Department of Applied Physics

Biomimetics

Architectural Considerations for Functional Nanocomposites

Jason R. McKee

Aalto University

DOCTORAL DISSERTATIONS

Aalto University publication series
DOCTORAL DISSERTATIONS 2/2015

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Architectural Considerations for Functional Nanocomposites

Jason R. McKee

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Science, at a public examination held at the lecture hall E (Y124) of the school on 30 January 2015 at 12.

Aalto University
School of Science
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Aalto University publication series
DOCTORAL DISSERTATIONS 2/2015

ISBN 978-952-60-6034-7 (printed)
ISBN 978-952-60-6035-4 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)
http://urn.fi/URN:ISBN:978-952-60-6035-4

Unigrafia Oy
Helsinki 2015

Finland

441 697
Printed matter

Aalto University

Abstract

Aalto University, P.O. Box 11000, FI-00076 Aalto www.aalto.fi

Author
Jason R. McKee

Name of the doctoral dissertation
Biomimetics - Architectural Considerations for Functional Nanocomposites

Publisher School of Science

Unit The Department of Applied Physics

Series Aalto University publication series DOCTORAL DISSERTATIONS 2/2015

Field of research Applied Physics

Manuscript submitted 7 October 2014 **Date of the defence** 30 January 2015

Permission to publish granted (date) 24 November 2014 **Language** English

☐ **Monograph** ☒ **Article dissertation (summary + original articles)**

Abstract

This thesis will focus on synthetic nanomaterials that combine hard nanocellulose reinforcement with soft molecularly engineered synthetic polymeric components. The architectural designs have all been inspired by natural nanocomposites, such as silk, animal bone and plant fibres. Typically, the design of natural structures are built around hard reinforcing nanodomains bound together by energy dissipating sacrificial networks. These natural materials consist of proteins, carbohydrates or brittle minerals. Separately each component is usually mechanically weak; however, when combined in the balanced and hierarchical ways, each component will synergistically contribute towards mechanically excellent networks, by combining strength, toughness and stiffness.

Hence, one of the main focuses in this thesis will be the structural design of the constituting components and how they relate to the mechanical properties of the overall composites. Another key feature is the compatibility issues between the reinforcing nanocellulose with the synthetic supramolecular networks. Each material has been designed in a way that yields a homogeneous dispersion of all colloidal components. This allows more efficient reinforcment as well as allows the components to more effectively together. And finally, specific functionalities were engineered into the nanocomposite materials either through the supramolecular binding or by the use of functional polymers.

In Publication I, highly dynamic supramolecular nanocomposite hydrogels were developed that uniquely combine: high stiffness, approaching those of solid elastic networks; self-healing within seconds; and temporal stability, allowing for self-healing of the exposed surface areas even after prolonged storage.

In Publication II, biomimetic sacrificial bonds were chemically engineered into one-component nanocomposites. This resulted in engineered fracture energy dissipation, which considerably increased the toughness of the glassy nanocomposite.

In Publications III & IV, functional nanocomposite hydrogels were formed by linking colloidal nanocellulose by adsorbing functional polysaccharides onto the surface. In the first example, a thermoresponsive nanocomposite with switchable modulus was shown. In the second example, both the modulus and yield-strain were enhanced by adding an interconnected sacrificial network into the nanofibrillar network.

These nanocellulose-based nanocomposites demonstrate promising new concepts for material design as well as never before seen combinations of mechanical properties and functionalities.

Keywords nanomaterials, supramolecular self-assembly, polymers, colloids

ISBN (printed) 978-952-60-6034-7	**ISBN (pdf)** 978-952-60-6035-4	
ISSN-L 1799-4934	**ISSN (printed)** 1799-4934	**ISSN (pdf)** 1799-4942
Location of publisher Helsinki	**Location of printing** Helsinki	**Year** 2015
Pages 134	**urn** http://urn.fi/URN:ISBN:978-952-60-6035-4	

Aalto-yliopisto

Tiivistelmä

Aalto-yliopisto, PL 11000, 00076 Aalto www.aalto.fi

Tekijä
Jason R. McKee

Väitöskirjan nimi
Biomimetiikka - Tutkimuksia toiminnallisten nanomateriaalien rakenteista

Julkaisija Perustieteiden korkeakoulu

Yksikkö Teknillisen fysiikan laitos

Sarja Aalto University publication series DOCTORAL DISSERTATIONS 2/2015

Tutkimusala Teknillinen fysiikka

Käsikirjoituksen pvm 07.10.2014 **Väitöspäivä** 30.01.2015

Julkaisuluvan myöntämispäivä 24.11.2014 **Kieli** Englanti

☐ **Monografia** ☒ **Yhdistelmäväitöskirja (yhteenveto-osa + erillisartikkelit)**

Tiivistelmä

Tämä opinnäytetyö keskittyy synteettisiin nanomateriaaleihin, jotka yhdistävät kovan nanoselluloosavahvistuksen pehmeisiin toiminnallisiin synteettisiin polymeereihin. Kaikki työssä esiteltävät molekulaariset arkkitehtuurit ovat saaneet innoituksensa luonnon nanokomposiiteista, kuten silkistä, luusta ja kasvikuiduista. Luonnonmateriaalit koostuvat tyypillisesti vahvistavista nanokokoisista alueista, jotka on sidottu yhteen supramolekulaarisilla uhrautuvilla sidoksilla. Niiden rakennusaineina ovat proteiinit, hiilihydraatit ja hauraat mineraalit. Komponentit ovat erillään yleensä mekaanisesti heikkoja, mutta sopivissa hierarkkisissa rakenteissa ne tasapainottavat ja tukevat toisiaan.

Näin ollen työn tärkeimpiä sisältöjä on edellä mainittujen nanokomposiittien osien rakenteellinen suunnittelu, jotta halutut mekaaniset ominaisuudet voidaan saavuttaa. Yhteensopivuusongelmat vahvistavan nanoselluloosan ja synteettisten supramolekulaaristen verkkorakenteiden välillä ovat myös yksi keskeinen teema. Jokainen materiaali on suunniteltu niin, että kaikki kolloidaaliset komponentit saadaan homogeenisesti dispergoiduksi polymeeriverkostoon. Tällöin verkkorakenne saadaan mahdollisimman tehokkaasti vahvistettua ja toimimaan samalla yhteen luonnon inspiroiminen supramolekulaaristen verkkorakenteiden kanssa. Lopuksi, nanokomposiitteihin saatiin spesifisiä funktionaalisuuksia supramolekulaarisen sitoutumisen tai funktionaalisten polymeerien avulla.

Ensimmäisessä julkaisussa kuvataan hyvin dynaaminen supramolekulaarinen nanokomposiittihydrogeeli, joka on hyvin jäykkä, kuten kiinteät elastiset verkkorakenteet, itsekorjautuu sekunneissa ja kykenee korjaamaan itsensä vielä pitkän säilytysajan jälkeenkin.

Toisessa julkaisussa yksikomponenttisia nanokomposiitteja muokattiin biomimeettisillä uhrautuvilla sidoksilla. Murtumisenergian dissipaation lisääntyessä lasimaisen nanokomposiittien sitkeys parani huomattavasti.

Kolmannessa ja neljännessä julkaisussa valmistettiin funktionaalisia nanokomposiittihydrogeelejä. Kolloidaalista nanoselluloosaa ristisilloitettiin fysikaalisesti adsorboimalla funktionaalisia polysakkarideja niiden pinnalle. Ensimmäiseksi valmistettiin lämpöherkkä nanokomposiitti, jonka moduulia voitiin muuttaa lämpötilan funktiona. Toiseksi sekä moduulia ja myötärajaa parannettiin lisäämällä nanofibrillaariseen verkkorakenteeseen itselinkittynyt uhrautuva verkkorakenne.

Nämä nanoselluloosaan perustuvat materiaalit tuovat lupaavia uusia konsepteja nanomateriaalien kehittelyyn sekä ennennäkemättömiä mekaanisten ominaisuuksien ja toiminnallisuuksian yhdistelmiä.

Avainsanat nanomateriaalit, molekylaarinen itseohjautuminen, polymeerit, kolloiditt

ISBN (painettu) 978-952-60-6034-7 **ISBN (pdf)** 978-952-60-6035-4

ISSN-L 1799-4934 **ISSN (painettu)** 1799-4934 **ISSN (pdf)** 1799-4942

Julkaisupaikka Helsinki **Painopaikka** Helsinki **Vuosi** 2015

Sivumäärä 134 **urn** http://urn.fi/URN:ISBN:978-952-60-6035-4

"I almost wish I hadn't gone down that rabbit-hole – and yet- and yet – it's rather curious, you know, this sort of life. When I used to read fairy-tales, I fancied that kind of thing never happened, and now here I am in the middle of one!"

-Alice

Acknowledgements

It is really hard to put into words my current feelings regarding the last three years. Perhaps the most apt description that comes to mind is a 'panicky blur', which is especially accurate for the last year or so. Now, do not get me wrong, I have immensely enjoyed working on my PhD and these have been the greatest years of my life. Yet, my full focus has been on this one goal since September 2011 and it feels like I never really sat down to think and plan the next steps. Rather, I have just pushed everything forward and improvised along the way. At this point, I should probably stop to enjoy the relief and make some plans… or wonder off to do something completely different with the same 'let's jump off a cliff and see what happens' mentality that I have followed pretty much my entire adult life. Details are not really my thing.

This thesis has been a massive undertaking and the number of people that have been a part of all this is truly staggering. You all have my most sincere thanks. Academy professor Olli Ikkala, thank you for everything. Thank you for unshackling my thoughts and allowing me the freedom I needed to pursue them. Thank you for all the help in highlighting and simplifying our message. I would never have achieved so much without your guidance and tutelage. Although things got a bit hectic at times and we were both on the point of breaking, we managed. I am currently leaving Molecular Materials to seek out my own fortunes. However, wherever I end up I hope we can continue to work together, as when all is said and done, this journey has been really fun.

This thesis comprises four articles, all of which have been done in collaboration with other groups. Hence, I would extend my most gracious thank you to Professor Heikki Tenhu and Dr. Oren Scherman for welcoming me to work with your groups and all the help you have offered. I would further like to thank Professor Tenhu for bringing me into the world of polymer chemistry and showing me that polymers are so much more that just plastic bags. It has been my pleasure working with both of you. I would also thank Professor Eero Kontturi, Professor Janne Laine, Professor Janne Ruokolainen and Dr. Sami Hietala for all the help and teaching on the materials and methods that I have used during the thesis. I would also extend my gratitude to Professor Robin Ras, Professor Mauri Kostiainen and Dr. Vladimir Aseyev for all the discussions, help and suggestions you offered me over the years. Dr. Vincent Ladmiral and Dr. Mona Semsarilar, thank you for your tutelage when I started working in academia all those year ago. Dr. Eric Appel and Emma-Rose Janecek, thank you for all the help you offered in our joint projects and for

making my stays at Cambridge so pleasant and productive. Mikko Karesoja, thank you for all the help and collaboration throughout my studies. Johanna Majoinen, Johannes Huokuna, Henna Rosilo, Lahja Martikainen, Dr. Marjo Kettunen, Dr. Antti Nykänen, Dr. Virgínia Silva Nykänen and Dr. Jani Seitsonen thank you for all the help you offered throughout this thesis as well as the collaboration between projects. Especially Johannes, the work you did can only be described as phenomenal. Timo Kajava and Orvokki Nyberg, thank you both for keeping the laboratory up and running smoothly. I can only wish you all best and hope we can continue to work together in the future, wherever that may take us.

I would like to extend my gratitude to Professor Sirkka Liisa Maunu and Professor Wim Thielemans for your preliminary examination of this thesis. Your comments and suggestion were invaluable and have helped shape this thesis into a much clearer and concise whole. Professor Lars Berglund, you have my most sincere thanks for accepting our invitation to be my opponent. I can only hope that we have a productive discussion when the time comes.

Room 15a: Jenni Koskela, Jukka Hassinen, Ville Liljeström, Tuukka Verho, Dr. Jaakko Timonen and Riikka Koski thank you for all the support, for keeping the insanity in check and that things did not get too strange over the years. The concept of locking large numbers of enthusiastic grad students into a tightly packed space has apparently paid off as we have all done some spectacular work. Though at the end, it seemed like only the bravest of professors dared enter our lair. I would also acknowledge everyone from our group Molecular Materials as well as everyone I have worked with from the Soft Matter and Wetting as well as the Biohybrid Materials groups. I wish you all the best.

I would thank the people who know me the best, my parents, Howard and Tuula as well as my sister Emma (+ dogs). You always encouraged me to pursue my own dreams and never forbade me anything, except to become an engineer in the forest or paper industry. Chalk that up to latent ‘teen rebellion’ or very cunning reverse psychology. I would also thank my grandparents, aunts, uncles and cousins for all the support and patience during the last few years. Thank you all for everything.

Finally, I would offer my most heartfelt thanks to my fiancée Tiina. If there is one person who knows how this process has shaped and changed me, it is you. Thank you for all the encouragement and support. I could not have done this without you. I can only hope that when you start working on your thesis I can be there for you.

Helsinki, 13 December

Jason McKee

Table of Contents

List of Publications

This doctoral dissertation consists of a summary and of the following publications, which are referred to in the text by their numerals

I. **McKee, J. R.**; Appel, E. A.; Seitsonen, J.; Kontturi, E.; Scherman, O. A.; Ikkala, O. Healable, Stable and Stiff Hydrogels: Combining Conflicting Properties Using Dynamic and Selective Three-Component Recognition with Reinforcing Cellulose Nanorods. *Advanced Functional Materials* **2014**, 24, 2706.

II. **McKee, J. R.**; Huokuna, J.; Martikainen, L.; Nykänen, A.; Karesoja, M.; Kontturi, E.; Tenhu, H.; Ruokolainen, J.; Ikkala, O. Molecular Engineering of Fracture Energy Dissipating Sacrificial Bonds Into Cellulose Nanocrystal Nanocomposites. *Angewandte Chemie Int. Ed.,* ***2014****,* 53, 5049.

III. **McKee, J. *R.;*** Hietala, S.; Seitsonen, J.; Laine, J.; Kontturi, E.; Ikkala, O. Thermoresponsive Nanocellulose Hydrogels with Tunable Mechanical Properties. *ACS Macro letters,* ***2014****, 3, 266.*

IV. Janecek E-R.; **McKee, J. R.**; Cindy C. Y. Tan; Nykänen, A.; Kettunen, M.; Ikkala, O.; Scherman, O. A. Hybrid supramolecular and colloidal hydrogels bridging length scales. *Manuscript is under review at Angewandte Chemie Int. Ed.*

Author's other contributions to articles related to combining functional polymers with colloidal chemistry:

V. **McKee J. R.**; Ladmiral V.; Niskanen J.; Tenhu H.; Armes S. P.; Synthesis of Sterically-Stabilized Polystyrene Latexes Using Well-Defined Thermoresponsive Poly(N-isopropylacryl-amide) Macromonomers. *Macromolecules* **2011**, *44*, 7692.

