Water-borne Self-assembled Polymer/Nanoclay-Based

Nacre-mimetics with Superior Mechanical and Functional
Properties

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen
University zur Erlangung des akademischen Grades einer Doktorin der Naturwissenschaften
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vorgelegt von

M.Tech.

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‘Strive constantly to serve the welfare of the world; by devotion to selfless work one attains the supreme goal of life. Do your work with the welfare of others always in mind.’

- The Bhagavad Gita
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<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>MTM</td>
<td>Montmorillonite</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly(vinylalcohol)</td>
</tr>
<tr>
<td>GPa</td>
<td>Gigapascal</td>
</tr>
<tr>
<td>MPa</td>
<td>Megapascal</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxymethylcellulose</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-by-layer</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
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<tr>
<td>µm</td>
<td>Micrometer</td>
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<tr>
<td>mm</td>
<td>Millimeter</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeter</td>
</tr>
<tr>
<td>CaCO</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>Copper sulphate</td>
</tr>
<tr>
<td>DS</td>
<td>Degree of substitution</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>ACC</td>
<td>Amorphous calcium carbonate</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>LDH</td>
<td>Layered double hydroxides</td>
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<td>--------------</td>
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<tr>
<td>PDADMAC</td>
<td>Poly(diallyldimethylammonium chloride)</td>
</tr>
<tr>
<td>CH</td>
<td>Chitosan</td>
</tr>
<tr>
<td>UV-VIS</td>
<td>Ultraviolet-Visible</td>
</tr>
<tr>
<td>GA</td>
<td>Glutaraldehyde</td>
</tr>
<tr>
<td>OH</td>
<td>Hydroxyl</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>FITR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>LB</td>
<td>Langmuir-Blodgett</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>LAP</td>
<td>Laponite</td>
</tr>
<tr>
<td>SUM</td>
<td>Sumecton</td>
</tr>
<tr>
<td>NHT</td>
<td>Sodium fluorohectorite</td>
</tr>
<tr>
<td>NTS</td>
<td>Sodium tetrasilicic mica</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>CPMAS</td>
<td>Cross-polarization magic-angle spinning</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width half maximum</td>
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<tr>
<td>WOF</td>
<td>Work-of-fracture</td>
</tr>
<tr>
<td>WAXS</td>
<td>Wide-angle x-ray scattering</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively coupled-atomic emission spectroscopy</td>
</tr>
<tr>
<td>VFT</td>
<td>Vertical flame test</td>
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<tr>
<td>FLIR</td>
<td>Forward looking infrared</td>
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<td>WAXD</td>
<td>Wide-angle x-ray diffraction</td>
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<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>----------------------------------</td>
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<tr>
<td>TTI</td>
<td>Time to ignition</td>
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<tr>
<td>pkHRR</td>
<td>Peak heat release rate</td>
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<tr>
<td>THR</td>
<td>Total heat release</td>
</tr>
<tr>
<td>TSR</td>
<td>Total smoke release</td>
</tr>
<tr>
<td>DTGA</td>
<td>Differential thermogravimetric analysis</td>
</tr>
<tr>
<td>ISO</td>
<td>International organization for standardization</td>
</tr>
<tr>
<td>ChNFs</td>
<td>Chitin nanofibrils</td>
</tr>
<tr>
<td>NPs</td>
<td>Nanoparticles</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>NaBH₄</td>
<td>Sodium borohydride</td>
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Summary

This thesis deals with the fabrication of water-borne self-assembled polymer/nanoclay-based nacre-mimetic nanocomposites, where the polymer serves as the soft matrix and the nanoclays act as hard reinforcements. The core/shell nanoplatelets are prepared via adsorption of a single polymer layer on top of the hard nanoclays by slow addition of dilute nanoclay dispersion into excess aqueous polymer solution and subsequent separation of excess polymer via centrifugation/redispersion cycles to maximize the fraction of reinforcements in the final material. The resulting core/shell nanoplatelets undergo concentration-induced self-assembly on a macroscopic length scale due to excluded volume effects during the evaporation of water.

In another approach, a large scale, one-pot, single step, and fast process is employed by omitting the intermediate extensive purification step and utilizing a careful direct mixing of optimized dispersions of polymer and nanoclay in a high-shear homogenizer followed by subsequent direct self-assembly into nacre-mimetic films. High shear homogenization allows direct preparation of concentrated, yet homogeneous gel-like dispersions of higher nanoclay content, suited for large-area and thick films prepared by doctor blading with essentially the same properties as films cast from dilute dispersions. While self-assembly via ‘perfect’ core/shell route is followed in the third chapter, a one-pot, direct mixing approach is used in the fourth, fifth, and sixth chapters of this thesis.

Present day polymer/nanoclay-based nacre-mimetics mostly concentrate on natural MTM nanoclay as hard phase, but MTM suffers from some disadvantages, e.g. its un-tuned aspect ratio, presence of iron or other metal oxides as contaminants leading to yellowish color, non-perfect surface charge distribution, and presence of fractions of larger agglomerates leading to imperfect exfoliation. However, synthetic nanoclays are devoid of such disadvantages. Therefore, herein, self-assembled artificial nacres are prepared using synthetic nanoclays with
aspect ratios covering three orders in magnitude (25-3500) and water soluble synthetic polymer, polyvinylalcohol (PVA), via ‘perfect’ core/shell approach. Comprehensive relationships among structure formation, deformation mechanisms and mechanical properties are established as a function of aspect ratio, and by tuning the viscoelastic properties of the soft phase via hydration. While nanocomposites reinforced with low aspect ratio nanoclay show superior toughness owing to pronounced inelastic deformation via platelet pull-out, those formed by higher aspect ratio exhibit superb stiffness up to 40 GPa and tensile strength exceeding 200 MPa, thereby attaining the elastic properties previously obtained only after tedious post-crosslinking. Also, the amount of polymer content in the nanocomposites based on differently sized nanoclays (very small vs. very large) influences the transition towards inelastic deformation and stable crack propagation. The well-defined ordered structure of the nacre-mimetics from meso to nanoscale is characterized by SEM, AFM, HRTEM, XRD methods. Tensile mechanical properties are thoroughly evaluated and compared using mechanical models. Also considering sustainable alternatives for future materials, polymers from petrochemical origin are replaced by renewable polymers in nacre-mimetics. Herein, one-pot, direct mixing approach is employed to fabricate self-assembled, large-area nacre-mimetics from completely nature based components, sodium carboxymethylcellulose (CMC) as a soft energy-dissipating phase and MTM as hard phase. The nanoscale periodicities of the alternating hard/soft layers are precisely tuned by changing the feed ratio of homogeneous dispersions of CMC and MTM. This allows studying the evolution of mechanical properties as a function of the lamellar nanoscale periodicity and hard to soft feed ratio. Remarkable mechanical stiffness (25 GPa) and strength (320 MPa) are obtained placing these materials among the top end of nacre-inspired materials reported so far. Enlarging the stacking distance between the nanoclays by adding slightly more polymer provides some inelastic deformation and higher toughness even at very low humidity. In addition, to efficiently stabilize the mechanical properties of CMC/MTM nacre-mimetics at high humidity (95 %RH), ionic
supramolecular bonds are introduced by infiltration of divalent Cu\(^{2+}\) ions. The mechanical properties in the highly hydrated state (stiffness = 13.5 GPa and tensile strength = 125 MPa) show comparable values to a range of non-crosslinked nacre-mimetics in the dry state. Moreover, the Cu\(^{2+}\)-treated nacre-mimetics demonstrate synergetic mechanical properties via simultaneous improvement of stiffness, strength and work-of-fracture (WOF), as compared to the pristine material. Some inelastic deformation takes place considering the highly reinforced state. This contrasts the typical behavior of tight, covalent crosslinks, and is suggested to originate from a sacrificial, dynamic breakage and rebinding of transient supramolecular ionic bonds.

In terms of functional benefits, synthetic nanoclay-based nacre-mimetics exhibit formerly impossible glass-like transparency and excellent gas barrier properties. While surface-pattern via inkjet printing and shape-persistent fire-blocking behavior are achieved from CMC/MTM nacre-mimetics. To investigate the fire-blocking behavior in detail, thick, layered, hybrid, brickwall CMC/MTM nanocomposite is coated on textile. The coating thickness is tailored using different concentrations of CMC/MTM (1–5 wt%) in the coating bath. While lower concentrations impart conformal coatings of fibers, highest concentration gives thicker continuous coatings on the whole textile surface. Fire barrier and retardancy behaviors are evaluated by thermogravimetric analysis (TGA), fire break-through test, vertical flame test (VFT), thermal imaging using forward looking infra-red (FLIR) camera, and cone calorimetry. Comprehensive studies elucidate the increasing fire barrier and retardancy with increasing coating thickness. Additional amphiphobic surface modification imparts oil and water repellence, as well as self-cleaning features on these fire barrier nanocomposite coatings on textile. Considering the simple and fully scalable, water-borne preparation pathway, this study enables rational design of future high-performance nacre-mimetic materials and opens avenues for eco-friendly, transparent, self-standing and strong advanced barrier materials.
Zusammenfassung


Darüber hinaus wurde ein einfacherer und schnellerer Prozess entwickelt, der auch in größerem Maßstab durchgeführt werden kann. Hierbei entfallen der aufwändige Zwischenschritt der Aufreinigung, indem eine optimierte Mischung der Polymer- und Schichtsilikat-Dispersion in einem High-Shear Homogenizer behandelt wird, welche im anschließenden Verfahren direkt zur Selbstorganisation von Perlmuttmimetika-Filmen führt. Durch den Einsatz von High-Shear Homogenizern lassen sich so auf direktem Wege konzentrierte und zugleich homogene Gel-ähnliche Dispersionen mit hohem Schichtsilikat-Anteil erhalten, welche sich zur Herstellung von großflächigen und dicken Filmen über Rakeln eignen. Sie weisen zudem weitgehend die gleichen Eigenschaften auf, wie Filme die über verdünnte Dispersionen erhalten wurden. Während die „perfekte“ Kern-Schale Route zur Herstellung von Perlmuttmimetika-Nanokompositen im dritten Kapitel verwendet wird,
werden in den Kapiteln vier, fünf und sechs dieser Arbeit Nanokomposite verwendet, welche durch die einfache und schnelle Methode des direkten Mischens erhalten wurden.

