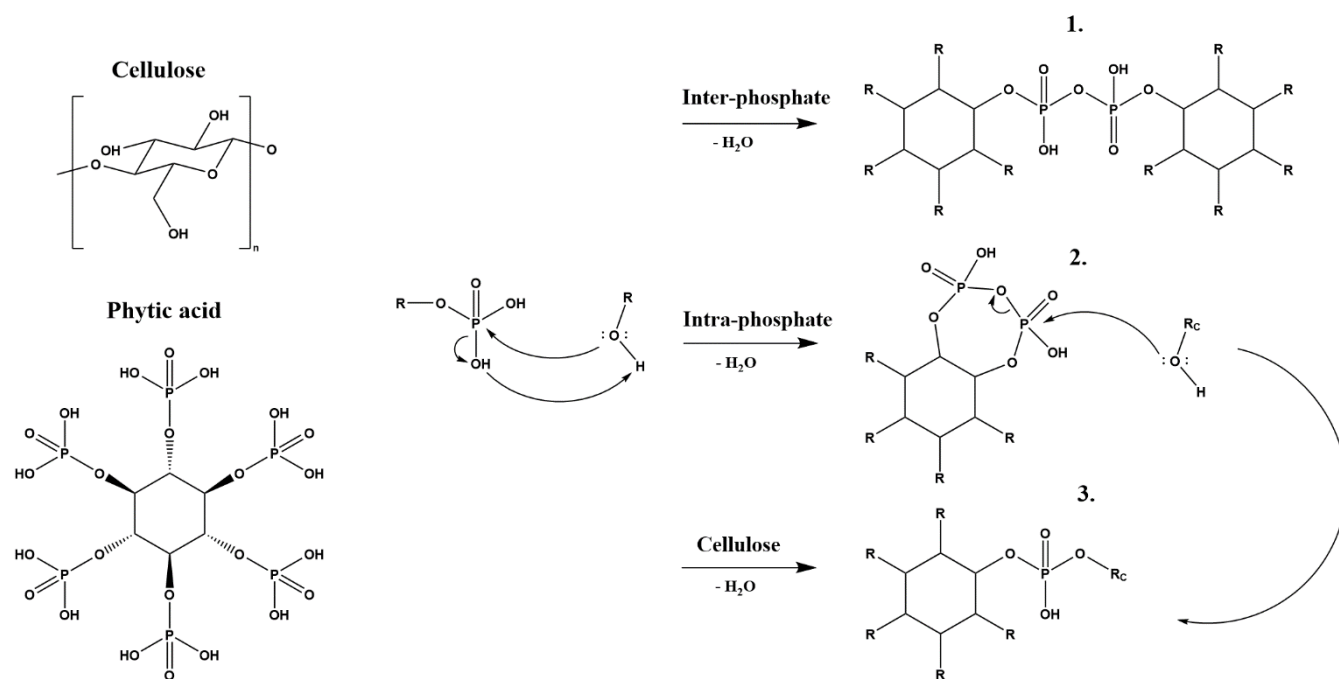


Figure 2. Molecular structures of cellulose and phytic acid with proposed mechanisms for dehydration condensation reactions between cellulose and phytic acid. The reactants are a phosphate group and either cellulose or another phytic acid molecule where R = either phosphate groups (PO_3H) or C2, C3 or C6 of cellulose. RC is defined as specifically C2, C3 or C6 of cellulose. Products 1, 2 and 3 are the proposed products of the reaction, depending on the mechanism of action described above the arrow. Product 2 is a highly reactive cyclic anhydride formed from intra-phosphorylation reactions, likely causing it to react further with cellulose generating product 3 as indicated with the arrow.