VI. Majoinen J.; Walther A.; **McKee, J. R.**; Kontturi, E.; Aseyev, V.; Malho, J. M.; Ruokolainen, J.; Ikkala, O. Polyelectrolyte Brushes Grafted from Cellulose Nanocrystals Using Cu-Mediated Surface-Initiated Controlled Radical Polymerization *Biomacromolecules* **2011**, *12*, 2997.

VII. Rosilo, H.; **McKee, J. R.**; Kontturi, E.; Koho, T.; Hytönen, V. P.; Ikkala, O., Kostiainen, M. A. Cationic polymer brush-modified cellulose nanocrystals for high-affinity virus binding. *Nanoscale* **2014**, *6, 11871*.

Author's Contribution

Publication I: *Healable, Stable and Stiff Hydrogels: Combining Conflicting Properties Using Dynamic and Selective Three-Component Recognition with Reinforcing Cellulose Nanorods.*

The author designed the architecture and synthesized all the components together with E.A.A. All characterization and measurements were done together with E.A.A, excluding the cryo-TEM imaging and elemental analysis. The author wrote the first draft with E.A.A. and finalized the manuscript together with E.A.A., O.A.S. and O.I. First authorship is divided between E.A.A. and the author.

Publication II: *Molecular Engineering of Fracture Energy Dissipating Sacrificial Bonds Into Cellulose Nanocrystal Nanocomposites.*

The author designed the architecture. The synthesis and characterization was performed together with J.H, excluding the TEM imaging and elemental analysis. The author wrote the first draft and finalized the manuscript together with O.I.

Publication III: *Thermoresponsive Nanocellulose Hydrogels with Tunable Mechanical Properties.*

The author designed the architecture together with E.K. All the samples and measurements were done by the author, excluding the cryo-TEM imaging. The author wrote the first draft and finalized the manuscript together with E.K. and O.I.

Publication IV: *Hybrid supramolecular and colloidal hydrogels bridging length scales.*

The author designed the architecture and synthesized all the components together with E-R. J. All characterization and measurements were done together with E-R. J, excluding the cryo-TEM imaging. The author wrote the first draft with E-R. J. and finalized the manuscript with E-R. J., O.A.S. and O.I. First authorship is divided between E -R. J. and the author.

1. Introduction

1.1 Thesis Outline

All results and discussions within this thesis revolve around the general concept of combining supramolecular chemistry with polymer networks, which are reinforced with colloidal cellulose nanocrystals (CNC) or nanofibrillated cellulose (NFC). One of the main focuses will be constructing architectures that combine molecular and colloidal components. Typically, the discussed architectures demonstrate enhanced mechanical or rheological properties due to nanocellulose reinforcement as well as molecularly engineered functionalities through specific synthetic polymer networks. Moreover, this work also addresses issues of chemical compatibility between the colloidal nanocellulose reinforcement and the matrix polymer, together with discussion on why compatibility should always be a central issue when designing new nanomaterials. Another central aspect of this thesis is the study of supramolecular interactions, which bind the polymer networks - how these physical bindings affect the mechanical properties in addition to imparting functionality. These aspects were studied for both supramolecular nanocomposite hydrogels as well as dry supramolecular nanocomposites.

This thesis consists of four chapters that explain the background of the ideas and suggestions behind publications I – IV. They explain why the architectures were synthesized as they were as well as the selection of components.

Chapter 1 introduces the components used in publications I-IV. It illustrates the chemical and physical properties of nanocellulose; a brief overview on polymer chemistry and synthetic methods; polymer networks; and finally an introduction to supramolecular chemistry as a way to bind networks together.

Chapter 2 introduces natural structures. This chapter mainly focuses on how the structures of natural nanocomposites affect their mechanical properties and functionalities. The discussion will mainly encompass the materials that inspired publications I-IV. It also highlights the complexity of natural structures and how exact replication is difficult to engineer, not to mention scaling up. It also contains examples of sacrificial networks.

Chapter 3 consists of ideas and suggestions on how to use natural materials as templates for synthetic materials through Publications I-IV. Also, this chapter will focus on the main challenges regarding the design and fabrication of new nanocellulose-based nanocomposites as well as the compatibility issues between nanocellulose and synthetic polymers.

Finally, *Chapter 4* will offer final conclusions and an outlook on the future of biomimetic nanocomposites, in general.

1.2 Nanocellulose

In nature, cellulose in its native form is located in large cellulose fibres. These fibres consist of bundles of smaller nanocomposite cellulose microfibrils (CMF), which contain crystalline cellulose, amorphous hemicelluloses and lignin (Figure 1.1).[1,2] The lateral dimensions of these large fibres are in the region of 20-60 µm, with lengths up to thousands of micrometers – whereas the single microfibrils are 5-30 nm thick.[3] The larger cellulose fibres consist of bundles of microfibrils; however, the microfibrils themselves are more organized. In the centre, there are ordered crystalline cellulose nanofibrils, which are bound together with hemicelluloses and lignin. The outer shell further consists of hemicellulose and lignin to bind the microfibrils together to form the larger fibre bundles.[1] It is these highly crystalline cellulose nanofibrils located within the microfibrils that have drawn the attention of material scientists over the last decade.[4] They are known as cellulose nanofibrils and form the elemental nanocellulose component from which all the plant based native nanocellulose constituents are extracted.

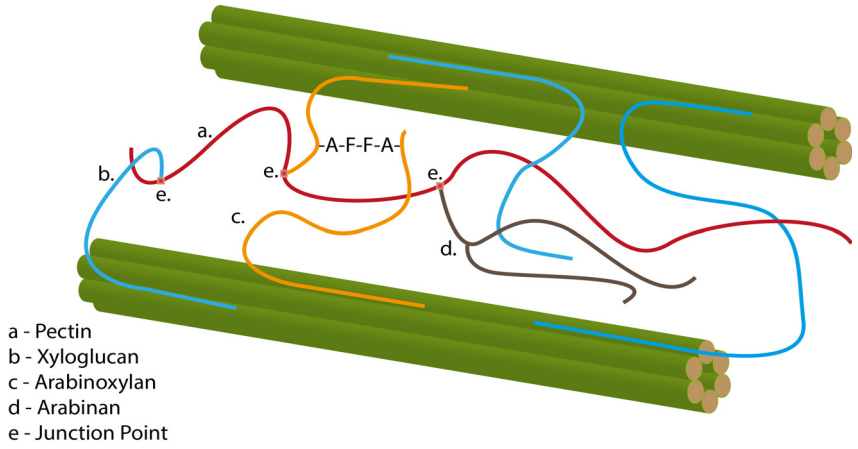

Figure 1.1. Schematics of cellulose microfibrils and their binding with soft hemicellulose biopolymers (Xyloglucan (blue) and Arabinoxylan (orange)). The hemicellulose strands have adsorbed to the cellulose microfibril surface and bound them together, by cross-linking with pectin (red) and by ferulic acid esters (A-F-F-A). The image has been adapted from T. Cosgrove, Nat. Mol. Cell Bio 2005, 6, 850. [1]

'Nanocellulose' is a fairly broad term that comprises numerous kinds of native nanofibrillar cellulose materials.[3-5] The main composition consists of a hierarchical assembly of cellulose chains aligned parallel to each other into a crystalline α-cellulose conformation. The lateral dimensions of single elementary nanofibrils are 3-5 nm while the lengths range between a few hundred nanometers to the micron scale - depending on the source material and extraction process. Elementary nanofibrils are extracted through a fairly simple process of sequential acid- and base-washes after the large fibres located in the cell walls are unravelled using mechanical shear. Single nanofibrils are obtained by fibrillation process, wherein high shear-forces mechanically break down the microfibrils into their base nanofibrillar structure.[6] Generally, this is done via numerous cycles of high-pressurized homogenization, which will yield a network of high aspect-ratio cellulose nanofibrils called nanofibrillated cellulose (NFC) – alternatively defined as cellulose nanofibres (CNF) or microfibrillated cellulose (MFC).

1.2.1 Nanofibrillated Cellulose

Single nanofibrillated cellulose fibrils have lateral dimensions in the range of some nanometers and lengths up to the micron scale. These high aspect-ratio fibrils consist of long cellulose I crystalline domains where cellulose chains are hierarchically aligned parallel to each other.[1,3] Between these well-defined crystalline domains are amorphous regions, which affect the rigidity of the colloidal fibril.[5,7,8] NFC fibrils have excellent mechanical properties, due to the grossly hydrogen bonded crystalline domains, with modulus values up to ~140 GPa and a tensile strength in the range of several GPa - approaching those of metals.[9]

Due to the high aspect ratio, NFC readily forms entwined colloidal networks. Hydrated networks of native NFC form strong hydrogels at low solids contents. At ~0.1 wt.% there is clear viscoelastic behaviour and at ~1 % the system behaves like an elastic hydrogel network, with dominating elastic modulus (G') across a broad frequency range.[10] Strain sweeps, on the other hand, demonstrate a classic shear-thinning behaviour, which is especially important for processing. Moreover, due to the rigid colloidal fibrils, NFC-based hydrogel networks demonstrate promoted storage modulus and viscosity at relatively low solids content. It should be noted that the rheological properties of nanocellulose-based hydrogels varies depending on the extraction process; degree of fibrillation; degree of crystallinity; solids content; and any other possible chemical treatment (e.g. TEMPO oxidation or carboxymethylation).[11,12] An example from Publication IV shows how a well-fibrillated (20 homogenizer cycles) sample of NFC at 1 wt.% will give a zero-shear modulus value of roughly 200-300 Pa, as determined by strain-sweeps at a frequency range of 10 s^{-1}.

At these conditions, shear-thinning will begin at roughly 20-30 % strain - indicating a very stiff, yet highly shear thinning network.

Due to the high stiffness and shear-thinning behaviour, nanocellulose can be considered for numerous applications in the food, drug, chemical and cosmetics industries as thickeners.

1.2.2 Cellulose Nanocrystals

Cellulose nanocrystals (CNC) are obtained by strong acid hydrolysis of the amorphous regions of nanocellulose fibrils, leaving only the crystalline region intact.[7,8,13] After acid hydrolysis, the resulting rod-like nanocrystallites tend to have lateral dimensions of 5-10 nm and lengths ranging from 50 to 1000 nm, with the dimensions primarily depending on the celluloses' origin. Publications I, II and III used CNCs extracted from Whatman's cotton filter paper hydrolysed using sulphuric acid.[14] The resulting sulfate CNCs have lateral dimension of 7 nm and lengths ranging from 50 to 300 nm. Due to the sulphuric acid treatment, the CNC surface areas were dotted with sulfate groups, providing the colloid a negative charge and thus excellent electrostatic stability in water.[15] Unlike NFC, CNCs do not form networks as easily due to their relatively low aspect ratio and in the case of sulfate CNCs, electrostatic stability.

The mechanical properties of CNCs are comparable with NFC.[16] Together with the good mechanical properties and their rod-like shape, CNC offer an exciting possibility for nanoreinforcement towards composite materials.[4,17] Indeed, to date CNCs have been successfully used as nanofillers in numerous functional nanocomposite materials.[18-21]

1.3 Synthetic Polymers

Publications I - IV demonstrate new methods on how to combine functional polymers with nanocellulose to make mechanically enhanced functional nanocomposites. Polymers are long molecules consisting of smaller repeating units.[22,23] Depending on the chemical properties of the repeating units, chain configuration and molecular weight – polymers can be tailored for a wide range of applications. Due to their size, they should, however, be approached from both a chemical and physical perspective. Polymer chemistry focuses on how to synthesize polymers and how their chemical structure can be tuned towards specific properties.[22] It also explains the coils chemical compatibility between themselves, other polymers and any possible solution or filler material. Polymer physics, on the other hand, explains how the polymer coils behave in different conditions; how the coil's conformation, dynamics or rigidity change

at different concentrations, solutions, temperature, pH, or ionic strengths.[23,24] These changes naturally affect the materials' properties and as such understanding them plays a central role in designing new functional materials.

One important chemical and physical aspect, with regards to this thesis, is how the polymers interact with natural colloidal fillers, which in many cases are chemically incompatible. Indeed, one of the main questions asked throughout the thesis is: how to homogeneously combine all the components in a manner that allows enhanced mechanical properties and simultaneously does not disrupt other possible functionality requiring dynamics at the molecular scale, such as self-healing. The other important aspect is how to effectively engineer said functionalities into materials, either through specific functional pendant groups or through functional polymers.

1.3.1 Polymer synthesis

Numerous polymerization methods have been devised to polymerize different types of monomers into different chain configurations.[22,23] The choice of polymerization method is non-trivial, as some methods work better with specific monomers while others allow for more diverse architectures. Some methods might yield more well-defined polymers, whereas others might be faster and cheaper. Considering the used monomers and final architectures, this thesis focuses solely on the free radical polymerization (FRP) and atom transfer radical polymerization (ATRP) of acrylamides (CH_2=CH-CO-NH-R), styrenics (CH_2=CH-Ph-R), acrylates (CH_2=CH-CO-O-R) and methacrylates (CH_2=C(CH_3)-CO-O-R).

Free Radical Polymerization

Free radical polymerization (FRP) is a classic method to quickly produce polymers from vinylidene motifs.[22] These monomers contain reactive vinyl groups (CH_2=CH-R), which can be activated either by radical initiators or active free-radical chain-ends. Once activated, the vinyl group will undergo rearrangement leading to sequential monomer addition, i.e. kinetic chain-growth until termination or radical chain transfer of the active centre of growth. In more detail, FRP consists of three specific stages: *(1) initiation,* wherein radicals are generated into the system, which activate centres of growth. *(2) Propagation*, wherein such centres of growth lead to macromolecular chains via the kinetic chain mechanism. And finally, *(3) termination* of the active chain ends either by combination of two active chain ends; disproportionation of the centre of growth; or reaction with any impurity, solvent or added chain-transfer agent. It should be noted that new chains are constantly

initiated and terminated over time. This means that once the reaction has been equilibrated to the reaction temperature and a steady radical flux is reached, the reaction will form new polymers with roughly the same chemical composition and molecular weight throughout the steady state phase. In other words, the reaction will continue at a steady state until either the initiator runs out or the monomer feed decreases due to low monomer concentration.