dass die Menge an Polymeranteil im Nanokomposit in Abhängigkeit der Größe der Schichtsilikate (kleines gegen sehr großes Seitenverhältnis) den Übergang zu inelastischer Deformation und stabiler Bruchdehnung beeinflusst. Die hochgeordnete definierte Struktur von Perlmuttmimetika von Meso- bis hin zur Nanoskala wird durch REM, AFM, HRTEM und XRD charakterisiert. Zug-Dehnungseigenschaften werden ausgewertet und mit mechanischen Modellen untereinander verglichen. Im Hinblick auf Nachhaltigkeit, sollen Polymere auf Erdölbasis durch Makromoleküle aus nachwachsenden Rohstoffen zusammen mit natürlich vorkommenden Schichtsilikaten verwendet werden. Aus diesem Grund wird die einfache und schnelle Direktmischung genutzt, um großflächige Perlmuttmimetika Nanokomposite zu erhalten, welche vollständig aus natürlich vorkommenden Materialien, Natriumcarboxymethylcellulose (CMC), hier als Polymer für die weiche, energieverteilende Phase, mit MTM als hartem Baustein, bestehen. Die Periodizität der harten und weichen Phasen im Nanobereich wird präzise durch die Zusammensetzung der homogenen Mischung aus CMC und MTM bestimmt, was eine Untersuchung der mechanischen Eigenschaften als Funktion der lamellaren Nanoperiodizität und des Anteils an harter und weicher Phase ermöglicht. Bemerkenswerte mechanische Steifigkeit (25 GPa) und Zugfestigkeit (320 MPa) können hierbei erhalten werden, was diese Materialien an die Spitze der permuttinspirierten Materialien setzt, die bisher berichtet wurde. Die Erhöhung des Ebenenabstandes zwischen den Schichtsilikaten durch Zugabe von geringen Mengen an zusätzlichem Polymer hat eine begrenzte inelastische Deformation und eine höhere Festigkeit zur Folge, auch bei geringer Luftfeuchtigkeit. Zusätzlich werden ionische supramolekulare Bindungen, welche durch die Infiltration von bivalenten Cu\(^{2+}\)-Ionen erzeugt werden, dazu genutzt, eine effektive Stabilisierung der mechanischen Eigenschaften bei hoher Luftfeuchtigkeit (95% rF) zu ermöglichen. Die mechanischen Eigenschaften im stark gequollenen Zustand (Steifigkeit = 13,5 GPa und Zugfestigkeit = 125 MPa) zeigen vergleichbare Werte zu einer Reihe von nicht komplexierten Perlmuttmimetikafilmen im trockenen Zustand. Des Weiteren zeigen Cu\(^{2+}\)
Zusammenfassung

behandelte Filme eine synergistische Verbesserung der mechanischen Eigenschaften, da sie eine gleichzeitige Erhöhung der Steifigkeit, der Zugfestigkeit und der Brucharbeit im Vergleich zu unbehandelten Filmen aufweisen. Trotz des hohen Verstärkeranteils zeigen die Proben eine inelastische Deformation. Dieser Unterschied zum typischen Verhalten von dichtgepackten, kovalenten Querverbindungen ist vermutlich auf das dynamische Brechen und Neubilden der supramolekularen ionischen Bindungen zurückzuführen (sacrificial break and rebind).

Im Sinne der funktionellen Eigenschaften sind Filme mit bisher unerreichter, glasähnlicher Transparenz und exzellenten Gasbarriereeigenschaften mit synthetischen Schichtsilikaten möglich. Perlmuttmimetika auf CMC/MTM-Basis führen zu formstabilen Feuerblockaden und Oberflächenstrukturierungen können durch Inkjet printing erreicht werden. Um die Feuerbarriereeigenschaften im Detail zu untersuchen wurden dicke, geschichtete Verbundwerkstoffe aus CMC/MTM Nanokomposite auf Textilien aufgebracht. Die Beschichtungsdicke wird durch verschiedene Konzentrationen von CMC/MTM (1 – 5 wt%) in einem Beschichtungsbad eingestellt. Während geringere Konzentrationen einheitliche Beschichtungen auf Fasern gewährleisten, werden durchgehende Beschichtungen, die die gesamte Stoffoberfläche umfassen durch die höchste Konzentration erreicht (5 wt%). Flammbarriere und Flammfestigkeit werden durch thermogravimetrische Analyse (TGA), Flammdurchbruchtests, vertikale Flammtests (VFT), Wärmebildanalyse durch eine vorwärts gerichtete Infrarotkamera (FLIR, engl.: forward looking infra red) und Kegelkalorimetrie evaluiert. Vergleichende Untersuchungen ergeben eine steigende Flammbarriere und Flammfestigkeit mit steigender Beschichtungsdicke. Zusätzlich führen diese flammbarriere Nanokompositbeschichtungen zu amphiphoben Oberflächeneigenschaften, die sowohl Öl als auch Wasser abweisen und somit zur Selbstreinigung auf den Textilien führt. In Anbetracht des einfachen und skalierbaren,
wasserbasierten Herstellungsverfahrens, ermöglicht diese Arbeit das Design zukünftiger Hochleistungsperlmuttermimetika und öffnet neue Wege für umweltfreundliche, transparente, tragfähige und fortschrittliche Barrierenmaterialien.
Introduction

1.1. Motivation

Natural materials with the astonishing complexity in their hierarchical structure and functional properties motivate us to build up the future generation advanced functional materials. The outstanding properties of these biological materials arise from their structural architecture at different length scales created from a limited set of elements especially with the help of proteins and enzymes in water at ambient temperature. The self-organization of the components with often brittle and weak properties into an ordered hierarchical structure allows to overcome the shortcomings of the constituting materials and enables synergetic mechanical behavior and/or the development of multifunctionalities. Mother of pearl (also known as nacre), spider silk, wood, crustacean cuticles and bone are some prime examples of nature’s load bearing materials. Nearly all of these bionanocomposites are characterized by ordered structures with large fraction of hard and reinforcing segments arranged in a minor amount of soft, energy-absorbing and lubricating biopolymer matrix. The interface between the hard and soft phase is strong and well controlled, and, moreover, the materials are capable of self-repair and exhibit high resilience and fatigue resistance. Due to their unique combination of stiffness, strength and toughness with low density, they set the paradigms for lightweight and strong engineering materials needed for energy efficient mobile technologies e.g. in automotive, aerospace engineering, etc. To serve this purpose, there have been considerable efforts for the fabrication of synthetic nanocomposites following the classical approach by mixing a minor amount of compatibilized reinforcing component (nanotubes/nanofibers/platelets) into a polymer matrix used as majority component. Despite progress, it has however remained extraordinarily difficult to obtain synergetic improvements
of stiffness, strength and toughness in such approaches, hence needing for biomimetic design principles at molecular level to prepare mechanically robust nanostructured composites.

Mother of pearl or nacre serves as a remarkable example among natural nanocomposites inspiring for a range of concepts. Nacre is composed of a brick-and-mortar architecture, in which 95 vol% of CaCO$_3$ platelets (brick) are arranged in a minority phase of multifunctional biopolymer (mortar), containing chitin nanofibrils that are bound with fusion proteins for efficient stress transfer to the inorganic platelets. The overall material is considered a near perfect union of hard and soft matter, and allows an outstanding combination of mechanical properties due to different toughening mechanisms occurring via crack deflection, platelet pull-outs, constrained microcracking, mineral bridge formation, and biopolymer stretching. Owing to the presence of ‘intelligent’ biopolymers, sacrificial bonds and self-healing properties can be found in nacre. Sacrificial bonds provide hidden length scales (unfolding of superstructures, stick/slip mechanisms) and represent the key to extra toughness and stiffness in biology. The Young’s modulus of nacre can reach up to 40-70 GPa, ultimate tensile strength is as high as 80-135 MPa and the toughness is three thousand times higher than that of an aragonite monolith. These synergistic advanced properties largely contrast the present-day engineering nanocomposites and explain their shortcomings. Although, such biological materials are exciting due to their unique properties but the obstacles in their economic production and lack of scalability limits their large-scale technology.

This brings the motivation for the fabrication of bio-inspired, layered nanocomposites by mimicking the relevant structural aspects of nacre using technically more feasible constituent materials and processes, aiming at the mechanical properties of nacre, and also incorporating new multifunctionality needed for the engineering world. The biomimetic nanocomposite approach differs profoundly from the classic approaches which are based on pure mixing of the components using lower amount of reinforcements. By contrast, in biomimetic approaches, highly ordered and layered structures are pursued, typically using high fractions
of reinforcements in a minority soft matrix with alternating hard and soft layers, balancing sufficient binding and dynamic fracture energy dissipation by control of molecular interactions in the soft phase.\textsuperscript{1, 2, 5, 9, 10} Therefore, the approach specifically involves material engineering at the nano and mesoscale requiring new science and technological options.

Though seashells are able to grow these complex materials in water at room temperature in a lengthy process,\textsuperscript{1} such slow growth manufacturing strategies are not applicable for man-made structural materials. Hence it is a major scientific and technological challenge to find new time-efficient, self-assembly strategies to prepare such similarly structured large-scale complex materials with high fractions of reinforcements and easily tunable nanoscale structures. Although various strategies have been employed to mimic the layered hard/soft composite structure of nacre via e.g. several sequential approaches, such as LBL\textsuperscript{11-19} and other multilayer deposition strategies,\textsuperscript{20, 21} ice-templating and sintering of ceramics,\textsuperscript{22-24} spray coating,\textsuperscript{25, 26} glow discharge plasma deposition,\textsuperscript{27} uncontrolled co-casting of polymer/clay mixtures,\textsuperscript{28, 29} or processes at interfaces,\textsuperscript{30, 31} most of these approaches are limited to very small scale and therefore, remain technologically inapplicable due to energy-intensive and laborious multistep procedures. Therefore, a simple, fast, and large scale fabrication process is required considering the needs in the application world. In addition, further possibilities arising from the excellent nanostructural control have to be identified along with excellent mechanical properties and multifunctionalities. The motivation and main objectives of this research work are elaborately described in the following section.