Results and Discussion

Covalent ester bonds from phosphorylation are formed via dehydration condensation reactions

A dehydration condensation reaction involves combining two molecules into one via the removal of water. In the present method, hydroxyl-rich phosphates from PA come into contact with both cellulose and other PA molecules. When hot-pressing or curing methodologies are then applied, a covalent cross-link between these molecules is formed as heat drives the removal of water. Figure 2 displays the proposed mechanisms and products which arise due to the dehydration condensation reactions between cellulose and phytic acid. Each mechanism depends on the environment and reactivity of nearby molecules. The high electronegativity of phosphorus in phosphate groups favors nucleophilic attack by both cellulose and other phosphate groups; hydroxyl groups on phosphates in particular being more nucleophilic. Thus, reaction product 1 is the most likely outcome when a high concentration of phosphates is present. However, the presented methodology involves a dilute system of phosphates and thus cellulose is also believed to undergo phosphorylation, generating product 3. An intra-phosphorylation reaction between phosphates is also possible in dilute systems, generating product 2. However, this structure is a highly reactive cyclic anhydride, similar to the product made when curing citric acid. The structure would be highly susceptible to nucleophilic attack by cellulose OH groups, thereby creating product 3 as shown by the curved arrow.

Dehydration condensation reactions can be verified by evaluating the intensity of the bands at 1630 and 3300 cm^{-1} in ATR-FTIR

spectroscopy (Figure 3). The band at 1630 cm^{-1} represents water bound to cellulose and phytic acid via hydrogen bonding while 3300 cm^{-1} describes the hydroxyl groups present on both cellulose and phytic acid. The band intensity at 3300 cm^{-1} was expectedly maximized on a cellulose substrate with phytic acid dried at room temperature (P20U). This in turn also maximizes the capacity for hydrogen bonding, increasing the intensity of the peak at 1630 cm^{-1} . When the substrate is cured by heating it at 160 $^{\circ}\text{C}$, bound water is evaporated, reducing this peak as seen in both the cellulose and cellulose with phytic acid (P160W and P160W). The intensity at 3300 cm^{-1} for P160W decreases below that of the substrate without PA (P160W), giving a strong indication that dehydration condensation reactions with cellulose hydroxyl groups have occurred and covalent ester bonds were formed. This can be further verified by the increase in ratio between the peak at 1060 cm^{-1} ($\delta_{\text{C-O-P}}$) and 915 cm^{-1} ($\delta_{\text{P-O-P}}$) for P20U and P160W.^{4, 21} As the ratio rises from 0.96 to 0.98, it indicates ester bonds to carbon are formed.

Inter-phosphorylation reactions between PA molecules generate product 1, a mechanism which is well supported in literature. This reaction may propagate, generating large oligo-phosphate chains provided sufficient nearby phosphates. However, we suggest two competing reactions which arise due to the low concentration of phytic acid distributed on the surface of the cellulose fibres. When phytic acid undergoes a dehydration condensation reaction, the phosphates change from being monoesters to di-esters. We can visualize this by tracking the shift of the monoester band at 1250 cm^{-1} to lower wavenumbers (1250-1210 cm^{-1}) for di-esters.²¹ In our system, we see a shift in the band from 1249 cm^{-1} (P20U) to 1243 cm^{-1} (P160W). The displacement of the band depends highly on the nature of the element forming the di-ester bond and the excess of unreacted phosphates.

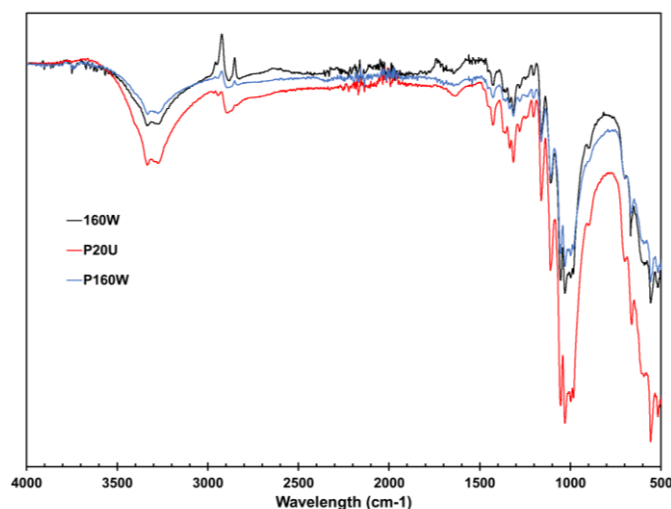


Figure 3. ATR-FTIR spectrum comparing a blank cellulose substrate exposed to 160 °C curing temperature and washed (160W), a substrate doped with phytic acid, cured at 160 °C and washed (P160W), and a substrate with phytic acid and dried at RT (P20U).