The chains' mean composition and molecular weights can be somewhat optimized, for example, by changing the stoichiometric ratios of [monomer]/[initiator] or by addition of a chain transfer agent. However, the final chains tend to have broad molecular weight distributions due to the highly reactive and unpredictable free radicals and possible chain-transfer reactions.[22] On the other hand, FPR allows for fairly long chains and the reactions are easy set up, requiring at the very least only an initiator and monomer. Moreover, due to the aggressive and non-selective nature of free radicals, FRP allows for a broad range of vinylidenes. For example, if the monomer side-group has a charge or proton donor/acceptor, it can complex with a metal-ligand catalyst, leading to the inhibition of chain-growth. With FRP this is rarely a problem. Regarding this thesis, the methyl-viologen (MV) based monomer used in supramolecular complexations is an electropositive π-conjugated monomer that can only be polymerized by aggressive FRP (Publication IV). Otherwise, it has to be added later on to a ready polymer as a side-group or end group(s), for example using nucleophilic addition (Publication II).

Atom Transfer Radical Polymerization

Over the last two decades, controlled radical polymerization (CRP) has revolutionized polymer chemistry.[25,26] Unlike FRP, CRP provides a degree of control over the polymerization, which allows for narrow molecular weight distributions, more specific molecular weights and more well-defined chains. Although there are numerous types of CRP mechanisms, this thesis will focus on atom transfer radical polymerization (ATRP), which is based on the well-established atom transfer radical addition (ATRA) cycle. ATRA proceeds via an activation de-activation equilibrium cycle, wherein a dormant alkyl halide (P-X) is activated by a transition metal-ligand complex (X(I)Y-L) (Figure 1.2). The active alkyl chain subsequently forms a radical ($P^{\cdot}$), which propagates via kinetic chain growth, similarly as FRP propagation. However, the active chain end will very quickly be capped off with the halide (P-X) - finishing off a single cycle during which, roughly, a few monomers are added to the chain. For a successful ATRA process, the equilibrium should lean heavily towards the de-active state (P-X), i.e. $[P\text{-}X] >> [P^{\cdot}]$.[27] Indeed, a FRP might only take 1 s from initiation to termination. ATRA chain growth, on the other hand, can take from anything between 10 minutes up to a few days depending on the reaction parameters. Unlike FRP, the molecular weight will grow as a function of time by first-order kinetics.[27] It should be noted that this process does not remove

uncontrolled chain-transfer reactions during the active phase – rather the activation-deactivation cycle allows for enough control that all the active chains will slowly grow together until the reaction is stopped or the monomer feed ends. This leads to narrow molecular weight distributions and better control over the final molecular weight. Also, this method allows for complex architectures, such as surface-initiated (SI) grafts[28], block-copolymers, and telechelic polymers.[25,26]

Atom transfer radical polymerization, more specifically, utilizes a broad range of Br or Cl – based alkyl halide initiators together with transition metal (Ni, Pd, Rh, Ru, Mo and most notably Cu) salts complexed with specific ligands (most notably nitrogen based).[29] It is a highly versatile and effective method to polymerize a broad range of acrylamides, styrenics, acrylates and methacrylates in a broad range of solvents. This allows for considerable freedom in tailoring polymers and complex architectures.

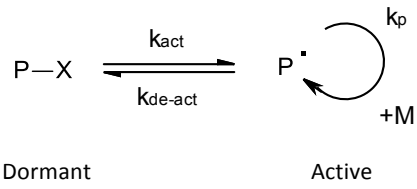

Figure 1.2. The basic mechanism for the activation de-activation cycle for the atom-transfer process.[25] Here, k_{act} is the activation rate constant, $k_{de\text{-}acd}$ is the deactivation rate constant, k_p is the rate constant of chain propagation, $+M$ is the addition of monomer units during the active state.

1.3.2 Chemical Modification of Cellulose Nanocrystals

Rod-like cellulose nanocrystals (CNC) form one of the main reinforcing components within this thesis. Pristine CNCs can be used as they are, in some cases, to reinforce soft polymer matrixes (Publication III).[17] However, to simultaneously embed functionality and increase the compatibility between CNCs and other components, polymer grafts have been shown to work superbly (Publications I & II). [30,31]

There are two main pathways to graft polymers onto surfaces: the 'grafting to' and the 'grafting from' methods.[28] With the grafting to method, polymers are first synthesized and then attached to the surface via a multifunctional linking agent. As the polymers are first synthesized separately, they tend to be more well-defined. Moreover, end-group and side-group modifications are more effective for free polymers than grafts, allowing for more uniform modification along the backbone. The drawbacks of this method are arduous synthetic procedures before the linking, which can include both chemical modifi-

cation of CNCs and end-group modification of the polymer. Additionally, there might be chemical incompatibilities between the surface and free polymer. Finally, the overall grafting densities might remain low due to steric hindrances.

Grafting to, on the other hand, relies on multifunctional initiators attached to the surface from which the grafts are polymerized.[30-33] This method was used in Publications I & II. The main advantage here are that the compatibility issues can easily be circumvented using this method. With CNCs, chemical compatibility is crucial and should always be taken into account whenever modifying surface areas.[20] Therefore, an ATRP-initiator bromo-isobutyryl bromide (BiBBr) was attached employing a two-step procedure in Publication I.[30] First, esterification in the vapour phase, i.e. chemical vapour deposition (CVD), to add small amounts of the multifunctional initiator. This process hydrophobized the CNC surface, allowing for further solvent esterification in dimethylformamide (DMF), finally yielding colloidal macroinitiator with a set of ATRP initiator motifs attached to the surface. Publication III, however, used only the CVD process, as this was found to be advantageous with regard to the mechanical properties.

Surface-initiated ATRP (SI-ATRP) is a powerful tool in coating surfaces with functional polymers.[28,34-36] Typically SI-polymerizations have drawbacks, mainly interpolymer chain-transfer, which can lead to a chemically cross-linked networks. According to Flory's gelation theory, it only requires one interparticle termination per chain or roughly 0.1 % occurrence to form microscopic gels.[23] This can be quite predominant within densely growing polymer brush, especially in the later phases of the polymerization where monomer diffusion can be hampered due to the surrounding polymer. In this regard, SI-ATRP has proven to be an effective tool, as the ATRA cycle shields the active chain-end from excessive cross-linking with neighbouring chains. More importantly, the slow chain propagation allows monomer to diffuse within the brush allowing for a steady feed and thus, a more uniform growth. SI-ATRP can be done for a plethora of nanoscale colloids, such as metal nanoparticles, silica particles, and CNCs.[37]

Regarding chemical compatibility, SI-ATRP is a highly effective method to change the chemical nature of the anionic CNCs.[38] Publication I demonstrates how to attain a dense cationic brush onto the anionic surface, whereas Publication III demonstrates how to graft a hydrophobic brush onto the hydrophilic surface. The material properties with regards to the grafts properties will be discussed later on in Chapter 3.

1.4 Supramolecular Chemistry

Supramolecular chemistry refers to the binding of smaller chemical constituents to form larger assemblies through weak reversible binding forces.[39] These forces include hydrogen bonds, hydrophobic interactions, Van-der-Waals forces, π- π-interactions and different types of electrostatic interactions. Through these forces, a plethora of different kinds of bindings, complexes, molecular assemblies and architectures have been realized.[40,41]

Molecular self-assembly is one of the most utilized notions in supramolecular chemistry.[39,42,43] Here, systems and architectures are formed without any guidance other than the surrounding environment through competing interactions, drawing them into energetically favourable conformations and packing.[41] Molecular self-assembly with polymers is divided into two main categories. Intramolecular self-assembly focuses on synthetic or biological polymers folding upon themselves. An excellent example here are proteins, which fold upon themselves to make highly specific structures through a wide range of supramolecular and competing interactions, such as hydrogen bonds, hydrophobic interactions and electrostatic interactions. Synthetic single-polymer self-assemblies have also been realized.[44] In contrast, intermolecular self-assemblies are much larger structures formed from numerous polymers communicating with each other through supramolecular interactions. Excellent examples are block-copolymers, which form periodic packing.[40] Viruses are also formed from proteins assembled into specific capsids-like structures.[45] Polymer micelles and vesicles are also formed through similar interactions, though these structures tend to be less well-defined.[46]

To successfully design a functional supramolecular architecture, there are important considerations that need to be addressed regarding the binding type, selectivity, equilibrium, degree of coupling and dynamics. [47-49] Therefore, the following aspects should all be carefully considered.

1.4.1 Supramolecular Binding

In addition to the different forces applied in the binding, there are also different types of binding modes (Figure 1.3).[48] Some are 'self-complementary', which bind or associate with chemically equivalent moieties. These units can either bind through dimerization (A:A) or through 'stacking', wherein 'double-sided units (A:B) bind, for example, via π- π-interactions or hydrogen bonds (e.g. urea stacking).[50,51] Special care needs to be taken with self-complementary groups, as there is always the danger of intramolecular binding within single chains, which can be detrimental for network formation. In contrast, 'complementary binding' occurs when two or three complementary components bind together. Two-component binding occures when two chemically different groups bind together (A:B), such as base-pairs in DNA,

two-component host-guest chemistry (e.g. cyclodextrins) or with electrostatic cationic-anionic interactions.[52-54] Three-component binding, on the other hand, requires a linking agent to bridge two chemically similar or dissimilar components (A:B:A or A:B:C), such as metal-complexation with ligands to bind two chain-ends together or host-guest chemistry, where a macrocyclic host binds one or two guests within a cavity.[55-57]

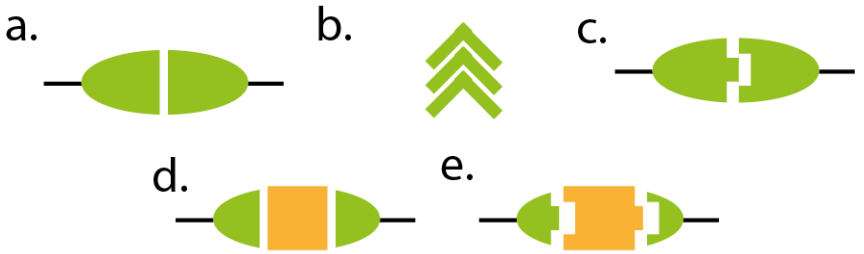

Figure 1.3. Self-complementary supramolecular binding: a) dimerization, b) stacking. Complementary supramolecular binding: c) complementary two-component dimerization, d), e) three-component binding.[48]

1.4.2 Molecular Recognition

Molecular recognition, or in other words selectivity of the binding, is a relatively new aspect of supramolecular materials chemistry. [39,53,58-61] Some interactions, such as bare electrostatic or hydrophobic interactions tend to be non-specific and non-directional. Although these interactions have been successfully used in materials to impart enhanced mechanical properties or functionality, they have drawbacks. As they tend to be non-specific, the binding can be easily disrupted, either by impurities, water screening, solvent or other similarly compatible substituent located within the network.[47,49] These aspects can be disadvantageous for the material and limit the choice of constituents; thus, narrowing the architectural and functional possibilities. In many cases, it is advantageous to use robust and selective binding to form well-defined materials. An excellent example of molecular recognition is seen through host-guest chemistry, wherein a macrocyclic host incorporates small-molecular guest motifs within a protected cavity.[48,62,63] These complexes can have high binding constants and rapid exchange dynamics - making them feasible for self-healing materials or stimulus-responsive materials.[56-58] Macrocyclic host-guest chemistry is also known for high selectivity, meaning that the self-assembly for such systems is driven by the recognition between the host and specific guest(s). Due to the high selectivity and binding constant, these types of complexes can withstand impurities, changes in the pH or ionic strength much better than bare ionic or hydrogen bonding sites, making them feasible candidates for molecular sensors or materials that require macroscopic recognition.[53] Also, Publication I shows how high selectivity can impart promoted temporal stability into the self-healing process.

1.4.3 Supramolecular Binding Equilibrium

The *physical binding equilibrium between* two or more motifs is quantified via the equilibrium association constant (K_{eq}) (Figure 1.4), calculated from the association rate constant (k_a) and dissociation rate constant (k_d):

$$K_{eq} = \frac{k_a}{k_d} \tag{1.1}$$

This equilibrium affects the degree of association, whereas the kinetics of association and dissociation affect the dynamics of the binding. Additionally, *the degree of association* is in direct proportion to the concentration of the binding groups $(K_{eq}c)^{1/2}$. This means, for example, that supramolecular networks require sufficient amounts of binding sites to exceed the critical concentration whereby a continuous percolated network is formed.

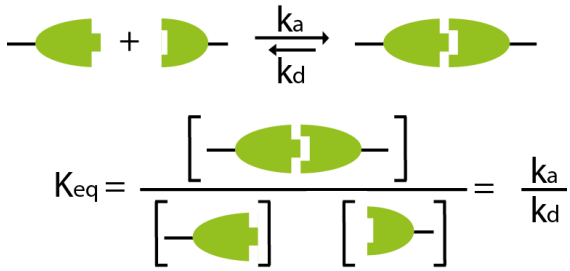

Figure 1.4. Schematics for the binding equilibrium (K_{eq}).[48]

1.4.4 Molecular Dynamics

Molecular dynamics broadens the binding equilibrium (K_{eq}) to also contain the exchange kinetics between associations (k_a) and dissociation (k_d), or in other words: the life-time of the binding. To construct dynamic networks, the physical cross-links should demonstrate rapid exchange between the 'active' and 'deactive' motifs, though with a high enough binding equilibrium ($[k_a] >> [k_d]$) to allow for a stable network. This will lead to networks with constant interchange between the active nodes.

This complex behaviour between the binding equilibrium, exchange kinetics, life-time as well as the external driving forces or thermodynamic parameters affecting the system can be combined via the Eyring theory and Arrhenius relationship. The Eyring theory shows how reaction rates (k) are proportional to the surrounding temperature (T):

$$k = \frac{k_B T}{h} exp\left(-\frac{\Delta G}{RT}\right) \tag{1.2}$$

This equation also gives important thermodynamic information on the Gibb's free energy (ΔG). Here, k_B is the Bolzman's constant, h is the Plank constant and R is the universal gas constant. The Eyring theory can also be written to include the reaction entropy (ΔS) and enthalpy (ΔH) via their relationship to the Gibb's free energy for constant temperature:

$$\Delta G = \Delta H - T\Delta S \tag{1.3}$$

$$k = \frac{k_B T}{h} exp\left(\frac{\Delta S}{R}\right) exp\left(-\frac{\Delta H}{RT}\right) \tag{1.4}$$

The activation energies (E_a) for k_a and k_d are especially important as they govern the minimum energy required for the binding to occur. Activation energies can be calculated via the Arrhenius relationship where A is a pre-exponential factor.

$$k = A\ exp\left(-\frac{E_a}{RT}\right) \tag{1.5}$$

This equation also focuses on reaction rates at different temperatures. Temperature is especially critical as low temperatures might inhibit k_d, which would drive the equilibrium towards k_a and subsequently loss of dynamics. On the other hand, too much energy and the system's equilibrium could be driven towards k_d until the physical binding is mainly dissociated and the network breaks down.