1.2. **Scope of the thesis**

This thesis deals with the preparation and characterization of water-borne self-assembled polymer/nanoclay-based nacre-mimetics with highly ordered layered nanostructure mimicking the brick-and-mortar structure of natural nacre using a simple, fast, and scalable approach. This work shows that superb control over the nanostructuration in nacre-mimetics is achieved via concentration-induced self-assembly of polymer-coated core/shell
nanoplatelets. Those are decisive to predefine the length scales of the final nanocomposite and reach well-ordered alternating hard and soft layers during evaporation-induced self-assembly. The aim of this work is also to expand the material property profiles beyond mechanical performance and use new concepts to achieve multifunctionality which is highly relevant for the future technologies. Such multifunctional properties include fire and gas barrier properties, anisotropic thermal, electric or ionic conductivity with superior transparency. In this regards, two-dimensional (2D) clay nanosheets are among the most interesting building blocks to realize these outstanding challenges due to their high interface, nanoscale dimensions and tunable aspect ratio. In this work, on one hand, synthetic nanoclays of widely varied sizes (25-3500 nm) are used as hard building blocks to advantage their benefits over several shortcomings arising from natural nanoclays, and to study the effect of nanoclay sizes on structure formation and mechanical properties of the nanocomposites. On the other hand, for sustainable alternative, renewable polymer like sodium carboxymethylcellulose (CMC) is used as a soft energy-dissipating phase replacing the petrochemical based polymers. Moreover, the preservation of mechanical properties at high humid condition is also shown by introducing ionic supramolecular bonds. This work also concentrates on implementing new concepts for multifunctional biomimetic materials including excellent gas barrier and fire-blocking properties, glass-like transparency, and printability. Furthermore, an application of nacre-inspired, hybrid brick-walls fire barrier coatings is also shown on textiles with amphiphobic and self-cleaning features.

Chapter 1 gives an introduction to this thesis and explores the motivation of the research in the field of water-borne self-assembled polymer/nanoclay-based nacre-inspired nanocomposites.

Chapter 2 describes briefly the evolution of natural nacre, its hierarchical structure, and outstanding mechanical properties of nacre relating to its structure. This chapter further
introduces the concept of nacre-mimetics and highlights the importance of understanding the preparation techniques and their impact on mechanical properties. It also discusses the challenges associated with these techniques.

Chapter 3 deals with the highly ordered nacre-mimetics based on PVA as a soft phase and synthetic nanoclays with aspect ratios covering three orders in magnitude (25-3500) as reinforcing agents. This study compares the advantages of using synthetic nanoclays over natural nanoclays and further links nanostructure formation, mechanical properties, and deformation mechanisms with platelet size and by tuning the viscoelastic properties of the soft phase via hydration. Regarding functionalities, formerly impossible glass-like transparency and excellent gas barrier properties are reported.

Chapter 4 shows a simple and quick large-scale preparation process of nacre-mimetics using high-shear homogenization. Large-area and thick films based on biobased sodium CMC and natural sodium MTM are prepared by direct mixing of varied feed ratios of CMC/MTM, to tune the nanoscale periodicities of the alternating soft/hard layers. The evolution of remarkable mechanical properties as a function of the lamellar nanoscale periodicity and fractions of hard to soft material has been thoroughly investigated. In terms of functional properties, high-transparency, shape-persistent fire-blocking, and the ability to surface-pattern via inkjet printing are reported.

Chapter 5 demonstrates how ionic supramolecular bonds, introduced by infiltration of divalent Cu$^{2+}$ ions...
allow efficient stabilization of the mechanical properties of CMC/MTM nacre-mimetics films at high humidity (95 %RH) exhibiting mechanical values which are comparable to a range of non-crosslinked nacre-mimetic materials in the dry state. Cu\(^{2+}\)-treated nacre-inspired materials display synergetic mechanical properties as compared to the pristine material and significant inelastic deformation originating from sacrificial, dynamic breakage and rebinding of transient supramolecular ionic bonds.

**Chapter 6** demonstrates a single-step, water-borne approach to prepare thick, self-assembling, hybrid, fire barrier coatings of CMC/MTM with well-defined nanostructure, and showcase their application on cotton fabrics. The coating thickness is tuned using different concentrations of CMC/MTM in the coating bath. While lower concentration imparts conformal coatings of fibers, a thicker continuous coating on textile surface is obtained from higher concentration. Comprehensive tests elucidate the increasing fire barrier and retardancy properties with increasing coating thickness. Further amphiphobic surface modification of the coating is done to impart oil and water repellency, as well as self-cleaning features.

**Appendix A** contains the work which I did as a side project. It shows the preparation of macrofibers wet-spun from the hydrogels of surface-deacetylated chitin nanofibrils via extrusion in a coagulation bath. The resulting biofibers display attractive mechanical properties with a large plastic region of about 12% in strain. These macrofibers are further utilized as biobased, renewable catalytic hybrids by exploiting the amine functions of the surface chitosan groups to host catalytically active noble metal nanoparticles.
1.3. **References and Notes**


Nacre-mimetic materials: inspiration from nacre and various fabrication processes - state of the art

2.1. Evolution of Natural Nacre

Nacre, also known as mother-of-pearl, is the inner lustrous iridescent layer found in many mollusc shells, most commonly in bivalves such as pearl oysters (*Pinctada margaritifera*), gastropods such as red abalone (*Haliotis rufescens*) and cephalopods such as nautilus (*Nautilus pompilius*) groups.¹ Many different kinds of shell structures are found in molluscs, which include prismatic, foliated and cross lamellar structure, columnar and sheet nacre. All of these structures are mainly made up of large amount of aragonite (orthorhombic, calcium carbonate (CaCO$_3$) crystals) or calcite (rhombohedral, CaCO$_3$ crystals) platelets and small amount of (≤ 5 wt%) organic materials.² These mollusc shells protect themselves from predators and other external mechanical forces and therefore, need to be stiff and strong to function as an efficient armor system. Among all the shell structures, nacreous structures emerge as the strongest materials exhibiting elastic modulus in the range of 40-70 GPa and tensile strength around 120 MPa for shell Turbo as opposed to ultimate tensile strength of 60 MPa for other non-nacreous structures.³ Due to their low density (2.5 g·cm$^{-3}$), mollusc shells appear as an ideal example of lightweight, mechanically robust and tough armor system and attract considerable attention of biologists, material scientists and engineers to mimic their structure and mechanical properties to produce artificial nacre.¹⁻⁵

2.2. Hierarchical Structure of Nacre

The hierarchical structure of nacre, spanning over multiple length scales from nano to macro, plays the key role in realizing its outstanding mechanical properties (Fig. 1). In the macroscale, the shell consists of a three-layered armor structure: (i) the outermost
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periostracum layer (composed of hardened protein), (ii) the hard prismatic middle layer (composed of columnar calcite) and (iii) the stiff but tough nacreous inner layer (composed of aragonite platelets and organic materials). This type of synergetic arrangements allows optimized protection of the sea shell. Although, the outer hard layer protects the shell by preventing penetration of any foreign substances under external mechanical forces, but undergoes brittle failure. However, the softer nacreous layer is relatively ductile and can protect the inner soft tissues of animals, even if the outer layer is damaged, by dissipating the mechanical energy through inelastic deformation. Next in the mesoscale, growth bands are observed which are represented by a few sub-layers of viscoplastic protein within the nacreous layers during periodic growth of nacre (Fig. 1b). These mesolayers play an important role in the mechanical performance of nacre by acting as powerful crack deflectors. The microarchitecture in the nacreous layer is described as brick-and-mortar structure where the densely packed layers of aragonite platelets (diameter \( \approx 8 \) µm and thickness \( \approx 0.5 \) µm) act as the brick and the organic layers (thickness \( \approx 20 \) nm) act as the mortar as shown in Fig. 1c,e. These platelets grow in different manner, depending on the species, to produce columnar or sheet nacre.

Barthelat et al. showed, by using several microscopic analyses, that aragonite platelets are not microscopically flat rather exhibit waviness (Fig. 1f) which generates hardening mechanism of nacre. The roughness measured by laser profilometry for red abalone can reach amplitudes of 200 nm covering a significant fraction of the platelets. Katti et al. further discovered that the platelets are not only stacked on each other but also interpenetrated forming interlocks between them as shown in Fig 1g. This platelet interlocking significantly contributes to increasing the fracture toughness of nacre. In the nanoscale, grains are observed within the nanostructure of the aragonite platelets having the size in the range of ca. 30 nm, delimited by a fine three-dimensional network of organic material (Fig. 1i). These
nanograins provide some ductility to the platelets leading to plastic deformation around the crack tip and result into high fracture toughness of nacre. The aragonite platelets grow in a ‘Christmas-tree’ pattern in nacre (Fig. 1h) following first the nucleation of aragonite crystals, then their successive arrest by means of a protein-mediated mechanism, followed by reinitiation of the mineral growth on the new surface layer.\textsuperscript{13-15}

Figure 1. The multiscale structure of nacre. (a) View of the inner nacreous layer of a red abalone shell. (b) Cross-section of red abalone shell. (c) Schematic of the brick-and-mortar microstructure. (d) Optical micrograph showing tiling of the platelets. (e) SEM image of a fracture surface. (f) TEM image of nacre showing platelets waviness (red abalone). (g) SEM of nacre showing interlocks.\textsuperscript{2} (h) ‘Christmas tree’ pattern observed on the growth surface of steady state tiled aragonite nacre. (i) TEM images showing single aragonite crystal with some nanograins. (j) Mineral bridges (marked by arrows) between tile layers. (k) Asperities (a fraction of which are remnants of mineral bridges). (a-f) and (i) Reprinted with permission from ref. 3. (h,j,k) Reprinted with permission from ref. 15.