This effect can also be visualized in the solid state ^{31}P -NMR spectrum (Figure 4a). As the OH group on the phosphate changes to a covalent ester bond with either C or another P, a shift in the primary phosphorus peak to the right is expected as the phosphorus becomes more deshielded. However, NMR results provide no indication of whether the ester linkage is to hydroxyls attached to carbon or another phosphate group. Rather, it provides substantial evidence that PA phosphates change from mono to di-ester linkages and therefore the presence of product 1 is still likely and should not be discounted.

The ^{13}C -NMR spectra in Figure 4b indicate the formation of di-ester linkages. Upon closer inspection, the C2,3 peak at 75 ppm begins changing when curing temperature is increased. 160W represents a singular peak, while the P160W peak looks to be splitting. This split can occur when a phosphorus group is present across an ester bond, causing a $^2J_{\text{C-O-P}}$ coupling. C6 on cellulose is the most likely subject for phosphorylation due to its steric availability and reactivity thus it also shows a trend towards splitting when observing P120W and P160W peaks at 66 ppm in ^{13}C -NMR. These results support the hypothesis that a covalent ester bond is formed between cellulose and phytic acid via high temperature curing. The dilute nature of the system causes this analysis and other analysis methods to be challenging as shifts are minor, due to the bulk of the material staying intact from the influence of phytic acid.

Washing cured substrates reveals changes in cellulose crystallinity and phosphorus content

The addition of phytic acid to cellulose fibres caused changes in cellulose crystallinity and rate of drainage during the washing step. Crystalline domains of cellulose at C4 and C6 are indicated by broad peaks at 63 and 84 ppm in solid state ^{13}C -NMR (Figure 4b).²² The addition of PA to the cellulose substrates caused both of these peaks to decrease in intensity, with curing at 160 °C decreasing even further. The formation of gaseous phosphoric acids at 160 °C likely

degraded the crystalline moieties further. This degradation was also notable during washing steps, as the time required to drain the water and ethanol were reduced.