In addition to the thermodynamic parameters, the chemical environment plays a critical part in disposing the binding equilibrium and molecular dynamics, as discussed in the previous chapter: *Molecular Recognition*. Screening of the active binding site, competing interactions, binding equilibriums within different solvents all affect the overall network binding properties. Therefore, it is critical to understand how the binding occurs (conditions, temperature, pH) and where (in solution, bulk, and what other constituent might also present). In this context, specific bindings can be tuned by varying the external parameters, allowing for switchable materials.[50,58] This thesis investigated three different types of supramolecular binding: one highly selective and dynamic host-guest interaction to bind soft hydrogel networks together allow self-healing (Publication I, IV). The other was a strong and stable binding located within a brittle glassy network to allow fracture-energy dissipation (Publication II). The third was a fairly unselective, non-directional adsorption of polymer onto a colloidal surface (Publication II, IV).

1.4.5 Host-guest Chemistry of Cucurbit[8]uril

Cucurbit[n]urils (CB[8], n=5-8, 10) are barrel-shaped macrocyclic oligomers which can physically bind specific guests within their cavity, similarly to calixarenes.[34-36] Depending on the degree of glycouril units, the cucurbit[n]uril acts as a supramolecular host for one specific guest (n<8) or two guests (n≥8). Overall, the binding forces consist partially of hydrophobic interactions within the cavity, similarly to cyclodextrins, as well as complex polar interactions between the guests, the cavity and the high-energy water molecules located at the cavity's rim.[34,64] CB[n] tend to bind electron poor or cationic species as first guest, due to the electron rich carbonyl rims. Upon formation of this 1:1 complex, the electron rich cavity becomes more electron poor, subsequently dispersing the high-energy water molecules beside the rim allowing for a electron-rich, second-guest to form a highly stable 1:1:1 ternary charge-transfer complex for CBs' (n>8). More specifically, CB[8] used in this thesis (Publications I & IV) can bind two guests: methyl-viologen (first-guest) and naphthalene (second-guest) with an overall K_{eq} up to 10^{14} M^{-1} (Figure 1.5).[64] This ternary complex demonstrates extremely rapid exchange between the guests, allowing for dynamic self-healing hydrogels.[56,57] It should be noted that due to solubility issues, CB[8] chemistry is predominantly done in water or the gas-phase.[35]

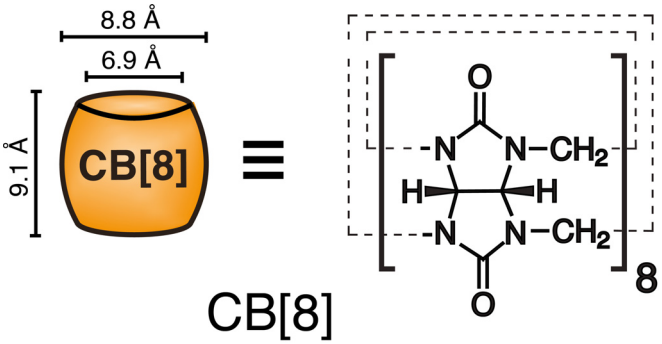

Figure 1.5. Chemical structure of cucurbit[8]uril with the dimensions.[48]

Architecturally, polymeric CB[8]-bound hydrogels typically consist of two complementary polymers with either the first- or second-guest as a pendant-functional side-group. These can then be bound together by adding CB[8]. With a large enough concentration of ternary complexes, a supramolecular network will be formed. Also, CB[n]s have been shown to be non-toxic, which makes them suitable candidate for biomedical applications.[48]

1.4.6 Hydrogen Bonding with Ureidopyrimidone

Hydrogen bonding is another well-established binding mechanism to impart functionality into polymer networks.[47] Depending on the chemical structure of the binding site, hydrogen bonds demonstrate a wide range of properties with regards to dynamics, strength and selectivity. Hydrogen bonds consist of a hydrogen donor, a hydrogen attached to an electronegative atom (F, O or N); and a hydrogen acceptor, a electronegative motif without a hydrogen attached to it (carbonyl, ternary amine). These interactions tend to be relatively weak (10-65 kJ/mol) when compared to covalent bonds (>300 kJ/mol).[48] However, due to the possibilities allowed by organic chemistry, numerous different types of bindings can be considered - demonstrating, for example, increased binding strength, selectivity, and directionality through specific arrays of binding sites (Figure 1.3). The following should be carefully considered when constructing supramolecular binding for polymer networks: Binding strengths can be tuned by changing the electronic structure of the binding sites. Also, the number of binding sites, i.e. arrays, affect both the selectivity and strength. Moreover, multiple binding sites are especially interesting, as specific structures have been shown to impart mechanical and stimulus responsive functionality into nanocomposite materials.[50] The surrounding polymer and solvent are also crucial, as polar solvents can screen the binding sites making them less effective (see: 1.4.2 *Molecular Recognition*). Similarly, other polar substituents attached to the surrounding polymer can have similar effects. Through these parameters and considerations, hydrogen bonds can be constructed to form highly dynamic binding, with weak constantly changing interactions,[47] as well as strong static binding[65] – or anything in between. One excellent example of a strong A:A binding is shown by ureidopyrimidone (UPy), which was used in Publication III.[65-67]

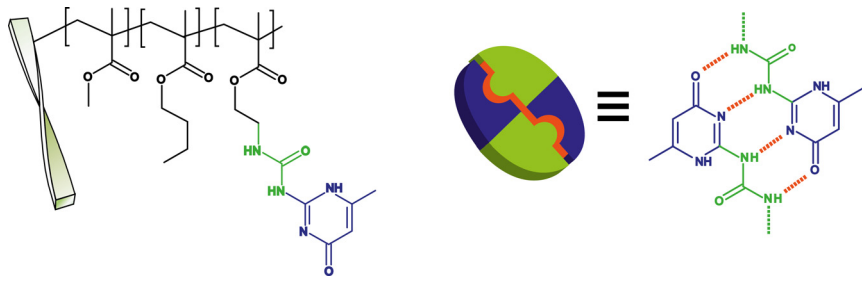

Figure 1.6. Chemical structure of UPy (see UPy dimer on the left) and an example on how to polymerize it as a pendant functionality into random copolymers. Image modified with permission from Publication II © 2014 Wiley-VCH Verlag GmbH & Co.

UPy demonstrates a self-complementary quadruple –AABB binding array (Figure 1.6), where A and B denote hydrogen bonding donors and acceptors respectively. The binding equilibrium, or in this case the dimerization equilibrium (K_{dim}), is extremely high ($K_{dim}=6\times10^7$ M^{-1}), as determined in chloroform.[65] UPy has been widely used to bind polymers together into self-assembled structures as well as functional supramolecular polymer networks.[65-67] UPy has been shown to impart UV-responsive self-healing, shape-resistant memory and fracture-energy dissipation properties into polymer networks.[50,51] Advantages of UPy-binding are a high binding constant, facile synthetic procedures and relatively good selectivity due to the quadruple array. One of the main drawbacks of UPy, however, are the bare hydrogen bonds, which become less effective within polar media. Hence, UPy is usually used in bulk nonpolar polymer networks or nonpolar solvents. Also, UPy can form three-component metal-ion complexes, which can be detrimental during ATRP-synthesis. Typically, UPy has been added into polymers as an end-group or pendant-functional side-group.[50,51,65,66]

1.5 Supramolecular Polymer Networks

An important aspect of networks, with regards to this thesis, is how they are bound together.[23] Polymers associate with each other in different ways, such as coil entanglement. However, networks are chemically cross-linked, forming more stable 'locked' networks by inhibiting the chain movement. Some networks might also contain supramolecular bonding units along the backbone, which physically 'glue' polymers together.[23] This thesis will focus on two types of networks: supramolecular hydrogels (Publications I, III & IV) and supramolecular thermoplastics (Publiction II) acting as functional matrix-networks containing nanocellulose reinforcement. Specifically, the bindings were mainly achieved through engineered polymer side-groups as well as less specific cellulose adsorption onto nanocellulose surfaces.

1.5.1 Supramolecular Hydrogels

Gels are three-dimensional networks, which have been expanded throughout the whole network by fluid, yet demonstrate no flow in the steady-state (zero-shear/strain).[23] Hydrogels are gels, which have been specifically expanded with water. Although hydrogels mostly consist of water, they demonstrate solid-like material properties, such as elasticity, stiffness and in some cases toughness[68] due to the chemically or physically cross-linked three-dimensional

network.[48] Such networks are characterized by rheology, which focuses on the flow of matter at different strain-values and frequencies. Regarding the rheological properties, the main question regarding molecular hydrogels is how the chains been bound together as well as the chain chemical composition.[69] Classically, hydrogels have been chemically cross-liked during or after polymerization of water-soluble monomers using myriad radical-induced chemical cross-links. The applicability of these strong yet irreversible cross-links tends to limit the utilization of such hydrogels, as the materials can, in some cases, be brittle.

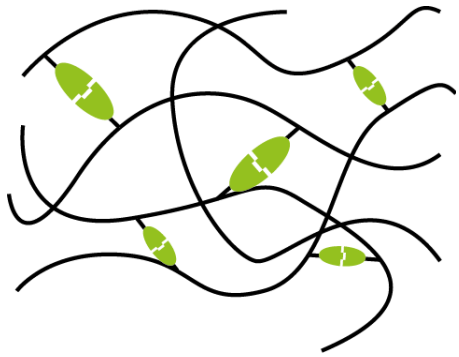

Figure 1.7. Schematic representation of a physically cross-linked network.

Supramolecular hydrogels, on the other hand, offer a choice of transient physical cross-links. Depending on the binding strength and molecular dynamics, these gels can form a wide range networks with reversible exchange between the physical cross-links (Figure 1.7).[49,53,56-59,69] These supramolecular exchanges can allow for relatively rapid reformation of broken networks, i.e. self-healing. Self-healing is especially pronounced with hydrated networks, due to rapid chain-movement – allowing the chains to keep pace with the supramolecular exchange. In addition to self-healing, supramolecular hydrogels typically demonstrate shear-thinning. The ability to break down the network for easier processability and subsequent rapid reformation is a highly desirable characteristic for materials. Another advantage is network formation - supramolecular networks rely on the molecular self-assembly between the binding units, whereas chemical cross-links need to be engineered separately by addition of cross-linking agents. Hence, dissolving the polymer is usually enough to form supramolecular networks. The ability to store just the dry polymer is desirable for long-term storage. Although the dynamic nature of supramolecular hydrogels offers numerous advantages, they tend to form softer networks, as the networks cannot withstand high shear-stress. These mechanical deficiencies can, however, be circumvented by applying colloidal reinforcement, whilst retaining the high dynamics, as shown in publication I.[49]

Publication I focuses on a supramolecular nanocomposite hydrogel that demonstrated enhanced rheological properties (high stiffness) due to CNC

reinforcement. Also, the gels demonstrated rapid self-healing due to highly dynamic CB[8] supramolecular cross-links as well as good temporal stability due to the high selectivity of the recognition sites. Publication III demonstrates hydrogels consisting of thermoresponsive methylcellulose (MC) that were physically bound together via CNCs. The ensuing gels offered higher stiffness as well as the ability to tune the modulus as a function of temperature: higher temperatures increased the modulus. And finally, Publication IV shows an interpenetrating and interconnected hydrogel network that consisted of colloidal NFC to reinforce the network and a softer interconnected CB[8] supramolecular hydrogel to allow energy-dissipative yielding. Together both networks behave synergistically, allowing for a higher modulus as well as promoted yield-strain.

1.5.2 Supramolecular Plastics

Recently, a new type of plastics have been discovered called vitrimers.[70] Vitrimers are a class in-between thermosets and thermoplastics, which rely on reversible chemical cross-links. At low temperatures they behave as classic thermosets, which are covalently cross-linked. At higher temperatures, these cross-links start to behave in a more dynamic fashion with rapid bond exchange, allowing the material to be processed. After cooling the material, the bond-exchange becomes so slow, essentially 'frozen', that the material once more behaves as a thermoset.

One of the main focuses of supramolecular materials has been towards selective directional binding as a method to achieved physically cross-link networks.[47,50,65-67,70-72] Indeed, the transitional physical cross-links should allow for considerable yielding within the network under physical strain, unlike the non-reversible chemical cross-links, which tend to break at high loadings. Here, the physical cross-links can undergo constant dissociation and association upon strain; thus, keeping the material together at much higher strain-values. Additionally, transient cross-links act as 'sacrificial bonds', constantly dissipating mechanical energy as they are dissociated. This means, that more energy is required to deform the material. Moreover, specific supramolecular units within the network can allow for chemically engineered functionality.[19,50,73]

Publication III demonstrates a supramolecular thermoplastic nanocomposite, which was reinforced with CNCs. The yielding matrix was formed purely from the glassy CNC-graftcopolymers with UPy pendant groups and bound together via interdigitation of the grafts and selective UPy-binding. The ensuing nanocomposite material demonstrated engineered fracture energy dissipation, which resulted from the sacrificial supramolecular binding.

2. Lessons from Nature

Nature has honed to perfection the designs and architectures of structural nanomaterials to synergistically combine strength, toughness and stiffness.[74-76] The most notable natural structured materials that influence modern material scientist are silk, pearl of nacre, wood, ligaments, tendons and animal bone. Although these materials demonstrate different mechanical aspects, the overall nanostructure is based around similar concepts of reinforcing nanodomains tethered to yielding dissipative networks all bound together in highly hierarchical self-assembled networks. Furthermore, all the components work together in synergy at different length-scales.

It is important to understand that with these low density and low weight natural materials, the structure is the key. All biological material components, organic and inorganic, are formed from low-weight elements (H, C, N, O, S, Si, Ca, P).[74] Therein, protein-based components can act as either the soft energy-dissipating matrix, bound together through a complex array of supramolecular chemistry. Proteins can additionally form hard reinforcing nanodomains, which reinforce the softer domains. These can be, for example, fibrillar or small crystalline self-assembled structures, such as β-sheets. The reinforcing domains can also be inorganic mineralized sheets, such as calcium carbonate ($CaCO_3$). Finally, in plant-based material cellulose forms colloidal level crystalline reinforcement in microfibres.