This growth pattern is later supported by the presence of mineral bridges (Fig. 1j) formed due to the continuous growth of aragonite platelets from their previous layers along the c-axis.
through the nanopores in the organic layers.\textsuperscript{16-19} These mineral bridges prevent crack extension in nacre and thus improve the mechanical properties in the organic matrix.\textsuperscript{20, 21} Moreover, as a result of these bridges, nanoscale mineral island-like structures, called nanoasperities (Fig. 1k) are formed. They control sliding resistance between platelets and hence promote ductility in nacre.\textsuperscript{2, 8, 21} Therefore, the structural architecture of nacre in each length scale spanning from nano to mesoscale has been associated with the strengthening and toughening mechanisms.

Bio-organic/polymer phase \textit{“mortar”:} The bio-organic structure of nacre has very strong influence on its mechanics but is so far not so well understood in comparison to the architectures. The organic matrix consists of proteins, with some glycoprotein and chitin nanofibrils. Different proteins control different aspects of shell formation process, e.g. providing nucleation sites for the growth of aragonite crystals, secretion of CaCO\textsubscript{3}, stabilizing aragonite crystals, organizing the crystals in overall three-dimensional structure.\textsuperscript{2} Careful cryo-TEM studies of the matrix of the bivalve Atrina suggested that interlamellar sheets are mainly made of highly oriented β-chitin nanofibrils followed by discontinuous layers of aspartic acid-rich proteins.\textsuperscript{22} The silk-fibroin like proteins associated with chitin may be responsible for the structural basis for the continuation of organic matrix framework around which the mineral is deposited.\textsuperscript{2} Evans,\textsuperscript{23} Metzler et al.,\textsuperscript{24} Suzuki et al.,\textsuperscript{25} and others studied the biominerization influenced by different proteins and the resulting materials in detail. As this is far beyond the scope of this work, the reader is referred to the above mentioned literature. The next paragraph contains the summary of the finding of these groups.

After detailed study of in vitro biomineralization, a complex called Pif-complex is reported which promotes aragonite growth in vitro in presence of chitin. The complex is made of two chitin binding proteins, Pif97 and N16 and one non-chitin binding protein, Pif80. It is summarized that first Pif80 protein acts and promotes aragonite formation. After around 8
µm, when chitin appears at the onset of lamellar nacre formation, the chitin binding proteins Pif97 and N16 start acting by exploiting the layer forming ability of N16 and connect the whole complex to organic framework. Therefore, all these four components (Pif80, Pif97, N16 and chitin) are equally important for the lamellar aragonite formation in nacre. These proteins contribute to mechanical strengthening in nacre by connecting the mineral part with the organic chitin nanofibrillar matrix which extends as continuous layer beyond individual aragonite platelets.

### 2.3. Mechanical Properties of Nacre Relating to its Structure

Extensive work has been done on the measurements of mechanical properties of nacre by using a variety of techniques including tension, three and four point bending, shear, and compression. The mechanical responses of the individual components have been measured by micro and nanoindentation on single aragonite platelet, and by single-molecule force spectroscopy on single organic molecules. Currey was the first to perform measurements on mechanical properties of nacre from a variety of bivalves, gastropods and cephalopods and suggested that the extraordinary fracture toughness of nacre originates from its microstructure and defined arrangement of aragonite platelets. He reported that the stress-strain curves of nacre describe an elastic region followed by a plastic region which subsequently leads to failure. Continued by the study of Jackson et al. on bivalve mollusc, *Pinctada imbricata*, who found that moisture absorbed in the organic matrix shows a significant plasticizing effect in the mechanical properties of nacre and thus leading to the plastic deformation, larger strain-to-failure and overall much higher toughness, albeit being accompanied with some reduction in tensile strength and stiffness. They reported Young’s moduli of 70 GPa and 60 GPa and tensile strength of 170 MPa and 130 MPa, under dry and wet conditions, respectively. Depending on degree of hydration, the work-of-fracture (WOF) of nacre varied from 0.35 to 1.24 kJ·m⁻², which is about 3000 times higher than that of
monolithic CaCO$_3$. Recent studies of the mechanical tests performed on nacre by Barthelat et al.\textsuperscript{10, 21} under wet and dry conditions are summarized in Fig. 2a,b. Results show that nacre under hydrated conditions exhibits first a linear elastic behavior with a Young’s modulus of 80 GPa and then undergoes a quite large plastic deformation with strain-at-break up to almost 1%. At tensile stresses of 60-70 MPa, the organic matrix starts to yield and the platelets slide past one other locally accompanied by strain hardening. Finally nacre fails due to platelet pull-out, as the aspect ratio of aragonite platelets is slightly below the critical value (critical aspect ratio depends on the ratio of average tensile stress in a platelet and yield shear strength), generating larger fracture toughness.\textsuperscript{28}

\textbf{Figure 2. Mechanical properties of nacre.} (a) Experimental tensile stress–strain curve for nacre and (b) associated deformation modes. (c) Experimental shear stress–strain curve for nacre and (d) associated deformation modes. Reprinted with permission from ref. 10.

Moreover, the strain of nacre at hydrated state is 10 times higher than the pristine aragonite.\textsuperscript{3, 10} This indicates that in spite of containing 95% of hard aragonite platelets, nacre exhibits a ductile-like behavior with relatively large failure strain. In order to achieve such large deformation, first, the organic/inorganic interface needs to be weaker than the platelets themselves to encourage platelet sliding over platelet fracture. Hence, strong platelets are required. Secondly, some hardening mechanism must operate at the platelet levels to spread the platelet sliding throughout the whole material. Espinosa et al.\textsuperscript{3} suggested that as the platelets behave as linear elastic, the inelastic behavior must arise from the shearing at the interfaces. To understand the interfacial shear behavior more clearly, they performed a simple shear test of nacre along the layers in both dry and wet conditions. They observed strong
hardening followed by large strain-at-break for hydrated nacre (Fig. 2c,d). Such high strain values indicate hardening mechanism at the interfaces which makes it progressively difficult for the platelets to slide past each other and therefore, activates higher number of sliding sites in nacre. Hence, it is understood that the mechanical performance of nacre is controlled by synergetic mechanisms at the interfaces.

**Relationship of Structure and Mechanical Properties of Nacre:** In order to relate the mechanical performance of nacre with its microstructure, several toughening mechanisms which produce resistance to shearing and hardening at interfaces from micro to nanoscale have been proposed as shown in Fig. 3. Three different kinds of models are discussed in the literature including several steps. One possible model contributing to major toughening mechanism is the biopolymer stretching. It is suggested that the organic molecules which have multi domain architecture with folded modules, consume significant amount of energy in an increased stressed condition and exhibit large elongation in a saw-tooth like pattern by unfolding each modules within a single molecule sequentially and therefore contribute to the high toughness of nacre (Fig. 3a). Second structural feature is the mineral bridges, which are associated with two major toughening mechanisms of nacre, i.e. crack deflection and platelets pull-out (Fig. 3b). The third structural feature which also contributes to the shearing resistance of the platelets at interface is the nanoasperities (Fig. 3c). Evans et al. and Wang et al. showed that nacre exhibits inelastic deformation in both shear and tension and the interposing arrangements of nanoasperities on the surface of aragonite govern the yield stresses during deformation and hence enhances ductility by controlling the sliding resistance. Further study by Li et al. indicated that the platelets are not brittle rather ductile which comes from the presence of large number of nanograins. Spacing between the nanograins increases under tensile load and the viscoelastic-plastic organic molecules
between them are stretched to provide enough space for nanograin rotation and deformation. This results in high deformability of the platelets and contributes to higher energy dissipation.

**Figure 3. Nanoscale and microscale toughening mechanisms.** Three types of nanoscale mechanisms controlling the frictional sliding of the interfaces of platelets, (a) biopolymer stretching, (b) aragonite bridges initially intact (left), and then showing some potential relocking after shearing (right), (c) aragonite asperities contact. (d) Scanning electron micrographs of a few dovetail like features at the periphery of the tablets. (e) Outline of the platelets contours, showing some of the stresses involved when nacre is stretched along the platelets. In addition to shear the interface is subjected to normal compression (black arrows), which generates resistance to platelet pull out. Equilibrium of forces at the interfaces requires tensile tractions at the core of the platelets. (a-c) Reprinted with permission from ref. 15. (d,e) Reprinted with permission from ref. 35.

Although these three mechanisms contribute to the shear resistance of the platelet interfaces from nano to microscale but unable to provide the necessary amount of hardening required to spread the platelet sliding over the whole nacre. Therefore, some other mechanisms are suggested to describe the observed non-linear deformation at macroscale. One of them is the resistance of crack propagation by platelet interlocking (Fig. 1g). Interlocks act as physical obstacles to the relative movement of mineral platelets and their progressive failure inhibit crack propagation by crack branching and blunting. As these interlocks are present throughout the whole nacre, it results into a bulk mechanical response of nacre contributing significantly to the fracture toughness and strength through energy dissipation at macro scale.\(^2\) Furthermore, the significant waviness of platelet surface (Fig. 3d,e) also leads to progressive interlocking and hardening in large scale during sliding.\(^3\)\(^,\)\(^10\)\(^,\)\(^33\) Waviness generates ‘dovetails’ like geometric features and makes the platelets thicker at their periphery. Under tensile load when the layers slide past one another and pull out the platelet
ends, the dovetail generates progressive locking and hardening over large volumes leading to toughening of nacre. Moreover, the inevitable flaws present in nacre like porosity and defective growth act as the sources of crack starters that eventually lead to catastrophic failure under tensile loading. But at high stress, a white region called process zone, is observed in the inelastic region ahead and behind of crack tip on the fracture specimen. The advancement of crack consumes large amount of energy dissipated in this process zone which further results into significant fracture toughening. Therefore, various different mechanisms have been proposed which contribute to the large amount of energy dissipation in nacre.