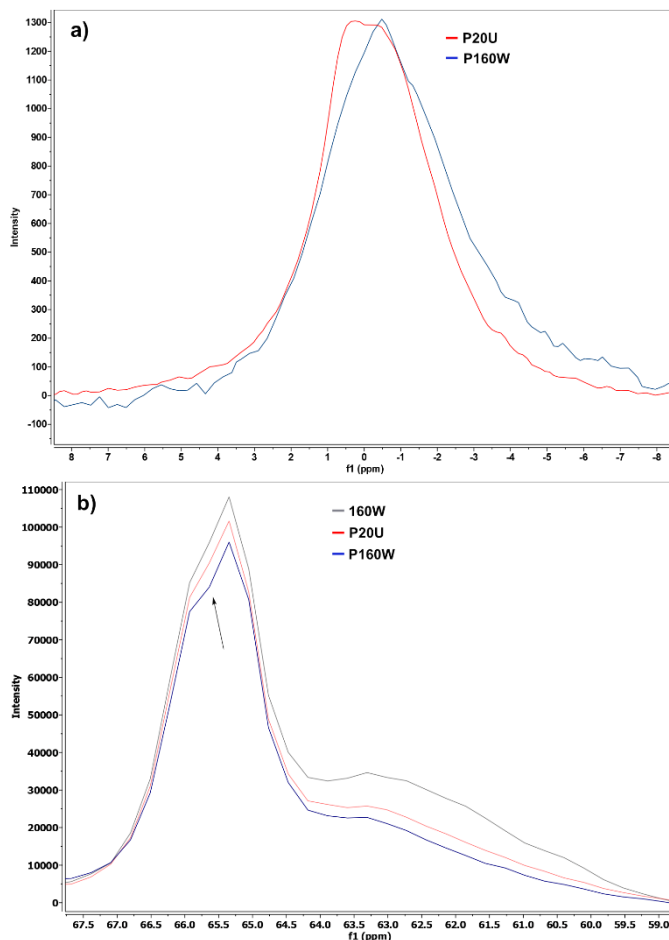


Figure 4. Stacked solid state NMR peaks of a) ^{31}P -NMR depicting a peak intensity shift from -0.45 ppm (P20U) to 0.24 ppm (P160W) after curing, and b) ^{13}C -NMR showing signs of cellulose C6 peak splitting indicated by the arrow and lower crystalline C6 intensity at 63 ppm. ^{31}P -NMR peaks were re-scaled to similar intensities and ^{13}C -NMR peaks auto-scaled to match interior crystalline moieties of C4 at 89 ppm.

Elemental analysis allowed quantification of phosphorus content retained on the substrates after washing. The decrease in of phosphorus content by washing was noticeably minimized on substrates treated with progressively high curing temperatures (Table 2). This result is further reflected by the higher intensity of the phosphorus signal in ^{31}P -NMR spectra. Notably, P20W substrates retained very little phosphorus, indicating that hydrogen bonding between phosphate and cellulosic hydroxyl groups was insufficient to retain PA on the fiber surfaces. Therefore, phosphorylation due to dehydration condensation reactions likely created covalently bound molecules which are increasingly difficult to remove from the cellulose matrix with higher curing temperatures. While covalent bonds to cellulose are proposed as the primary product of this reaction, the formation of inter-phosphorylated PA chains may create large structures which have reduced solubility in water and ethanol and are physical restrained within the cellulose network due to entanglements and frictional forces. This would also potentially allow phosphorus to be retained in the cellulose substrates without covalently bonding it to cellulose molecules.

Unwashed cellulose substrates also revealed a decrease in phosphorus content with increasing curing temperature. At 160 °C, PA molecules begin to degrade into phosphoric acids, with boiling points at similar temperatures. Thus, without a phosphorylation reaction, the phosphate groups would quickly evaporate. The fact that there is only a 0.36% loss in phosphorus content between P20U and P160U supports the hypothesis that this reaction is taking place. However, loss of 0.12% phosphorus in both P80U and P120U cannot be fully explained.

Table 2. Phosphorus content (%) elemental analysis of PA doped cellulose substrates.

	Unwashed	Washed
P20	1.78	0.05
P80	1.66	0.08
P120	1.65	0.27
P160	1.42	0.70

Flame-retardancy of cured PA substrates is retained after washing

The flame-retardancy mechanism of organophosphates and phytic acid is well understood. In general, the thermal stability of phytic acid is low in comparison to cellulose and other materials due to the hygroscopicity of the multiple phosphate groups. As temperature increases, the molecule begins to decompose, forming phosphoric acids. These acids catalyse the dehydration of cellulose, causing the onset of carbonization. As the accelerated carbonization of cellulose occurs, a char layer is formed on the surface of the fibers. This char creates a physical barrier against heat and oxygen, which prevents further degradation of the fibers.⁵

According to a study by Daneluti and Matos²³, the onset of phytic acid carbonization was found to be around 160 °C for pure phytic acid when analysed via thermogravimetric analysis (TGA). They also noted a visual darkening of the solution when the solution was treated at 150 °C, which they ascribed to carbonization of the phytic acid. We suggest that this carbonization reaction occurs gradually as temperature increases. The cellulose substrates displayed a progressive visual darkening at each higher curing temperature and TGA curves changed significantly (Figure 5a). Unwashed substrates doped with PA gradually rose in carbonization onset with increasing curing temperature as shown in Figure 5b. This indicates a reduction in the initial ability of the material to cause carbonization, which correlates well with the phosphorus content found in elemental analysis. However, the interesting point is the material properties after washing. As curing temperature increased, the change in property values was incrementally minimized (Figure 5). P160W in particular changed by less than 5% however this result lacks consistency when compared to the reduction of nearly 50% in phosphorus content found by elemental analysis in Table 2.