Separately, each component is usually mechanically weak or lacks some mechanical aspect (strength, stiffness or toughness). However, when combined in the right way, each component works synergistically leading to mechanically excellent networks that can surpass many man-made materials by combining strength, stiffness, toughness and lightweight composition. Indeed, with recent advancements in electron microscopy, spectroscopic analysis and computational modelling, a better understanding of the subtle nanomechanics within natural materials has brought about a plethora of new questions regarding material design and architectures.[77-79] Hence, another central aspect of this thesis is the understanding of natural networks, their architectures and most importantly, how their structure relates to functionality.

2.1 Mechanical Aspects

Sacrificial bonds, hidden length-scales and stress transfer are all mechanisms that help increase the mechanical aspects of nanomaterials through several deflection mechanisms.[80,81] Indeed, the structures of natural materials have evolved around these mechanisms, which allow synergistic combinations of high stiffness, strength and toughness using only lightweight components. These biological aspects were the main focus points around which Publications I-IV were built upon.

2.1.1 Energy Dissipation through Sacrificial Bonds and Hidden Lengths

Many natural nanocomposites have inherent toughening mechanisms that increase the amount of energy required for the deformation. The increased energy is partially a result of 'sacrificial bonds', defined by their ability to break before the main structure.[80-82] Typically, the bonds are formed from complex supramolecular interactions. The mechanism works by dissipating mechanical force, by opening the sacrificial bonds rather than deforming the surrounding network, thus keeping the main structure intact. Hidden lengths, on the other hand, are small 'loose' domains, links or chains that have been constrained from stretching through a sacrificial bond. Typically, a combination of sacrificial bonds and hidden lengths works by sequential opening of the physical binding, which unravels the hidden length until it is stretched (Figure 2.1a). Finally, the hidden length will further deflect the energy towards another sacrificial bond nearby. This forms a system that slowly unravels - constantly dissipating mechanical energy, while keeping the actual structure intact. In some cases, sacrificial bonds are transient. This can lead to a system, which constantly reforms broken bonds, allowing for an even more efficient energy-transfer.[80]

There are numerous types of supramolecular architectures for dissipating mechanical energy through sacrificial bonds and hidden lengths. The most efficient architectures can be explained using the single-strand model where the physical binding occurs between two colloidal surfaces[81] (Figure 2.1b): (1) This case contains loops bound by sacrificial nodule points, as discussed in the aforementioned hidden length example. By rupturing the weakest point, the coil will sequentially unravel. This will lead to successive 'force ruptures'. The rupture sequence is driven by the binding equilibrium of the sacrificial bond, with the weakest opening up first and the strongest last. Hence, there will be a gradual increase in the amount of energy required for each successive rupture. (2) This case is based on numerous sacrificial bonds attached to the surface. Once stress is induced, the sacrificial bonds will sequentially rupture in the order with which they are attached to the surface. Again, this will lead to

sequential force ruptures. (3) Here, the chains are covalently attached to the colloid surface and dissipate energy in the yielding phase. The sacrificial bonds will rupture in order. Hidden lengths result from the distances between the binding sites. (4) In this case, all the bonds will rupture at the same time as they are loaded parallel to each other. However, the amount of stress in comparably higher for the first break when compared to the first three cases. Moreover, it can allow 'hopping', i.e. reformation of the supramolecular binds, as the chains slide past each other, thus keeping the structure intact even after the bindings rupture.

The dissipative mechanics found in nature can be transferred to synthetic materials by embedding supramolecular interactions into polymer networks. The binding architectures used in Publications I-IV can be envisioned using the single-strand model.[81] These architectures will be discussed more in Chapter 3.

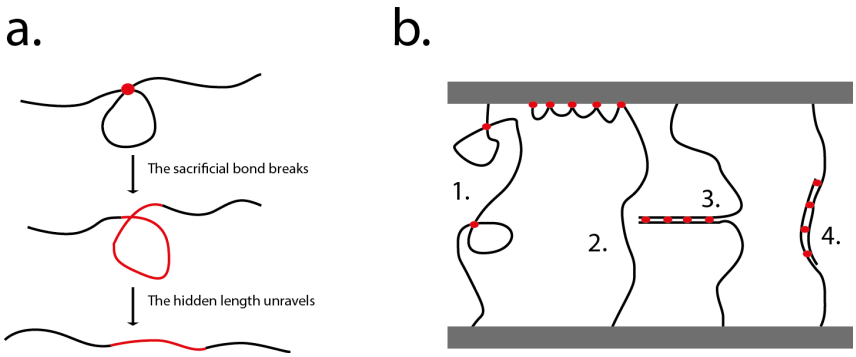

Figure 2.1. a) Schematics for opening sacrificial bonds with ensuing unravelling of the hidden length. b) The four sacrificial architectures: 1 Loops bound with supramolecular binding that also contain hidden lengths. 2. Surface adsorption via arrays of supramolecular bindings. 3. Sacrificial bonds in the yielding phase, where they will rupture in order. 4. Sacrificial bonds in the yielding phase, where they will rupture simultaneously.[81]

2.1.2 Stress-transfer in Natural Nanocomposites

Combining stiff colloidal motifs with a softer yielding networks typically leads to a combination of the two properties through stress transfer mechanisms. An excellent example of stress transfer can be found from nacre, which combines ceramic platelets with soft proteins.[83,84] Ceramics, such as $CaCO_3$, are very stiff and strong; however, they demonstrate no yielding. This means that ceramic materials have little tolerance to cracks or surface flaws. On the other hand, many polymers tend to be flaw-tolerant as well as offer yielding; however, they tend to be soft – requiring only small amounts of stress to deform the matrix. Hence a combination of both properties would be highly desirable. Nature has found a way to effectively combine the best of both

worlds through a hierarchical bricklayer architecture. This nanocomposite network offers excellent strength and flaw tolerance by reinforcing the softer network through partially transferring the load to the stiff platelets - as well as allowing the stress to propagate around the platelets through a sacrificial network. Moreover, the structure is formed through self-assembly, whereby each platelet is surrounded by the protein matrix. Any platelet crack will therefore not propagate catastrophically as the energy is dissipated directly into the soft matrix (Figure 2.2). And finally, the whole network is interconnected, i.e. the yielding matrix is tightly bound to the platelet surfaces. This increases the energy required to pull out platelets or slide them past each other. Nacre is an excellent example of how stiff reinforcing domains work together with softer domains to enhance the mechanical properties. Similar types of stress transfer mechanics are observed throughout nature where stress is partially transferred to different reinforcing domains.

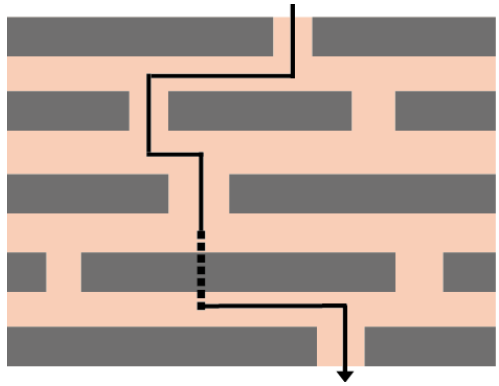

Figure 2.2. Schematic representation on the stress-transfer mechanics in nacre, where the stress is partially transferred to stiff platelets and deflected around the platelets (grey) through a sacrificial domain. Even in the presence of a crack, the stress is dissipated, thus allowing efficient fracture energy dissipation.

With regard to efficient stress-transfer in synthetic nanocomposites and the nature between the hard colloidal reinforcement and the yielding matrix, the main lessons learnt from nacre and nature in general are: (1) Homogeneous distribution of the reinforcing phase allows for more efficient fracture-energy dissipation as cracks will be immediately dissipated to the surrounding polymer matrix. Also, it allows efficient stress-transfer throughout the whole material. (2) Interconnectivity is important as it enhances the pull-out forces. Hence, the soft matrix should be tightly bound to the reinforcing surface, while allowing energy dissipation in the bulk-phase. Another possibility is to have a large array of sacrificial bonds attached to the surface.

Publications I-IV all demonstrated excellent compatibility between the hard and soft domains, with homogeneous distributions of nanocellulose. Moreover, each architecture was also fully interconnected.

2.2 Animal Bone

Bones are interesting as they demonstrate remarkable mechanical properties through a synergy between different lengthscales (Figure 2.3).[79,85,86] Moreover, they demonstrate localized mechanical aspects, depending on where the bone is located and how much stress is applied and from which direction. Regarding the highest length-scales, bones are formed from a 'spongy' network (*trabecular* or *cancellous bone, 80 % porosity*) within the bone, which can withstand compression; and a hard compact mineralized bone (*cortical bone, 6 % porosity)*, which offers excellent stability against bending and buckling.[74] Depending on the local requirements, bones have different degrees of cortical bone and cencellous bone.

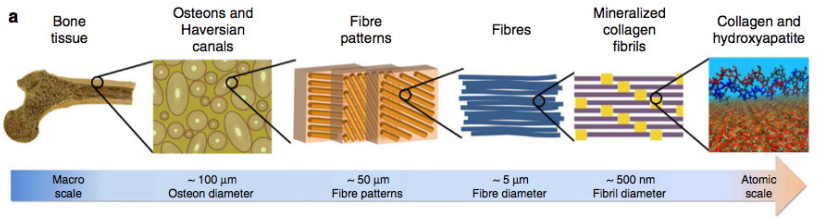

Figure 2.3. Schematics of the different length-scales in animal bone. By permission from Nature Publishing group.[79]

The most exciting aspects of bone, regarding this thesis, are found in the lower length-scales, which are formed from of hard mineralized collagen fibres bound together by a softer physically cross-linked protein matrix. On this level, mineralized collagen fibres are glued together via a non-fibrillar soft supramolecular network.[85,86] This length-scale allows for highly effective fracture energy dissipation.[80,86] More specifically, when a force is applied, the non-fibrillar glue keeps the collagen fibrils together thus keeping the network intact, while simultaneously dissipating energy through sacrificial bonds.[80] Afterwards, the supramolecular glue will reform with the collagen fibrils, thereby restoring the network at least partially to its original status. The next level down consists of the actual mineralized collagen fibre assembly, which reinforce the network.[79,85] Here, single collagen fibrils are bound together via mineral hydroxyapatite, forming a hard mineralized fibre structure to reinforce the network, thus increasing the strength and stiffness.

Finally, single collagen fibrils are formed from a triple helix consisting of three protein chains entwined around each other via intermolecular hydrogen bonds.[79] Due to the helical conformation and supramolecular interactions, collagen can also dissipate energy under stress allowing for one more protective yielding layer against catastrophic break. They also offer some degree of elasticity against bending and pulling. Indeed, bone is an excellent example of different length-scales working together in synergy to enhance the mechanical aspect of the network. Also, the different energy dissipations and stress transfer aspects offer excellent inspiration for materials scientist. Especially an energy dissipating reinforcing motif would be an exiting prospect.

2.3 Silk

Silk is a well-known nanocomposite material, formed from reinforcing protein β-sheets bound to a soft protein matrix, consisting of less ordered nanodomains involving sacrificial bonds and hidden lengths (Figure 2.4).[87,88] The reinforcing domains are small (3 nm) protein β-sheets, which are tightly bound via a hierarchical hydrogen bonded matrix.[89] These hard crystallites reinforce the softer yielding domains, allowing for efficient stress-transfer. Moreover, under uniaxial stress, the crystallites will orient and start to slide past each other, while the softer domains unravel around them, constantly transferring stress. During this process, some of the less-ordered β-sheets will also start to unravel, bringing into play additional energy dissipation. Typically, silk matrixes consist of roughly 50 % of reinforcing β-sheets and 50 % of a softer, less-ordered supramolecular network.[90,91] Though this can vary a fair amount depending on the silk type. Due to the synergistic dissipative mechanism and stress-transfer, silk demonstrated remarkable mechanical properties, considering that it is formed purely from proteins. This again shows the importance of how relatively weak soft-matter can exceed human-engineered materials with the right structure.

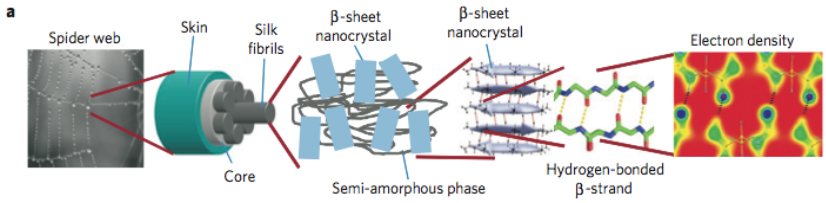

Figure 2.4. Schematics of the structure of silk from the macroscopic scale to the molecular scale. By permission from Nature Publishing group.[89]

2.4 Wood and Plant Fibres

The detailed structure of plant fibres has been given in chapter 1.2 *Nanocellulose*. Wood and plant fibres also work in several length-scales. The network of macro-fibres is what makes outer plant cell walls strong. In the highest length-scale (cellular level), wood comprises, for example, of hierarchically oriented elongated cells along the xylem channel. These cells have a thin cell wall consisting of a network of macroscopic wood-fibres. The lateral dimensions of these large fibres are in the region of 20-60 μm, while the lengths can be thousands of microns. This network acts as a scaffold that gives the cells their shape and also glues the cells together via hemicellulose and a strong lignin network, thus inhibiting cell movement. Indeed, the cell matrix is fairly static - any growth happens through expansion of the cell wall via

controlled creep of the fibres and localized cell division. These macroscopic fibres are themselves composites consisting of bundles microfibrils bound together via soft hemicelluloses and lignin and strengthened via crystalline cellulose fibrils. These nanocomposite microfibrils offer good dissipative deformation together with efficient stress-transfer, due to the interactions between the strong crystalline fibrils and the tethered softer yielding hemicellulose network. More specifically, the linear fibrillar packing allows for excellent axial strength and stiffness parallel to the fibres orientation, whereas the supramolecular network allows for yielding and bending of the fibre. With woodfibres, similar mechanical functions happen in multiple length-scales, from the nanofibrils to the microfibrils and macrofibers. Understanding these basic structural elements allow for the fabrication of efficient biopolymer-based materials.