2.4. Fabrication processes of nacre-mimetic materials

The outstanding combinations of mechanical properties of nacre arising from the interplay of its hierarchical structure inspired material scientists and engineers to mimic the brick-and-mortar structure in artificial materials. There are some primary inspirations which need to be met to mimic nacre, e.g. the ordered layered structure of the reinforcements to maximize mechanical strength in one direction, the concept of alternating hard and soft layers to allow efficient crack deflection and maximization of the fraction of inorganic. Thinking further, one also has to consider the importance of the mineral bridges, the designs of intelligent synthetic polymers as artificial mortar and matching the dimensions of synthetic analogues with the natural role model to progress further to fully mimic the remarkable performance of nacre. Although nacre grows naturally in water in a lengthy process, but to make the nacre-mimetics technologically feasible, simple, fast and scalable processes based on the advanced fabrication strategies and self-assembly procedures are required. Indeed, in the last years, various diversifying preparation strategies have been reported, e.g. ice-templating techniques, sequential deposition techniques such as LBL, and other multilayer deposition techniques, biomineralization, spray coating, glow discharge plasma deposition, uncontrolled co-casting of polymer/clay mixtures, processes at interfaces.
and solution based self-assembly methods, as well as an increased understanding on how mechanical performance correlates to the hierarchical structures encoded into the nacre-mimetics. But it is also important to mention that to achieve the similar mechanical behavior of nacre, especially the higher toughness, the highly ordered structure of nacre needs to be mimicked at various length scales. Mimicking nacre at numerous length scales is very difficult and compared to other methods, only ice-templation and sintering were able to mimic so far the maximum number of the structural features, e.g. organic layer thickness, mineral bridges, and nanoasperities. Several inorganic building blocks have been used as hard phase to fabricate artificial nacre e.g. layered silicates nanoclays, ceramic nanoparticles (Al₂O₃, hydroxyapatite), layered double hydroxides (LDHs), CaCO₃ crystals, graphene nanosheets etc. In the following section, the significant and mostly used preparation techniques of nacre-mimetic layered composites using the above mentioned building blocks are discussed.

### 2.4.1. Ice-templating

A recently reported technique to mimic nacre-like hierarchical structure in either lamellar or brick-and-mortar fashion using several micrometer thin ceramic layers is ice-templating or sometimes named as freeze casting method. This technique is developed on the basis of the physics of ice formation to create porous or layered hybrid materials. There is a critical particle size during the freezing of suspensions and above this value, the suspended particles is trapped by the moving water-ice front. As water undergoes lamellar crystallization, under steady-state conditions, it is possible to grow ice crystals in the form of platelets with a very high aspect ratio. Based on these key points, large porous lamellar ceramic scaffolds are prepared from aqueous suspension of 50 wt% Al₂O₃ and organic additives by precisely controlling the freezing kinetics. The suspension is first cooled to -80 °C where the growing ice crystals expel the Al₂O₃ particles producing a lamellar microstructure oriented parallel to
the direction of the freezing front. The particles trapped in between the ice provide surface roughness resembling to that of asperities of nacre (Fig. 5d). Ice crystals are then eliminated by freeze drying and heated at 400 °C to remove the organic additives and obtain a lamellar ceramic scaffold. Finally sintering is done at 1500 °C to densify the ceramic lamellae having 1 µm thick ceramic bridges between the lamellae similar to the mineral bridges of natural nacre.\textsuperscript{38} This four step mechanism to form ceramic scaffold by ice-templating is shown in Fig. 5a.\textsuperscript{38, 67} Like the lamellar structure, brick-and-mortar structure can also be prepared by infiltrating these ceramic scaffolds with polymer followed by pressing the scaffolds in the direction perpendicular to the lamellae and removing the polymer by sintering.

**Figure 5. Ice-templating and sintering of ceramic slurry to prepare nacre-mimetics.** (a) The four steps of ice-templating: preparation of slurry, solidification, sublimation and sintering. (b) The Al\textsubscript{2}O\textsubscript{3}/PMMA lamellar composite structure oriented over several centimeters produced by freeze casting a ceramic suspension and polymer infiltration (lighter phase: ceramic; dark phase: polymer). (c) The ‘bricks-and-mortar’ structure made by pressing and subsequent sintering the lamellar scaffolds with ceramic content up to 80 vol\%. (d) The microscopic roughness of Al\textsubscript{2}O\textsubscript{3} lamellae in the ceramic walls produced by freeze casting a ceramic suspension containing sucrose. A comparison between the toughening mechanism in (e) artificial Al\textsubscript{2}O\textsubscript{3}/PMMA ‘bricks-and-mortar’ structure and (f) natural nacre. (a) Reprinted with permission from ref. 67. (b-f) Reprinted with permission from ref. 38.
Munch et al.\textsuperscript{37} and Launey et al.\textsuperscript{38} infiltrated both lamellar and brick-and-mortar scaffolds with poly(methyl methacrylate) (PMMA) by a free-radical polymerization to prepare Al\textsubscript{2}O\textsubscript{3}/PMMA nacre-inspired hybrid materials (Fig. 5b,c). The average thickness of polymer layers was obtained 10-20 µm in the lamellar structures and only 1-2 µm similar to that of nacre in the brick-and-mortar structures. The resulting materials showed very good combination of high strength and fracture resistance exhibiting flexural strength of 116 MPa for the lamellae structure and 210 MPa for the brick-and-mortar structure and > 1% inelastic deformation before failure. The elastic modulus was calculated to 115 GPa in the direction perpendicular to the ceramic layers whereas, the crack-initiated fracture toughness was almost twice as high as what could be expected using the rule of mixtures on Al\textsubscript{2}O\textsubscript{3} and PMMA.\textsuperscript{38}

The fracture mode shows that the crack does not propagate through the ceramics bricks, rather follows the path around them leading to deformation via platelet pull-out as seen in nacre (Fig. 5e,f).\textsuperscript{37, 38} Launey et al.\textsuperscript{39} further extended this method to alumina/Al-Si systems having 36 vol\% of Al\textsubscript{2}O\textsubscript{3} content and obtained flexural strength around 300 MPa and fracture toughness higher than 40 MPa•m\textsuperscript{1/2}, exceeding that of nacre. The flexural properties were further increased by decreasing the thickness of ceramic lamellae, and controlled by several factors, e.g. freezing kinetics, particles size, suspension concentration, and/or by chemical grafting of methacrylate group onto the Al\textsubscript{2}O\textsubscript{3} surfaces to introduce stronger covalent binding between organic and inorganic phases. This grafting increases the strength and toughness due to the stronger interfacial adhesion which controls the interfacial sliding in a similar manner as in nacre.\textsuperscript{68}

Hence, ice-templating method produces composites which are able to mimic several structural features of nacre introducing platelet roughness and ceramic bridges. The brick-and-mortar structure of the hybrid is similar to that of nacre though the dimensions and the polymer content are much higher. The hybrid shows an impressive combination of high
strength and toughness due to wide distribution of damages and efficient stress release through the soft polymeric phase. This process can be scaled-up to prepare larger material than few centimeters. However, the main obstacle could be the uniform infiltration of organic phase into the ceramic scaffold without forming porosity for the samples longer in the direction parallel to the lamellae. Furthermore, the composite prepared by this process does not contain tablet waviness, the volume fraction of the ceramic phase present is rather low compared to natural nacre, and the process is laborious and energy intensive.

2.4.2. Sequential deposition techniques

Layer-by-layer deposition technique: Layer-by-layer (LBL) assembly technique is simple, versatile and relatively inexpensive method to prepare advanced functional thin films with tunable structural flexibility for specific applications. It allows accurate control of the composition and thickness to fabricate complex multilayered structures. A clean substrate is first sequentially immersed into two dilute solutions of oppositely charged nanoscale materials. These materials adsorb onto the substrate by interacting with each other through electrostatic interaction, hydrogen bonding, charge transfer, covalent bonding etc. producing nanometer thick monolayers. One or more intermediate washing steps are used after the deposition of each layer to remove all irregularly adsorbed materials or excess multilayers. The process is repeated until a multilayered structure is obtained. The coating is then detached from the substrate to get the free standing thin film. LBL can be applied to a wide range of materials e.g. nanoparticles, nanowires, nanosheets as the hard phases with soft polymeric phases and also allows to incorporate higher fractionation of inorganic phase in the hybrid materials.