The weight loss once carbonization occurs is ascribed to the loss of OH groups. Here, there is again a clear trend of flame-retardant properties being retained with increased cross-linking degree. However, we do not observe a similar trend with regards to unwashed samples compared to carbonization. Here, the weight loss remains constant, indicating that the cross-linking of phytic acid and

to some extent the phosphorus content does not affect the formation of the char layer and the dehydration. At high temperatures in TGA we see that the combustion onset and residual weight follow the same trend as carbonization.

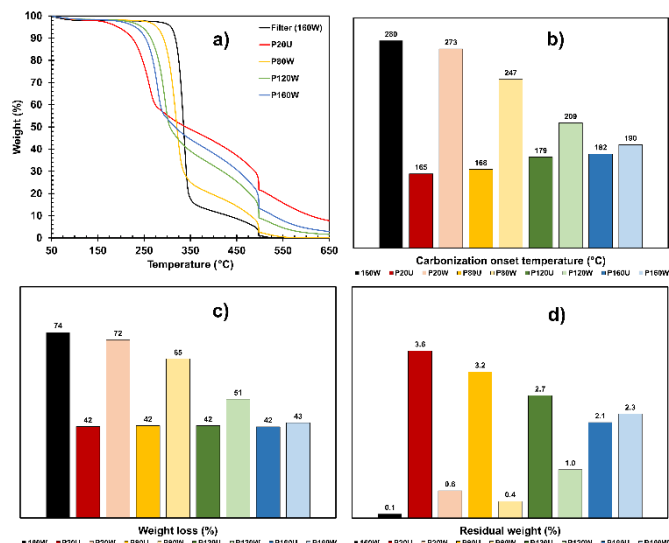


Figure 5. TGA analysis of cellulose substrates doped with phytic acid in air for a) carbonization onset temperature, b) weight loss in percent due to carbonization, c) residual weight in percent at 800 °C and d) the full TGA graph showing points of analysis. The number following P is the curing temperature while U are unwashed samples and W are washed.

Conclusions

Curing of phytic acid on cellulose substrates at temperatures up to 160 °C causes phosphorylation due to dehydration condensation reactions. The formation of large aggregated phytic acid structures is typically suggested in literature as the product of this reaction, however this work proposes the formation of covalent ester bonds between cellulose and phytic acid as the primary product in dilute systems. The result of these phosphorylation reactions is the formation of cellulose fibres which retain phosphate groups after washing. Curing at 160 °C was found to be the most effective temperature for phosphorylation, yet the formation of phosphoric acids at this temperature affects flame-retardant properties and crystallinity of the cellulose networks.

The drive towards using bio-based materials to functionalise cellulose fibres and fabrics has made phytic acid a promising option when functionalizing these materials towards flame-retardancy or metal chelation. Furthermore, using non-toxic processes to bind phytic acid to these substrates is the next developmental step necessary to lay out the foundation for future works using these concepts. Phosphorylation reactions with hydroxyl group containing substrates using curing or hot-pressing techniques will be essential toward progressing green practices and processes.

Keywords

Multifunctionality, polyphosphate, fire, flame retardant, drying, cellulose, FTIR, NMR, TGA,

Author Contributions

Elliott Orzan: Conceptualization, Methodology, Investigation, Writing- Original Draft, Writing – Review & Editing.

Stefan Spirk: Conceptualization, Writing – Review & Editing, Supervision

Aitor Barrio: Investigation, Writing – Review & Editing.

Tiina Nypelö: Conceptualization, Writing – Review & Editing, Supervision, Funding acquisition

Conflicts of interest

There are no conflicts to declare.

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