3. Architectural Considerations for Synthetic Nanocomposites

3.1 Biomimetic Nanocomposites

Nanocomposites are multiphase materials with one or more solid phase(s) having at least two dimensions less than 100 nm.[92] Due to the relatively larger surface area to volume, or the high aspect ratio of the reinforcing domains, nanocomposites tend to offer distinctly different properties when compared to their more classic composite counterparts. The increased interfacial area between the reinforcing domain and the softer yielding domain can be considered to be of an order of magnitude higher than with more classic composite materials. Hence, the reinforcing properties tend to be more effective. For example, by combining nanocellulose with compatible polymer matrixes, the ensuing materials typically demonstrate increased strength and stiffness.[17] Especially interesting are high strength nanomaterials with specific chemically engineered functionalities, such as the ability to self-heal or specific stimuli responsiveness.[19-21,49,50,84,93] The main reason to utilize nanocellulose as a reinforcing unit is to exploit the high aspect ratio and stiffness of the hierarchical (semi)crystalline structure of CNCs and NFC via stress transfer mechanisms. Herein lies one of the main architectural questions: how to embed nanocellulose into softer matrixes involving supramolecular networks so as to attain the full benefit of the nanoreinforcement. Here, nature has paved the way for highly efficient models.

Natural structural materials consist of complex hierarchical architectures on numerous length-scales. Hence, their exact replication is challenging for synthetic materials, even in small-scale synthesis. Specifically, the replication of numerous length-scales has proven to be exceptionally challenging as well as to engineer toughness. Therein 'biomimetics' aims to identify some of the most essential aspect of biological materials in technologically feasible manner.[75] These inspirations can either relate directly to similar structural elements; or materials can be engineered to demonstrate similar properties as natural materials, though with a different architectural approach. These properties can be various mechanical aspects, such as increased strength, stiffness toughness or engineered fracture-energy dissipation. Self-assembly, surface wetting and optical functionalities are also highly desirable properties for materials.[94,95]

3.2 Reinforcement Through Cellulose Nanocrystals

There are two main methods to combine CNCs with polymers. CNC-reinforcement can be added in the pristine form, i.e. no chemical modification, or by increasing their compatibility via chemical modification of the surface. Using pristine CNCs saves synthetic steps and allows for more facile material fabrication. This is a feasible pathway for scaling up, as shown in publication III. However, this method limits the possibilities for water-soluble polymers which, are compatible with the anionic surface. This prohibits most polyelectrolytes as they will either form complexes with the anionic surface (polycations) or possibly lead to phase separation due to low interaction between the hard and soft domains (poyanions). Phase separation and incompatibility are both fairly prevalent for dry CNC reinforced materials. Also, uncontrolled complexation and incompatibility can prohibit network formation. In this context, it is important to construct architectures where all the components are fully compatible as well as taking into consideration the aforementioned suggestions regarding natural nanocomposites (see Chapter: *2.1 Mechanical Aspects*). Compatibility will lead to better stability and better mechanical properties. Therefore, by drastically changing the chemical nature of the reinforcing nanorods, a much broader spectrum of matrix polymers can be envisioned. This will inevitably lead to a broader range of possibilities and functionalities, as shown in Publications I & II.

3.3 Cucurbut[8]uril-bound Nanocomposite Hydrogels

Three-component molecular recognition is the driving force behind the assembled nanocomposite hydrogel presented in Publication I. The studied architecture was unique, demonstrating a never before seen combination of conflicting properties of high stiffness, rapid self-healing and good temporal stability. These properties came to fruition by combining three components: first-guest methylviologen-functional poly(vinyl alcohol) (PVA-MV) (5 mol.% MV loading) (Figure 3.1a); cellulose nanocrystals (CNC) with cationic poly(dimethylaminoethyl methacrylate) second-guest naphtyl-functional copolymer grafts (CNC-*g*-P(DMAEMA-*r*-NpMA) (~ 9 mol.% Np loading) (Figure 3.1b); and cucurbit[8]uril (CB[8]) (figure 3.1c) to bind the guest-functional polymers together (Figure 3.1d). The resulting nanocomposite hydrogel demonstrated increased modulus values: one order of magnitude increase when compared to similar molecular CB[8] hydrogels.[56,57] Generally, molecular gels bound by CB[8] tend to have zero-shear elastic moduli (*G'*) of ~0.1-1 kPa, whereas the CNC reinforced nanocomposite hydrogels had a *G'*~10 kPa, i.e. properties approaching those of solid networks (Figure 3.2). Due to the highly dynamic supramolecular binding of CB[8], the network demonstrated rapid self-healing. During strain-induced rupture (150 % strain), the network

broke down (*G”>G’*) and once the high strain was lowered (0.01 %), the network re-knitted itself to the original values within 6 seconds, demonstrating one of the fastest self-healing processes to date (Figure 3.3). Finally, due to the high selectivity of the ternary binding, the self-healing occurred without passivation side-reactions, such as screening of the active sites. This allowed rapid healing of the exposed surface-areas even after four months storage in 100% humidity, i.e. good temporal stability.

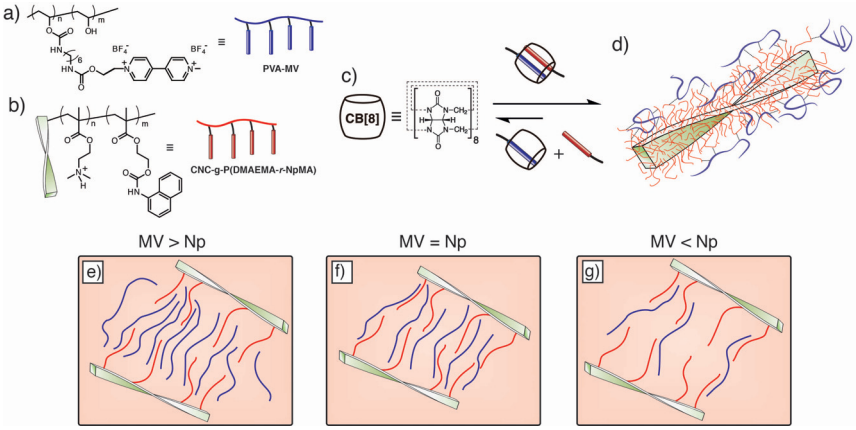

Figure 3.1. Schematics and architecture for the molecular recognition-driven supramolecular hydrogels. a) Poly(vinyl alcohol) (PVA) containing the first-guest methyl viologen functionality (PVA-MV). b) CNCs containing random copolymer grafts of protonated dimethylaminoethyl methacrylate (DMAEMA) and second-guest naphthyl methacrylate (NpMA) (CNC-*g*-P(DMAEMA-*r*-NpMA)) with DMAEMA/NpMA 10/1 mol/mol. c) CB[8] as the host to bind the network together. d) Selective supramolecular cross-links based on three-component recognition to bind all the components into dynamic hydrogels. Here, the modified PVA bridges the CNC-grafts together. (e-g) Effect of the bridging based on the Np/MV ratio showing less efficient bridging with non-stoichiometric guest ratios (e & g) and the effective equimolar Np/MV ratio (f) where the system demonstrates the highest *G*’ and solids content. Image reprinted with permission from Publication I © 2014 Wiley-VCH Verlag GmbH & Co.

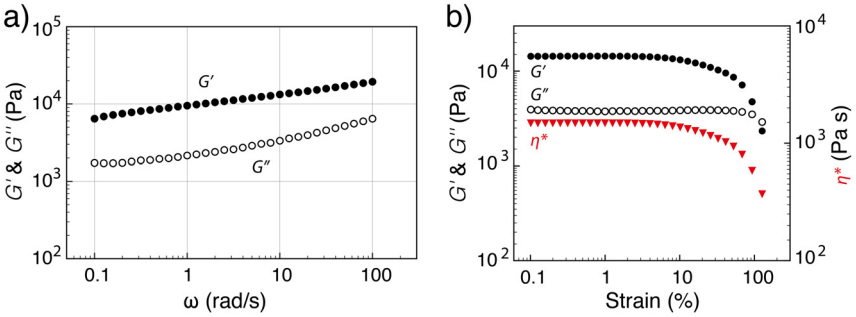

Figure 3.2. Rheology of CNC-*g*-P(DMAEMA-*r*-NpMA)/PVA-MV/CB[8] with the guest ratio of 1.1, i.e. close to their stoichiometric binding in CB[8]. a) Frequency sweep shows that *G´* is essentially constant and *G´* >> *G´´*. b) Strain-sweep with *G*’, *G*” and the complex viscosity η*, collected at 10 rad/s. Image reprinted with permission from Publication I © 2014 Wiley-VCH Verlag GmbH & Co.

3.3.1 Functionality Through Molecular Recognition

Combining rapid healing, stiffness and stability can all be explained through the three-components molecular recognition. Firstly, the network formation required all three aforementioned components. Single components or any two components together formed either a free-flowing solution or colloidal dispersion. Once the gel formed by incorporating all the components, it formed a self-regulating structure, which incorporated a specific amount of water depending on the guest ratio (figure 3.3d). In other words, the degree of PVA bridging between CNC-grafts was driven by the ternary complexation (Figure 3.1 e-g). In this case, a roughly equimolar ratio of first and second guests were found to form the most efficient bridging. This was observed as the highest solids content and subsequently, the highest zero-strain modulus value (~14 kPa). Our hypothesis here was that the PVA-MV drew the CNCs closer together and expelled the excess water to form the dense supramolecular networks. Consequently, the denser the network, i.e. higher solids content, the higher the modulus. In contrast, nonstoichiometric amounts lead to less efficient bridging, which was observed as lower solids content and thus lower zero-stain *G'* values. This means that the mechanical properties were not proportional to the amount of reinforcing CNCs, as shown in more classical nanocomposites. Instead, the structure was driven by molecular recognition - similarly to some natural materials constructed from proteins. Additionally, due to the dense nanocomposite structure the reinforcing CNCs offered good stress-transfer, whilst the binding supramolecular network constantly dissipated mechanical energy. It should also be noted that these high values could not be achieved with molecular CB[8] gels due to solubility issues of the CB[8] guest.

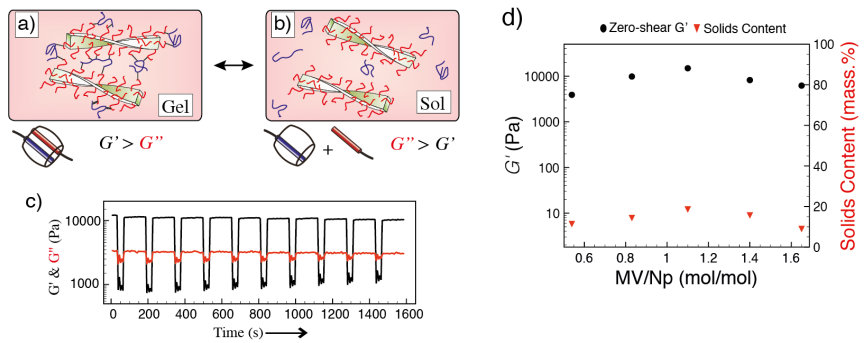

Figure 3.3. Rapid reversible sol-gel transitions as demonstrated by step-strain rheology. a) Schematic representation of the hydrogel cross-linking based on the ternary CB[8] binding *vs.* b) the sol-state whereby high strain results in dissociation of the ternary complex. c) Periodic sol-gel transitions, upon application of low strains (0.05%, 30 s) and high strains (500%, 120 s) for the sample with 1.1 guest ratio. b) Low-shear *G'* values as well as the solids contents as a function of increasing CNC-*g*-P(DMAEMA-*r*-NpMA) content. Image modified with permission from Publication I © 2014 Wiley-VCH Verlag GmbH.

Healing with this architecture was extremely rapid. Strain-induced ruptures were healed within 6s to the original network values. This rapid healing could be attributed to the well-established exchange-dynamics of CB[8] and the dense brush network, which allowed for more guest motifs to be located in one volume unit that with more traditional molecular gels.[56,57] This allowed for a more efficient exchange between binding motifs.

3.3.2 Selection of Components for Complementary Colloidal Gels

To construct a functional nanocomposite network out of the three aforementioned components (Figure 3.1) requires some important considerations. Starting from the CNC-graft, a cationic polyelectrolyte was chosen for a few reasons. Firstly, it gave the CNC-grafts good electrostatic stability. This allowed for a good homogeneous dispersion within the nanocomposite matrix as the cationic brush disallowed interdigitation between the CNC-grafts as seen from Cryo-TEM (see Publication I Figure S8).[96] Additionally, the open cationic brush yielded a more accessible domain for the neutral PVA-MV. According to isothermal titration calorimetry, almost all the guests were part of a ternary complex, meaning that the PVA managed to bind fairly close to the CNC surface. A neutral graft might not have been as accommodating. Furthermore, the hydrophobic naphthyl-guest could have easily drawn a netral graft to phase-separation, whereas an anionic graft would have led to uncontrolled complexation with the cationic methyl-viologen guest.[56] The neutral first-guest functional PVA-MV was chosen as it has previously demonstrated to work effectively with cationic CB[8] hydrogels[56] and it demonstrated no network formation with the cationic CNC grafts at the studied concentrations.

The graft also allowed for a biomimetic dissipative deformation (see Chapter *2.1.1 Energy Dissipation through sacrificial bonds and hidden lengths, case 4*). Due to the dynamic binding, the high strain did not fully break the ternary complexes; rather, it gradually shifted the binding equilibrium toward the dissociated state. Hence, even at very high strain-values, part of the mechanical energy was always diverted towards keeping the ternary complexes dissociated. In contrast, once non-transient covalent crosslinks are broken, the mechanical energy is henceforth directed towards deforming the network.

3.4 One-Component Supramolecular Nanocomposites

One of the main advantages of nanoreinforcement for solid materials is increased strength and stiffness. Yet, these mechanical enhancements tend to make the material brittle. Moreover, the materials demonstrate little fracture energy dissipation as they have not been engineered to compensate with the

change chemical and physical properties. Usually, the reinforcing motifs are hard colloids, which demonstrate little yielding (e.g. nanoclay, nanocellulose, silica). When the colloids are mixed into a polymer matrix, they offer good reinforcement through stress-transfer; however, they will partially discontinue the yielding matrix – leading to harder and stronger, yet more brittle materials.[19,50,84,93] This is especially prevalent if the polymers are incompatible with the colloidal surface or the system is not interconnected. Synthetic nanocomposite combinations that focus specifically on engineered dissipative deformation through sacrificial bonds are scarce. Typically, CNC-nanocomposites are constructed by mixing pristine CNCs with functional polymers. Although, the materials tend to demonstrate enhanced strength and stiffness, they lack the synergy nature has to offer, leading to brittleness. One way to increase toughness and fracture energy dissipation is to combine a dissipative supramolecular network together with the reinforcing domains.[81]

Another important lesson learned from nature is connectivity. With silk, nacre and plant fibres the hard domains are directly attached to the soft yielding network. This allows for more efficient stress transfer and energy dissipation as the whole network is interconnected and working together under deformation. In most cases, unmodified CNCs offer little interaction, other than the stress-transfer, though typically at the cost of limited yielding. This can be explained, for example, with smaller amounts of mechanical energy required for pull-out forces as the matrix is not fully compatible with the colloidal surface. One possibility is to modify the surface of CNCs with smaller molecules in order to enhance their compatibility with more non-polar media. This helps to create a more uniform dispersion. However, the CNCs will remain unbound. Hence, attaching the sacrificial network directly the reinforcing CNCs, either through covalent binding (Publication I & II) or via strong physical interactions (Publications III & IV), should offer better mechanical improvements.