Layered silicates mainly sodium montmorillonite (MTM) are extensively used as hard phase to fabricate the layered nanostructures due to lost cost and high mechanical properties of these nanoclays. MTM, with a general formula (Na,Ca)$_{0.33}$(Al$_{2-y}$,Mg$_{y}$)Si$_4$O$_{10}$(OH)$_2$.nH$_2$O, is
a smectic monoclinic clay-like material having two tetrahedral sheets of Si$^{4+}$ sandwiching a central octahedral sheet of Al$^{3+}$ or Mg$^{2+}$. The thickness of the individual platelet is ca. 1 nm and the aspect ratio is more than 100. A net negative charge is generated due to charge deficiencies when metal ions are exchanged for other types e.g. Al$^{3+}$ by Mg$^{2+}$ and Si$^{4+}$ by Al$^{3+}$. Therefore, these negatively charged nanoclays can be combined with positively charged polyelectrolytes upon electrostatic attraction by LBL assembly. Major progress in fabricating nacre-mimetics by LBL self-assembly has been done by Kotov and coworkers. They used sequential deposition of different polymers, e.g. cationic polyelectrolyte poly(diallyldimethylammonium chloride) (PDADMAC), strong rigid cationic polysaccharide chitosan (CH), and neutral poly(vinylalcohol) with MTM nanoclay to prepare layered structures.$^{40, 41, 45}$ Tang et al.$^{46}$ prepared 5 µm thick PDADMAC/MTM films by LBL technique where the film thickness is tailored by increasing the number of deposition steps or layers, e.g. 50 layers make 1.2 ± 0.1 µm thickness. The layered composites show an initial large plastic deformation under relatively low stress (< 10 MPa) due to the breakage of polymer-polymer or polymer-clay weak short-range van der Waals interactions. When stretched further, they undergo significant hardening due to sequential breakage of sacrificial ionic crosslinks of the polyelectrolyte, similar to the behavior observed in nacre. The composites showed ultimate tensile strength of 109 ± 8 MPa and Young’s modulus of 13 ± 2 GPa, slightly lower than that of nacre due to having relatively lower inorganic content and flat platelet surface. Therefore, no additional frictional sliding coming from the rough platelet surface, as observed in nacre, was possible. Later, to obtain higher mechanical properties by enhancing the interfacial strength and load transfer from matrix to MTM platelets, Podsiadlo et al.$^{45}$ replaced PDADMAC by a much stronger polymer, chitosan (CH) and also increased the incorporation of MTM to nearly 80 wt% in CH/MTM composite. But contrary to their expectation, mechanical properties of CH/MTM composites were much lower than PDADMAC/MTM composites and even showed lower strength than pure chitosan film. Poor
mechanical properties of CH/MTM composites originate from the molecular rigidity of CH chains. As CH chains were adsorbed on MTM surfaces in highly elongated configuration due to their molecular rigidity, therefore, could not find an optimal conformation for better interaction and efficient stress transfer.\textsuperscript{45} Later they replaced CH by a neutral polymer poly(vinylalcohol) (PVA) and prepare nacre-mimetics with 70 wt\% MTM content by LBL. They obtained higher mechanical properties (tensile strength = 150 MPa and Young’s modulus = 13 GPa) due to the effective hydrogen bonding and van der Waals force of attraction between PVA and MTM.\textsuperscript{41} They further enhanced the mechanical properties of these uncrosslinked PVA/MTM films by using covalent crosslinking with glutaraldehyde (GA). Though covalent crosslinking increases tensile strength and Young’s modulus significantly to 400 ± 40 MPa and 106 ± 11 GPa, respectively, but the material remains brittle.\textsuperscript{40} Later, they introduced ionic crosslinking into the polymeric matrix which creates a double network of sacrificial bonds and strikingly increased the mechanical properties of the uncrosslinked PVA/MTM films. Though, as compared to covalent crosslinking, ionic crosslinking provides lower mechanical improvement but emphasizes on the importance of molecular engineering of the composites and the necessity of high degree of control over their nanoscale organization.\textsuperscript{41} Grunlan and coworkers explored LBL technique extensively for the fabrication of ordered layered and brick-and-mortar structured gas and fire barrier nanocoatings using different cationic polymer like chitosan, branched poly(ethylamine) and anionic nanoclays e.g. MTM, Laponite platelets.\textsuperscript{70-74} The only drawback for the practical application of this technique is the time consuming sequential deposition steps needed to achieve a film with practical thickness (1µm/day). To overcome this problem, a fastest growth pattern was achieved by using exponential LBL assembly of poly(ethyleneimine), poly(acrylic acid) and sodium MTM into a complex tricomponent film.\textsuperscript{43} Though the film growth rate was 100 times faster than the linear LBL but led to lower inorganic content of 10 wt\% as a result of exponential growth.
Furthermore, this technique in combination with other low-energy methods is also used to get sophisticated structural design like in natural nacre as discussed below.

**Spin-coating and monolayer deposition:** In this process surface modified inorganic platelets are used along with organic constituents to form nacre-like structure. Use of functional inorganic platelets not only fabricates the biologically inspired structures but also exhibits additional functionalities like catalytic, magnetic, optical and fire retardant properties. Bonderer et al.\(^4\) fabricated chitosan/Al\(_2\)O\(_3\) films using sequential deposition technique. Alumina platelets were first modified with hydrophobic amine silane to increase their ability to be adsorbed at the air/water interface and to improve better adhesion on chitosan through hydrogen bonds. After obtaining the two dimensional monolayer of modified alumina platelets at the interface, it was transferred to a substrate by dip coating followed by the deposition of an organic layer by spin coating from chitosan solution. These two steps were then repeated sequentially to obtain a free standing film with total thickness of a few tens of micrometers. Inorganic platelets were well-aligned in the film up to a content of less than 20 vol\%, whereas higher concentration led to voids and misalignment. They showed that tensile strength of the hybrid materials depends on the operative failure mode which is determined by aspect ratio of the inorganic platelets, \(s\). Composites fail under the platelet fracture mode when \(s > s_c\) (where \(s_c\) is the critical aspect ratio of the platelets), as the maximal stress on the platelets exceeds their tensile strength. Therefore, the composites are strong but brittle and thus flaw intolerant, whereas materials with \(s < s_c\), undergo rupture under the platelet pull-out mode and are generally weak but ductile and thus flaw-tolerant as shown in Fig.6. Therefore, by using alumina platelets with an average aspect ratio of about 40 (\(s < s_c\), five times higher than the aragonite platelets in nacre, \(s \sim 8\)), and comparable matrix strength, and also by achieving efficient load transfer to alumina platelets through strong interface, they maximized the strength of the composites higher than that of natural nacre.
Figure 6. Deformation modes of chitosan/Al₂O₃ films (a) Fracture mechanisms based on aspect ratio. (b) Estimated tensile strength of platelet-reinforced composites. Tensile strength of polymer matrix composites reinforced with CaCO₃ and Al₂O₃ platelets is estimated in (b) (black and blue surfaces, respectively) on the basis of shear lag mechanical model. Reprinted with permission from ref. 47.

The tensile strength and the Young’s modulus of the composite with 15 vol% of alumina were 300 MPa and 10 GPa, respectively and the ultimate fracture strain was as high as ~ 20% resulting from the extensive plastic flow of the chitosan. Therefore, the work-of-fracture of these materials was one order of magnitude higher than that of nacre. However, lower inorganic content (< 20 vol% instead of 95 vol%) led to the modulus 10 times lower as compared to nacre. This technique is also used for other systems like PVA/layered double hydroxide (LDH)⁵⁹, CH/LDH⁴⁸, etc. where the CH/LDH composite is also used as light emitting diodes by exploiting the red light emitting capability of Eu-Cl rare-earth platelets under irradiation of 360 nm UV-light. Nacre-mimetic composites are also prepared combining LBL with Langmuir-Blodgett (LB) self-assembly.⁷⁵

2.4.3. Biomineralization

This process, also known as template inhibition technique, is used for the preparation of bulk materials as well as free standing films. This low temperature water based process involves raw materials easily available in nature.³ In this technique, an organic phase acts as a template
for the nucleation and growth of inorganic crystals from their supersaturated solution and influences the crystal size, type and morphology. The organic phase accelerates or inhibits the growth of the inorganic crystals depending on its concentration, molecular weight, density of the functional groups and also whether the macromolecules are adsorbed on the surface or present in solution.\(^5\) To prepare the nacre-mimetic composites, first the polymeric solution is added to a supersaturated solution of the inorganic crystal, and then the mixture is left at 25 °C for several days for the crystals to grow during water evaporation.\(^5, 50\) As this preparation technique is beyond the scope of this work, reader is referred to the corresponding literature for more details.\(^50-52\)

Although, biomineralization appeared as a simple and successful method to produce bulk composites mimicking the structure of nacre, the limitation of this technique are the slow processing rate requiring a day or more to produce micron scale materials and the poor mechanical properties as compared to what was expected from their structure.\(^68\)

**Biomineralization combined with sequential deposition:** As a further development of this approach, biomineralization combined with sequential deposition techniques are used to prepare polymer/CaCO\(_3\) composites. Kato et al.\(^53\) have successfully applied the template-inhibition strategy to induce thin film crystallization of CaCO\(_3\) on the solid matrices and fabricated layered polymer/CaCO\(_3\) composite films by alternating spin coating of polysaccharides and thin-film crystallization in the presence of an acidic polymer such as poly(acrylic acid). As CaCO\(_3\) grows like small polycrystalline crystals in the composite films unlike the single platelet crystals in nacre, free standing films with excellent mechanical properties have not been fabricated so far. Recently Finnemore et al.\(^64\) presented the first successful biomimetic attempt to replicate nacre by using CaCO\(_3\). They prepared artificial nacre with striking optical iridescence by using layer-by-layer deposition of porous organic films followed by the interplay of polymer-mediated mineral growth. Their approach of
fabricating artificial nacre is highly comparable to biogenic nacre both in its morphology and
growth rate as shown in Fig. 7. Natural nacre consists of 250-500 nm thick aragonite platelets
separated by 30-90 nm thick organic layers and each of these platelets are part of a single
crystal where crystallinity extends through platelets stacks, mediated by holes in the organic
layers. The stack of periodicity gives rise to hallmark iridescence of natural nacre and
structural hierarchy is responsible for its tremendous tough and strong mechanical behavior.
The SEM images depict the fractured surfaces of biogenic nacre in Fig. 7b, and the artificial
nacre fabricated by them in Fig. 7e. The images exhibit multilayers of 400 nm thick CaCO₃
platelets with a nanogranular structure resulting in a stack of crystalline calcite layers,
interconnected through porous organic films (Fig. 7f) similar to that of natural nacre. The
main advantage of this approach was the fabrication of the porous organic inter-crystalline
layers which allowed bridges between the mineral films to form, providing vertical crystalline
mineral continuity which enhances the mechanical stability of nacre.

![Figure 7. Comparison of natural and artificial nacre. (a) Photograph showing bright iridescence of natural nacre. (b) SEM image of fractured surface of a stack of mineral platelets. (c) Organic inter-crystalline, film which allows for vertical crystal continuity between platelets. (d) Artificial nacre, exhibiting a similar coloration as in (a). (e) SEM image of a fractured surface showing seven aligned CaCO₃ platelet separated by organic films. The surface graininess is comparable to natural nacre. (f) SEM image of a PVP film on calcite showing the similar pore distribution as in (c). (g) AFM height image of the porous film. Reprinted with permission from ref. 64.](image)

Although the fabricated composite showed mean plain strain modulus of 38 GPa which is
smaller than that of natural nacre (69 GPa) but nanoindentation test showed plastic
deformation for this artificial nacre indicating the fracture toughness similar to the toughening
of aragonite in natural nacre. Furthermore, by controlling the layer periodicity, nacre-like optical iridescence has been reproduced in these artificial nacres. Therefore, this process showed a successful way to closely replicate nacre by following a biomimetic route.