3.4.1 Architectural Considerations

Publication II shows a nanocomposite architecture based on a one-component design.[28] Here, glassy chains were polymerized from CNC surfaces with supramolecular UPy binding units as pendant groups along the polymer backbone. Hence, a separate matrix polymer was not required as the network was formed purely though interdigitation and the ensuing supramolecular binding (Figure 3.4). It should also be noted that this one-component architecture unavoidably leads towards a homogeneous dispersion of CNCs. More specifically, the graft copolymer mainly consisted of a random blend of poly(methyl methacrylate-r-butyl methacrylate) (PMMA 69 mol.%, PBMA 30.3 mol%) with a small amounts of UPy-functional methacrylate (UPyMA 0.7 mol.%) to form: (CNC-*g*-P(MMA-*r*-BMA-*r*-UPyMA)) (Figure 3.4). Such one-composite architectures require specific considerations for effective network formation.[28] As such architectures are bound through interdigitation, they

require fairly long grafts. Longer grafts allow for more efficient interdigitation and this allows for better yielding within the bulk-phase. Indeed, the degree of polymerization has been directly linked to increased toughness of one-component nanocomposites.[28]

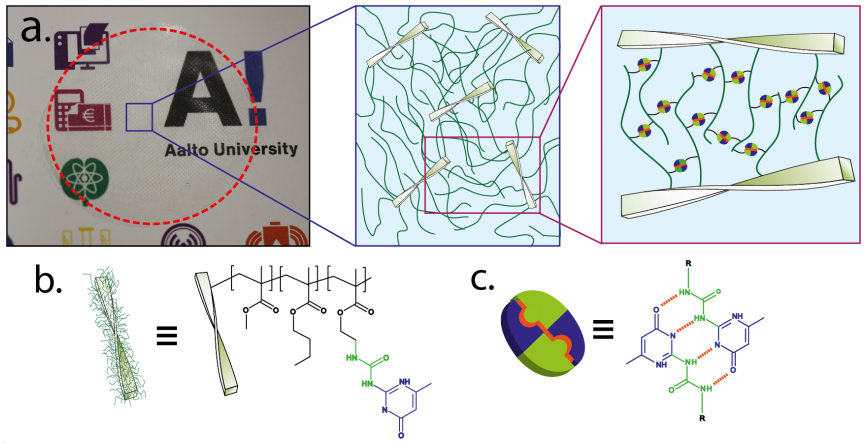

Figure 3.4. a) Image of a heat-pressed film consisting purely of CNC-*g*-P(MMA-*r*-BMA-*r*-UPyMA). The outer borders of the film are visualized with a red dashed line. b) Chemical composition of CNC-*g*-P(MMA-*r*-BMA-*r*-UPyMA). c) The dimerization of UPy via four hydrogen bonds. Image reprinted with permission from Publication II © 2014 Wiley-VCH Verlag GmbH & Co.

Another important factor is the grafting density. It has been demonstrated how to polymerize highly dense brushes from CNCs via sequential chemical vapour deposition and solution esterification of multifunctional ATRP-initiators.[30] Although a high grafting density could be beneficial for specific complexation reactions or to yield better solution stability for CNC, it can be detrimental for materials – especially for the discussed one-component architecture. Publication II suggested that a lower grafting density facilitated interdigitation and thus: inter-colloidal supramolecular binding – leading to less brittle networks. The amount of UPy was kept low (0.7 mol.%), as it has a very high binding equilibrium and most likely very low dynamics due to the locked glassy network. Hence, the hypothesis here was that large amounts of UPy would eventually make the network brittle as it would behave more like a chemically cross-linked network.

3.4.2 Engineered Fracture Energy Dissipation

The architecture shown in Publication II allows for biomimetic deformation.[85,86,97] The current hypothesis is that when uniaxial stress is applied, the CNC-grafts will orient parallel to the strain and slowly slide past each other, constantly reinforcing the network, similarly to silk and wood fibres (Figure 2.4a). At the same time, the physically interconnected network will dissipate

energy by selective cleaving of the UPy-binding sites. This process was shown to increase the toughness through a continuous 'unzipping' between interdigitated brushes (stick-slip mechanism) (Figure 3.6). Stress-strain tensile tests showed a maximum stress of 29±3 MPa with a maximum strain up to 8-25 %. The biomimetic toughening process was observed through plastic deformation in stress-strain measurements and extended process-zones as strain whitening. Moreover, electron microscopy highlighted the pull-out-forces behind the yielding process and how the material extended micron-sized process-zones away from the crack-ends (Figure 3.5 b). Similar materials without the UPy-binding were highly brittle and demonstrated no plastic-deformation whatsoever. This indicated that this was a feasible manner of approach towards strong, stiff and tough nanomaterials.

Although the sacrificial bond mechanics discussed previously (see Chapter *2.1.1 Energy Dissipation through sacrificial bonds and hidden length, case 4)* indicates that all the sacrificial bonds dissociate simultaneously, this is not the case here according to the mechanical stress-train curves. The most likely explanation is the high molecular weight grafts. They demonstrate behaviour in between random coils and brushes, i.e. when deformed the chains slide past each other as well as gradually uncoiling even after the maximum yield-strain, i.e. hidden lengths.

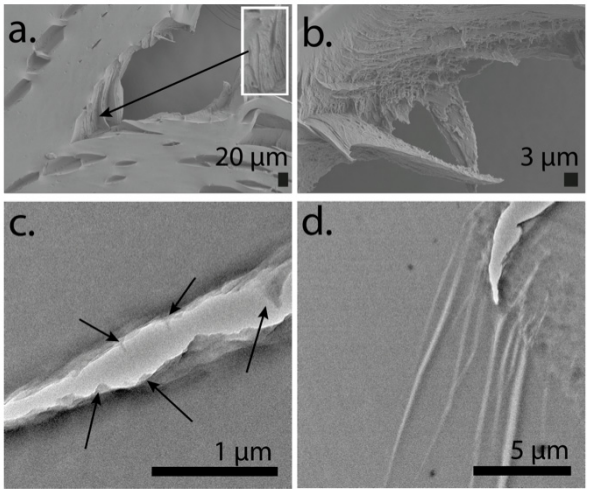

Figure 3.5. a) SEM image of fracture surface after uniaxial stress for relaxed samples. Note that aligned fibrillar structures are observed near the crack tips, suggesting aligned CNCs. b) Serrated surface features within the fracture surfaces indicating pull-out mechanisms, imaged by SEM for relaxed samples. c) TEM images of micron sized cracks after uniaxial elongation of 500 nm thick slices of CNC-*g*-P(MMA-*r*-BMA-*r*-UPyMA) films, showing pull-outs (see arrows) for relaxed samples. d) Crack end demonstrating numerous filaments of plastic deformations spreading away from the crack end to extend the process zone, imaged by TEM for relaxed samples. Image reprinted with permission from Publication II © 2014 Wiley-VCH Verlag GmbH & Co.

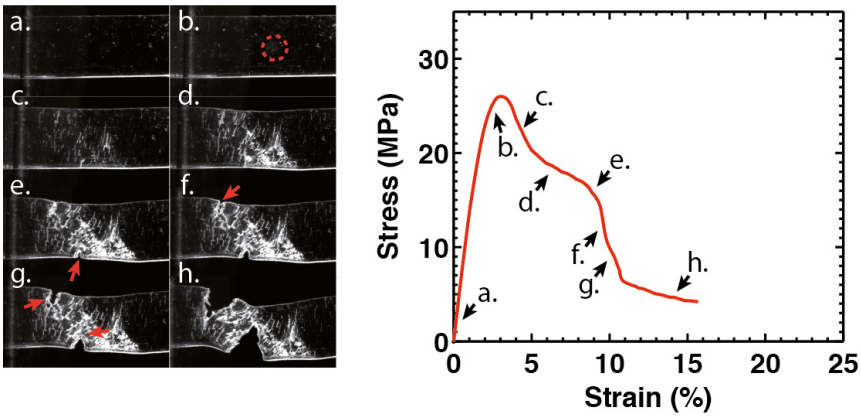

Figure 3.6. . (a-h) Photographs on stress whitening in the strongly deformed areas during an on-going tensile test, as observed from 100 mm thick heat-pressed CNC-*g*-P(MMA-*r*-BMA-*r*-UPyMA) films. Note the strain whitening, subsequent crazing, and the necking adjacent to any formed cracks (b-d). The red circle (b) demonstrates the nucleation of a stress whitening area; the red arrows (e-g) demonstrate the rapidly propagating cracks, which are seen as steeper slopes in the corresponding red stress-strain curve. (right) A stress-strain curve, corresponding to the photographs a-h. Image reprinted with permission from Publication II © 2014 Wiley-VCH Verlag GmbH & Co.

3.5 Binding Nanocellulose with Functional Polysaccharides

Natural wood-fibre structures offer templates for functional nanomaterials.[1,75] In nature, hemicelluloses absorb cellulose nanofibrils through numerous hydrogen bonding arrays to form tightly cross-linked networks. This allows for a tight binding between the reinforcing and yielding domain. Through similar adsorption bindings, nanocomposite architectures can be envisioned, as shown in Publications III & IV.[98,99] For example, Publication III shows how to bind CNCs together using thermoresponsive methylcellulose to engineer thermoresponsive nanocomposite hydrogels. Publication IV, on the other hand, shows how to engineer energy dissipative hybrid supramolecular network consisting of colloidal NFC and supramolecular hydrogels. Here, a second-guest functional polysaccharide adsorbed to the surface on NFC and simultaneously formed the dynamic CB[8] network into the hybrid architecture. This led to an interconnected nanocomposite hydrogel.

This adsorption occured via the aforementioned biomimetic sacrificial bonding architecture (see Chapter *2.1.1 Energy Dissipation through sacrificial bonds and hidden length, case 2*). However, it is difficult to quantify how effective it was as there are no data in the binding equilibrium or exchange dynamics between polysaccharides and nanocellulose surfaces. By physically cross-linking nanocellulose with linear polysaccharides, a clear increase in the modulus values occurred. However, there were negligible changes in the yield-strain. Tentatively, this would point toward a fairly static binding, which would demonstrate little dissipation.

3.5.1 Thermoresponsive Nanocellulose Hydrogels

To test the hypothesis of binding polysaccharides with nanocellulose surfaces, thermoresponsive methylcellulose (MC) was combined with CNCs by simply dissolving dry MC powder into CNC dispersions of specific concentrations. Within a few hours of mixing, networks with increasing viscosity formed. At room temperature (20 °C), the samples behaved like viscoelastic fluids with increasing low-shear moduli with higher CNC loading (Figure 3.7). The increased moduli were attributed to the increased amounts of hydrogen binding sites with respect to increased CNC concentration, i.e. increased surface adsorption. Cryo-TEM images showed a fully homogeneous distribution of CNCs within the MC matrix, indicating excellent compatibility between the linear polysaccharides and anionic CNCs at 20 °C (see Publication III Figure S6).

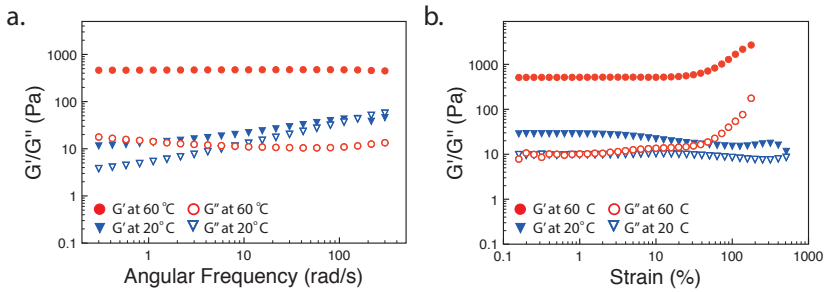

Figure 3.7. Typical dynamic oscillatory rheological characterization for the nanocomposite hydrogel with a 1.5 wt.% cellulose nanocrystal loading with 1.0 wt.% methyl cellulose: (a) frequency dependent oscillatory measurement at 60 °C (red) and 20 °C (blue), indication gelation in the first case and a viscoelastic network in the second; (b) strain dependent oscillatory measurement at 60 °C (red) and 20 °C (blue). Image reprinted with permission from Publication III © 2014 American Chemical Society.

By increasing the temperature above the cloud-point (CP), a clear change in morphology was observed for each CNC/MC sample* as well as the pure MC reference sample. Here, the samples turned more turbid, in a similar manner as thermoresponsive polymers in solution. Typically, thermoresponsive polymers phase-separate upon heating them above their respective cloud-points. There are different types of thermoresponsive polymers categorized by which properties affect the thermal transition.[100] For example, the transition of poly(*N*-isopropyl acrylamide) (PNIPAM) is relatively static when compared to methylcellulose – showing only slight deviances in the transition temperature at different concentrations and molecular weights.[101] Methylcellulose, on the other hand, demonstrates a highly complex transition, which is affected by the molecular weight, concentration, degree of methoxy substitution and the heating rate.[102,103] Hence, the transition is challenging to quantify.

* Each aqueous CNC/MC sample contained 1 wt.% MC, with incrementally higher CNC concentrations ranging from 0.2 wt.% to 3.5 wt.%. The reference sample contained 1 wt.% MC.

Furthermore, the transition tends to happen over a broad temperature range unlike PNIPAM and other similar synthetic polymers, which undergo a fairly sharp coil-to-globule transition upon passing the cloud-point. MC, on the other hand, undergoes a coil-to-fibril transition.[102-104] This results in a distinct increase in the modulus values. Switchable thermoresponsive gelation is a desirable property in materials, especially if this increased modulus can be further increased and tuned with CNC nanoreinforcement.

By heating the MC-CNC nanocomposite hydrogels to 60 °C, a clear change in the network morphology occurred, similarly to the reference sample. Frequency-sweeps showed a clear change from viscoelastic fluids (20 °C) to elastic hydrogels (60 °C), wherein $G' \gg G''$, $G' \sim \omega^0$ (Figure 3.7). Additionally, the zero-shear modulus values demonstrated an order of magnitude increase for each sample when heated to 60 °C (Figure3.8a). Cyclical heating-cooling cycles further demonstrated a fully reversible transition up to 75 °C (Figure3.8b).

This study demonstrated the feasibility of fabricating functional nanomaterials by polysaccharide adsorption onto nanocellulose surfaces using facile fabrication methods.

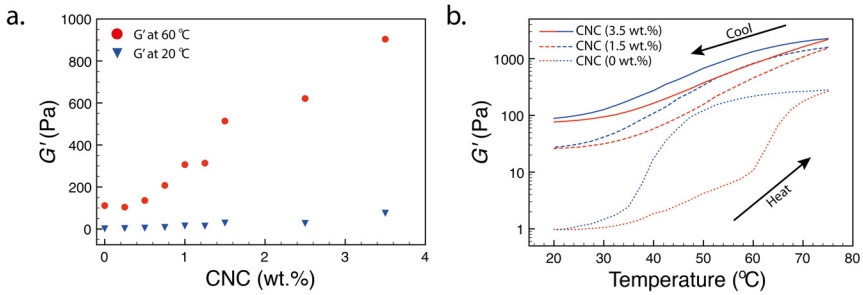

Figure 3.8. (a) Zero-shear *G'* values for hydrogels with increasing cellulose nanocrystal loadings at 60 °C (red) and 20 °C (blue) with fixed amount of methyl cellulose (1 wt.%), as determined via strain dependent oscillatory rheometry. (b) Cyclical measurements consisting of zero-shear *G'* values at different temperatures for three different samples with different CNC loading, as determined via strain dependent oscillatory rheometry. Image reprinted with permission from Publication III © 2014 American Chemical Society.

3.5.2 Combining Supramolecular Networks with Colloidal Hydrogels Through Cellulose Adsorption

Currently, one of the main questions regarding nanofibrillated cellulose is how to rationally engineer the mechanical and rheological properties. Pristine NFC hydrogels, for example, show fairly high modulus values with respect to their solids content (0.2-0.4 kPa at ~1 wt.%). The networks, however, tend to offer short linear viscoelastic regimes up to only ~20-30 % strain at 1 wt.%.*

* These values correspond with the NFC used in Publication 4: native hardwood nanofibrils after 20 passes through a homogenizer.

Publication IV shows a hybrid architecture wherein an interpenetrating and interconnected supramolecular network was engineered within a NFC hydrogel to increase both the stiffness and yield-strain. The dynamic supramolecular network consisting of: (1) a cationic first-guest functional random copolymer consisting of poly(styrenetrimethyl-amine hydrochloride) and MV functional styrenics (PSTMV) (5 mol.% MV loading);[56] (2) second-guest functional hydroxyl-ethyl cellulose (HEC-Np)[57] (1 mol.% Np loading) with (3) CB[8] to bind the molecular constituents together (Figure 3.9). Hence, the hybrid nanocomposite material consisted of reinforcing colloidal length-scales and bridging dissipating molecular length-scales. The network was formed by first combining standard amounts of PSTMV (0.5 wt.%), CB[8] (0.1 wt.%) with varying amounts of NFC (0-1.5 wt.%). Due to the electrostatic stability of PSTMV, there was no apparent interaction between the molecular components and NFC at this point except for the 1:1 complex between MV and CB[8]. This is important as it allowed for good mixing and thus a fully interpenetrating system. Next, a fixed amount of HEC-Np (0.15 wt.%) was added to form the 1:1:1 ternary complex and to bind the ensuing dynamic network to the colloidal NFC via non-specific adsorption to the nanocellulose surface. This tethered both networks together to form the hybrid supramolecular nanocomposite structure.

According to strain-sweeps, the hybrid supramolecular nanocomposite network showed distinctly higher modulus values and, more importantly, broader linear viscoelastic regimes than the corresponding NFC reference (Figures 3.10 & 3.11). Indeed, by combining the two networks, the increased modulus values were greater than their sum – indicating an efficient synergy between both networks leading to promoted stiffness as well as yield-strain. The promoted stiffness resulted from the interconnected supramolecular network 'gluing' the NFC domains together. Additional strain energy was also required to break down the network, thus promoting the elasticity due to the presence of the supramolecular CB[8] bonds with their capability to rapidly dissociate and reform upon deformation.[64]

The interconnectivity was determined by a NFC, PSTMV and HEC-Np control without CB[8] or using only CB[7], which can only bind one guest. These two components showed only a slight increase in the low-strain modulus, though distinctly smaller than with all four components, indicating physical binding between NFC and HEC-Np. However, there was no apparent increase in the yield-strain (Figure 3.11). This also demonstrated that the promoted rheological properties were driven by the dynamic CB[8]-binding. Indeed, the addition of more dynamic CB[8] interactions showed a clear relationship with higher yield-strain values (Figure 3.10) - with increased dynamics, more efficient energy dissipation occurred.

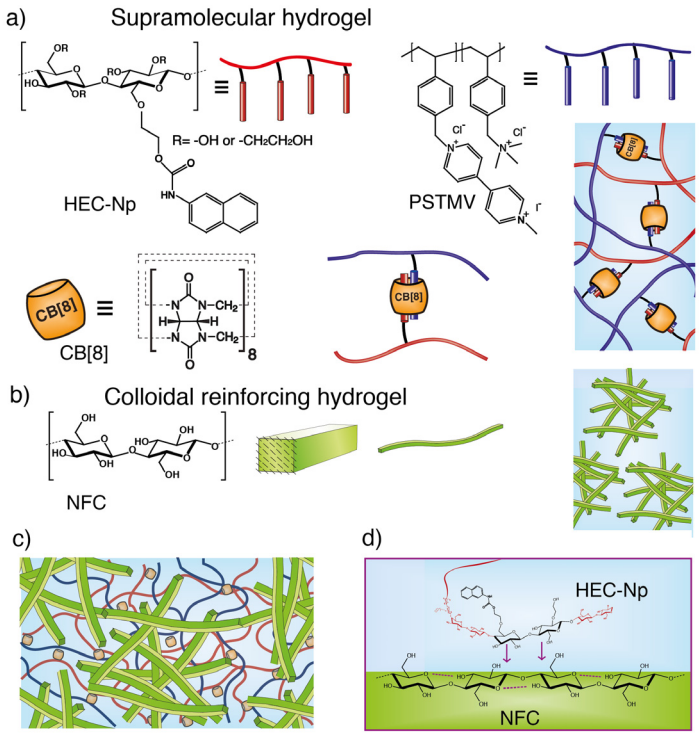

Figure 3.9. (a) Schematic representation of the dynamic supramolecular hydrogel consisting of: second-guest functional HEC-Np (fixed amount 0.15 wt.%); first-guest functional PSTMV (fixed amount 0.5 wt.% loading); (c) CB[8] host motif (fixed amount 0.1 wt.%). Also showing the molecular network bound by the ternary complexation of CB[8]. (b) The colloidal reinforcing nanofibrillated cellulose (variable amount 0-1.5 wt.%). Also showing the structure consisting of flocks bound by single NFC fibrils. (c) The interconnected hybrid supramolecular nanocomposite network consisting of the molecular supramolecular gel and NFC flocs. (d) Surface adsorption of HEC-Np onto nanocellulose surface.

SEM of the freezedried aerogels show how the pure NFC had a highly fibrillar structure, similar to previous literature precedents (see Publication IV Figure S3). However, the nanocomposite network contained a mixture of fibrillar and sheet-like structures, indicating the presence of a molecular polymer. Additionally, the aerogel did not reveal any apparent phase-separation also indicating good mixing and compatibility.

This architecture offers insights on how to engineer yielding towards molecularly engineered biomimetic composite materials. By selecting a similar type of interconnected and interpenetrating dissipative network, more efficient yielding could be engineered into dry NFC materials. However, the binding mechanics and connectivity need to be carefully evaluated, as all components need to be compatible and the binding needs to be specifically designed to effectively function at high strength and strain, i.e. effectively work against the deformation of the nanofibrils.

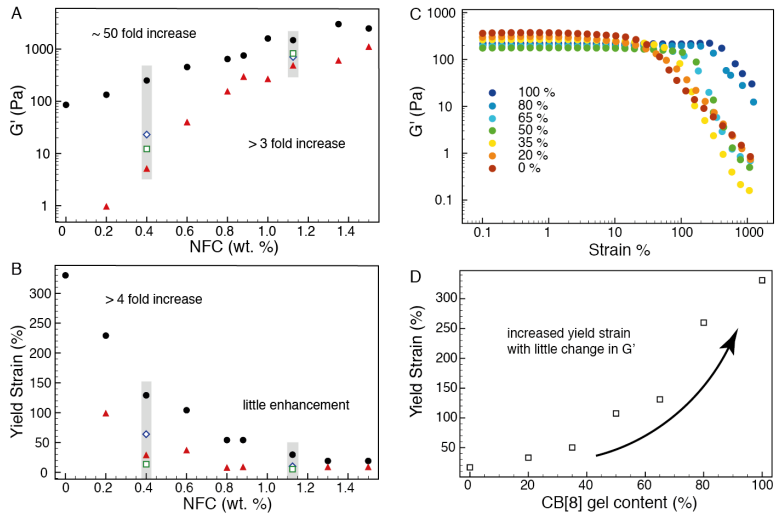

Figure 3.10. (a, b) (Black circles) Hybrid supramolecular hydrogels with specific NFC loading and standard amount of CB[8] constituents; (red triangles) pure NFC reference. The references, highlighted in grey box: (blue diamonds) all the components except CB[8] host and (green squares) the reference CB[7] with all components except CB[8]. (a) Low strain limit G' values. The G' values were determined in the linear regime (0.1-1 % strain) at 10 rad/s. (b) Shear thinning strain values determined at 10 rad/s. (c) constant total amount of solids (1.15 wt.%) with changing wt. % of supramolecular gel vs. NFC. (d) yield-strain of the constant total solid content gels with changing percentage of CB[8] gel vs. NFC.

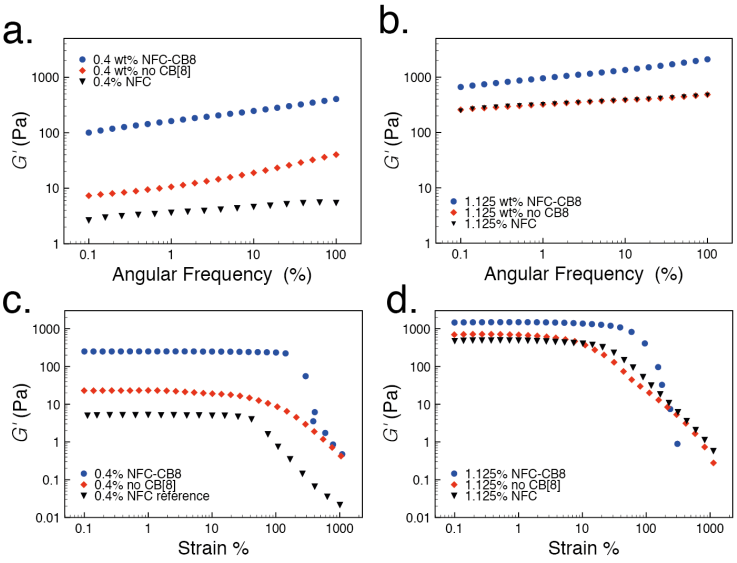

Figure 3.11. Characterization by dynamic oscillatory rheology: (blue circles) hybrid nanocomposite hydrogel with 0.4 or 1.125 wt.% NFC loading; (red diamonds) corresponding reference sample with all components except CB[8] host; and (black) corresponding NFC reference. (a), (b) Frequency sweeps as determined at 10 % strain for the samples that contain 0.4 and 1.125 wt.% NFC. (c), (d) Strain sweeps, as determined at 10 rad/s for the samples that contain 0.4 and 1.125 wt.% NFC samples

4. Conclusions and Future Perspective

Natural materials are wonderfully complex as seen throughout this thesis. However, there is still a long way to go for the fabrication of biomimetic materials insired by nature that combine excellent strength, stiffness and toughness through synergistically utilizing nanomechanics through several length-scales. This thesis focuses on the aspect of combining nanoreinforcement with supramolecular sacrificial networks. It should be noted that all results discussed within this thesis are preliminary glimpses on what the future has to offer material scientists, with regards to synthetic biomimetic architectures. To conclude, the main findings discussed within this thesis are:

1. Compatibility between all the components will lead to a more homogeneous distribution of the colloidal reinforcement. This can be effectively achieved by polymer grafts attached to the colloidal reinforcing domain, which allows for a broad range of chemical compatibilities from polyelectrolytes in aqueous solutions to hydrophobic thermoplastics in bulk.

2. Using supramolecular polymers with specific architectures can act as efficient sacrificial networks that dissipate energy. Special care, however, needs to be taken with the amount of binding sites, the type of binding, binding equilibrium and dynamics, selectivity, the location within the network and chains (pendant groups, backbone or end-groups).

3. Interconnected colloidal level reinforcing phases and yielding networks. Both domains should be strongly interconnected together, either through covalent interactions or strong physical interactions.

4. Specific supramolecular interactions or functional polymers can be effectively used to engineer functionality into nanocomposites, such as the ability to self-heal or thermoresponsive properties.

Future studies on biomimetics should broaden the concept of sacrificial bonds with more systematic studies on the relationship between the binding equilibrium, binding dynamics and the network they are embedded in. More specifically, how the network properties should be taken into account when choosing the sacrificial binding. Will softer networks work more efficiently with dynamic interactions or more static bindings or a mixture of both? What

about glassy networks where the chain movement is locked? Most likely, dynamic interactions will not do much, as the chains cannot keep up with the exchange dynamics. Rubbers are interesting as static interactions could increase the stiffness whereas dynamic interactions might increase the yielding. Here, a large array of binding types would be highly efficient similar to nature; however, this is synthetically challenging.

Another interesting idea is to use nanoreinforcement, which is also constructed using sacrificial supramolecular principles, similar to the helical structure of collagen and the ß-sheets of silk. Such synthetic architectures have already been constructed; however, the main challenge is how to embed them into the polymer matrix effectively: interconnected matrix with a homogeneous distribution of the reinforcing motif.

Finally, the main dream is to construct synthetic materials that contain all of the aforementioned aspects. Also, the material should be lightweight, offer promoted mechanical properties when compared to more classic polymer-based materials as well as being scalable and cheap to fabricate. Essentially, we are at the point where we are only starting to understand the full complexity of nature: how the materials work and why. Transferring these functions to synthetic materials will take a lot more time and work. One exciting possibility for future materials will be hybrids that contain both engineered natural components together with chemically engineered components. The first examples have already been shown, based on engineered protein binding or using viruses as functional templates.

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Aalto-DD 2/2015

ISBN 978-952-60-6034-7 (printed)
ISBN 978-952-60-6035-4 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

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