### 2.4.4. Solution based self-assembly

Most of the techniques described above found great success to mimic nacre in great extent but limited to very small scale production due to energy-intensive, laborious and time consuming multistep processes. Recently Walther et al.\(^6^1\),\(^6^2\) introduced a fast, facile and scalable approach to fabricate polymer/MTM based nacre-mimetics via self-assembly of core/shell nanoplatelets as shown schematically in Fig. 8. The core/shell nanoplatelets are obtained by adsorption of soft polymers onto inorganic nanoclays via either electrostatic or hydrogen bonding and the excess polymer is removed by centrifugation. Then a concentration-induced self-assembly of these core/shell platelets is followed on a macroscopic length scale during water removal due to excluded volume effects. The nacre-mimetics with 70 wt% inorganic content are prepared either by vacuum filtration (or paper making), doctor-blading or simple painting techniques into a fraction of sub-millimeter thick film rapidly. The PVA/MTM hybrid films with nacre-like brick-and-mortar microstructure prepared by this environmentally friendly, energy efficient, and economic process show very good mechanical, gas-barrier properties, optical translucency and extraordinary shape and fire-resistance performances.\(^6^1\) PVA/MTM films exhibit Young’s modulus and tensile strength of 27 GPa and 165 MPa, respectively, strength exceeding that of nacre. The mechanical properties of PVA/MTM films increase further remarkably after crosslinking with borate leading to a Young’s modulus and tensile strength of 45 GPa and 245 MPa, respectively, and a strain-to-failure of 0.9%. Compared to nacre, they obtained 2-3 folds higher tensile strength and similar strain, and modulus approaching to that nacre. To restrict the platelet-sliding, they crosslinked PVA with glutaraldehyde (GA) and boric acid and found no significant improvement in
mechanical properties with GA compared to uncrosslinked PVA/MTM. It is related to the increase in MTM interlayer spacing by GA which prevents further the increase in the mechanical properties. However, crosslinking with boric acid leads to significant increase in strength as well as stiffness, but sacrifices the toughness of the film. The higher stiffness is attributed to the presence of little disorder with respect to nanoclay platelets in the film which might be acted as little protrusions on the surface plane and therefore, exhibit necessary interlocking and strain hardening.

Figure 8. Preparation of self-assembled brick-and-mortar structures based on concentration-induced self-ordering of polymer-coated core-shell nanoplatelets. (a) First the nanoclay platelets are coated with polymer via adsorption. Excess polymer is removed by washing. The key element is the individual polymer coated clay platelets, which form nacre-mimicking film via self-assembly. Reprinted with permission from ref. 61, Copyright © 2010, American Chemical Society.

In another work, Walther et al.\textsuperscript{62} prepared PDADMAC/MTM composites by the same method and exchanged the monovalent Cl\textsuperscript{-} of PDADMAC by counterions of different valences, e.g. SO\textsubscript{2}\textsuperscript{4-}, PO\textsubscript{3}\textsuperscript{4-} or polymerizable styrene sulfonate (StSO\textsubscript{3}\textsuperscript{-}) at the polymer/nanoclay interface by infiltration. They showed that multivalent counterions can strengthen the assembly and tailored the interfacial strength by creating interpenetrating network of counterions. The mechanical properties increase with increasing the valences and highest values are obtained for PO\textsubscript{3}\textsuperscript{4-} ion (tensile strength = 151 MPa and stiffness = 32 GPa) compared to Cl\textsuperscript{-} of PDADMAC (tensile strength =106 MPa and stiffness = 13 GPa). Yao et al.\textsuperscript{63} further extended this process to chitosan/MTM nacre-like hybrid films prepared by vacuum filtration or water-evaporation process. The mechanical properties of chitosan/MTM
films are lower than the PVA/MTM films prepared by either LBL or vacuum filtration because the stereochemistry of the six rings in the chitosan chain creates an obstacle to the hydrogen bonding formation of some OH and NH$_3$ groups of chitosan with SiO$_4$ tetrahedrons on the surface of MTM. Moreover, they also did not observe the covalent bond formation between chitosan and MTM via Al-O-C bonds as seen in PVA/MTM films. However, the Young’s modulus and ultimate tensile strength of chitosan/MTM films are respectively 3–5-fold and 2–3-fold higher than that of the conventional films prepared by simply mixing. These films also show light transmittance and fire retardancy.

Like nanoclays, graphene oxides (GO) also have two dimensional sheets like structure and very good mechanical strengths as well as electrical properties, and therefore, appear as very good inorganic building blocks for preparing nacre-mimetic materials. Wang et al.$^{65}$ and Xu et al.$^{66}$ transferred this approach to polymer/GO or reduced GO nanocomposites finding improvements in mechanical as well as functional properties, such as, electrical conductivities.$^{65}$

Though progress has been made in mimicking the hierarchical structures and the outstanding mechanical properties of nacre following the above mentioned fabrication techniques, still there are lots of challenges to be met, such as, mimicking the structural features, in terms of, platelets waviness, mineral bridges and nanoasperities of nacre into man-made nanocomposites; successfully designing the layered structure at various length scales; and further controlling the interface to initiate strain hardening for higher toughness in artificial nacre. Also not much work has been done – to molecularly engineer the soft phase to obtain the synergistic mechanical properties using sacrificial bonding, – also to tune the hard phase by incorporating various synthetic nanoclays apart from natural MTM, and studying the effect of their aspect ratios and compositions on structure formation and deformation modes in nacre-mimetics. Therefore, a single step, rapid self-assembly process needs to be optimized.
via incorporation of higher content of suitably selecting inorganic phases, and tailored soft phases to fabricate mechanically robust nacre-mimetics in a fast and large-scale manner with tunable structure from meso to nanoscale.

References and Notes


Chapter 3

Nacre-mimetics with synthetic nanoclays up to ultrahigh aspect ratios

3.1. Introduction

The excellent mechanical performance of biological materials originates from a hierarchically ordered arrangement of well-tailored hard and soft building blocks.\(^1\)\(^-\)\(^3\) The hard matter serves as the load bearing and reinforcing part, whereas energy can be dissipated into the soft segments. As a direct consequence, many of these materials combine high toughness with excellent strength and stiffness. For instance, in nacre, the layered arrangement of platelet-shaped CaCO\(_3\) crystals and biopolymers in a brick-and-mortar structure leads to a synergistic mechanical performance.\(^4\) The Young’s modulus can reach up to 40-70 GPa, ultimate tensile strength is as high as 80-135 MPa and the toughness is three thousand times higher than that of an aragonite monolith.\(^4\)\(^-\)\(^7\)

Considering the lightweight character of mechanically strong and tough biomaterials, finding corresponding biomimetic materials that allow large-scale and facile preparation for future load bearing applications is of preeminent importance.\(^8\) For nacre-mimetics, highly ordered, layered nanocomposite structures with high level of reinforcements, and with tailored interfaces and preferentially tailored molecular energy dissipation mechanisms are being pursued. However, this is a major scientific and technological challenge as precise nanostructuration at such biomimetic compositions with high fractions of reinforcements is hard to combine with large-scale processing methods. Various efforts have been undertaken to mimic the layered hard/soft composite structure of nacre\(^9\) via e.g. several sequential approaches, such as LbL\(^10\)\(^-\)\(^18\) and other multilayer deposition strategies,\(^19\)\(^,\)\(^20\) ice-templating and sintering of ceramics,\(^21\)\(^-\)\(^23\) spray coating,\(^24\)\(^,\)\(^25\) glow discharge plasma deposition,\(^26\) uncontrolled
co-casting of polymer/clay mixtures,\textsuperscript{27,28} or processes at interfaces.\textsuperscript{29,30} Unfortunately, many of these approaches are limited to very small scale and remain technologically infeasible due to energy-intensive and laborious multistep procedures. Moreover, considering the needs in the application world, we also have to identify further possibilities arising from the excellent nanostructural control. The goal is to expand the property profiles beyond pure mechanical performance and implement new concepts for multifunctional biomimetic materials, highly relevant for future technologies. Such properties include fire and gas barrier properties, anisotropic thermal, electric or ionic conductivity, while at the same time possibly reaching glass-like transparency and maintaining excellent mechanical properties. 2D clay nanosheets are among the most interesting building blocks to realize these outstanding challenges owing to their high interface, nanoscale dimensions and tunable aspect ratio. Previous reports mostly concentrated on individual functional properties, such as gas barrier,\textsuperscript{27,31-37} fire shields\textsuperscript{35-39} and photothermal activity\textsuperscript{25} while still often falling short of addressing and realizing multifunctional property profiles with best and optimized performance in different areas.

Recently Walther et al. introduced a fast, facile and scalable concept to achieve superb control over nanostructuration in nacre-mimetics via self-assembly of core/shell nanoplatelets formed by adsorption of soft polymers onto hard nanoclays.\textsuperscript{36} The resulting core/shell nanoplatelets undergo concentration-induced self-assembly on a macroscopic length scale during water-removal due to excluded volume effects. Such self-assembled artificial nacre is characterized by maximum exfoliation and at the same time maximum amount of inorganic reinforcements arranged in a highly ordered fashion. The polymer shell pre-encodes the properties of the soft energy-dissipating layer on the reinforcing nanoplatelets. Recent studies shed light on how polymer dynamics and supramolecular binding scenarios within the soft phase influence the macroscopic mechanical properties, and how sacrificial bonds and synergetic mechanical performance can be targeted based on controlling molecular
interactions.\textsuperscript{40-43} The overall process is environmentally friendly and economic. We further simplified the method to a direct mixing approach of highly concentrated dispersions (>10 wt\%) using suitably tailored nanoclay and polymer.\textsuperscript{44}

However, much in contrast to previous work on understanding and evolving the soft phase\textsuperscript{42,45}, very little is still known on the possibilities arising from changing the nanoclay. Research on clay-based nacre-mimetics has so far almost exclusively focused on using montmorillonite (MTM), a natural Bentonite clay that mostly exfoliates into 1 nm thick clay sheets with an average diameter of a few hundred nanometers in water. MTM however suffers from major drawbacks. First of all, its aspect ratio cannot be tuned. This is however of profound importance for an in-depth understanding of the mechanical properties of such advanced, nanostructured composites with nanoconfined polymer layers and subtle nanomechanics. In addition, the optical quality is poor as natural MTM is contaminated by iron or other metal ions and their corresponding oxides leading to a yellowish color. Furthermore, the non-perfect surface charge distribution and presence of fractions of larger agglomerates can lead to imperfect exfoliation and contamination with unwanted larger particles, requiring fractionation steps and leaving ambiguities in determining clear structure/property relationships.\textsuperscript{46,47} All these factors, absorption due to contamination, light scattering due to larger particles and non-complete exfoliation inevitably lead to colored and at best only translucent films once a certain thickness is reached.

Here we demonstrate distinct advantages of using synthetic nanoclays with widely different aspect ratios up to 10000 for self-assembled artificial nacre based on polyvinylalcohol (PVA)-coated nanoclay. Such synthetic nanoclays are free from color contamination unlike natural clays, possess homogeneous charge distribution on the surface and fully exfoliate into single nanosheets in water. We establish the relationships among structure formation, nanostructuration, deformation mechanisms and mechanical properties as
a function of aspect ratio and also by tuning the viscoelastic properties of the soft phase through exposure to different levels of hydration. We show that nanocomposites reinforced with low aspect ratio nanoclay have superior toughness owing to pronounced inelastic deformation via platelet pull-out. On the contrary, nacre-mimetics formed by ultralarge synthetic nanoclay open avenues to superb stiffness up to 40 GPa and tensile strength exceeding 200 MPa, thereby attaining elastic properties previously only being in reach after tedious post-crosslinking. We further correlate how the amount of polymer in differently sized clays (very small vs. very large ones) influences the transition towards inelastic deformation and stable crack propagation. Excellent gas barrier properties and glass-like transparency complement the scope of mechanical properties and provide design principles for using synthetic nanoclays for multifunctional biomimetics materials as, e.g., needed for flexible, advanced barrier materials.

3.2. Experimental

Materials. Polyvinylalcohol (PVA, \(M_w = 85-126 \text{ kDa}, 98\% \text{ hydrolyzed}; \text{ Aldrich})\); Laponite RD (LAP) and Na-Cloisite (montmorillonite, MTM, both Rockwood Industries), Sumecton (SUM; Kunime Industries Co. Ltd.), sodium fluorohectorite (NHT) and sodium tetrasilicic mica (NTS, both Topy Industries Ltd.) were used as received. MilliQ water was used in all experiments.

Exfoliation of LAP and SUM and MTM nanoclays. LAP and SUM were dispersed in MilliQ water (0.5 wt\%) and stirred for 2-3 hours to yield completely exfoliated dispersions. MTM was stirred vigorously overnight, then left for 4-5 days to allow sedimentation of large agglomerates, and finally decanted. The homogenous supernatant dispersion was used to prepare the nanocomposites.

Exfoliation of NHT and NTS nanoclays. Cleaning was done similarly as reported\(^52\) with slight changes in the centrifugation speed and time. A 5 wt\% aqueous solution of each
nanoclay was centrifuged at 12,000 rpm speed for 90 minutes. After the centrifugation, the dispersion exhibits three different phases (see Supplementary Fig. 11). The middle viscose phase contains the desired clean nanoclay with 10-13 wt% solid content, which was then used to prepare 0.5 wt% exfoliated dispersions.

**Fragmentation of NTS nanoclays.** A 5 wt% cleaned NTS dispersion was passed through a microfluidizer (Microfluidicscorp MRT CR5) applying 1400 bar shear cycles for 10 and 20 passes to obtain two batches of NTS nanoclay dispersion having two different sizes. SEM characterization yields the corresponding aspect ratios to 280 and 60.

**Preparation of self-standing films of pristine nanoclays.** A 0.5 wt% exfoliated nanoclay dispersion was poured into petri dishes and dried at ambient conditions.

**Preparation of nacre-mimetic films via solution casting.** A 0.5 wt% exfoliated nanoclay dispersion was slowly added to 1 wt% aqueous solution of PVA under continuous magnetic stirring. This process was easily scaled up to 2 - 4 L and the dispersion was stirred for at least overnight for complete polymer adsorption on the nanoclay surface. Excess polymer was removed by centrifugation at 11000 rpm (for LAP and SUM) and at 5000 rpm (for MTM, NHT and NTS), followed by washing (2x) and redispersion in MilliQ water. The dispersions were then poured into petri dishes and dried at ambient conditions.

**Preparation of nacre-mimetic films by direct mixing and film casting.** To tailor the weight fractions of PVA/LAP and PVA/NTS to exactly the same values, a 0.5 wt% exfoliated nanoclay dispersion was added slowly to 0.5 wt% aqueous solution of PVA under continuous magnetic stirring until the desired weight ratio was obtained. The dispersion was stirred overnight for complete polymer adsorption on the nanoclay surface, poured into petri dishes and dried at ambient conditions.
Methods

Field-emission scanning electron microscopy. Field-emission scanning electron microscopy was performed on a (i) Hitachi S-4800 field emission microscope (1.5 kV) after sputter-coating a thin Au/Pd layer on the cross-section of the film and (ii) on a Hitachi SU-9000 (30 kV) both in transmission and scanning mode without sputtering.

Thermogravimetric analysis. Thermogravimetric analysis was done using a NETZSCH TG 209C instrument under continuous flow of 25 mL/min of N₂ at a heating rate of 20 K/min.

Atomic force microscopy. Atomic force microscopy was performed on a Veeco Multimode in tapping mode conditions using standard silicon cantilevers (PPP-SEIH-W from Nanosensors).

Transmission electron microscopy. Transmission electron microscopy was performed on a JEOL JEM-3200FSC Cryo-TEM, operating at liquid nitrogen temperature. Zero-loss filtered images were obtained at an acceleration voltage of 300kV. All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 4000, Gatan) combined and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.4). Microtomed ultrathin sections were obtained using a LEICA 125 Ultracut microtome. The samples were embedded into epoxy resin prior cutting.

UV-Visible spectroscopy. UV-Visible spectroscopy was performed on a V-630 UV/Vis Spectrophotometer from Jasco. A clear coat (Proshine, Manhattan, refractive index = 1.41) was applied on top of the PVA/NTS film.

1D wide-angle XRD. One dimensional wide-angle XRD was performed using an Empyrean setup from PANalytical. An Empyrean Cu x-ray tube LFF HR (line source of 12×0.04 mm²) provided CuKα, radiation with \( \lambda = 1.542 \, \text{Å} \) at 40 kV voltage and 40 mA current. Bragg Brentano parallel-beam geometry was used.
**2D wide-angle XRD.** Two dimensional wide-angle XRD was performed on a Bruker AXS Nanostar-U Instrument equipped with a microfocus X-ray source (Incoatec ImSCu E025) operating at \( \lambda = 1.54 \ \text{Å} \). A pinhole setup with 750 mm, 400 mm, and 1000 mm (from source to sample) was used and the sample-to-detector distance was 27 cm. The scattering patterns were corrected for the beam stop and background (Scotch tape) prior to evaluations. The samples were measured at 10-15° (tilt angle) beam inclination with respect to the plane of the films. Intensity distribution profiles in the azimuthal angle were used to calculate the degree of orientation of the nanoclays in the polymer matrix. Degree of orientation is calculated using the following equation (1):

\[
\eta = \left( \frac{180 - \text{FWHM}}{180} \right) \times 100
\]  
(1)

where FWHM is the full width at half maximum of the peak in the azimuthal intensity profile.

**Dynamic light scattering.** Dynamic light scattering was carried out on an ALV/CGS-3 Compact Goniometer at 23 °C and 90° scattering angle.

**Tensile mechanical tests.** Tensile mechanical tests were carried out on a DEBEN minitest equipped with a 20 N load cell. All measurements were conducted at room temperature and specimens were conditioned at required humidity for a minimum of 2 days. The specimen sizes used were in the range of 2 cm x 1.25 mm x 20-30 μm. At least 5 (mostly 9) specimens were tested for each sample at a nominal strain rate of 1 mm/min. The slope of the linear region of the stress-strain curves was used to determine the Young’s modulus, \( E \).

**Water sorption isotherms.** Water sorption isotherms were performed with a HIDEN ISOCHHEMA IGAsorp device at 28 °C in a range of 5–93 % RH. Samples (ca. 9 mg) were exhaustively dried (60 °C) and quickly placed into the machine. The procedure consists of continuous monitoring of the mass of the adsorbed moisture at a particular relative humidity.
and reaches ca. 95% of the equilibrium mass value before it jumps to the next set %RH. The last 4-5 points of mass values are quasi-static.

**Oxygen barrier properties.** Oxygen barrier properties were measured by MOCON (Paul Lippke Handels-GmbH, Neuwied, Germany), using an Ox-tran 2/21 oxygen permeability instrument for PVA/NTS and by Oxygen Permeation Analyser (Systech 8001, Systech Instruments Ltd., U.K.) for PVA/LAP and PVA/SUM (in accordance with ASTM Standard D-3985) at 23 °C and at 80 %RH. The active area of measurement was 5 cm².

**Solid-State $^{13}$C CPMAS NMR.** Solid-State $^{13}$C CPMAS NMR experiments were performed on a Bruker AV700 NMR spectrometer under cross-polarization magic-angle spinning (CPMAS) condition and spinning at 5 kHz. To improve the efficiency of $^{1}$H-$^{13}$C cross-polarization under MAS a ramp (90/100) contact pulse was applied on the $^{1}$H radio-frequency channel. The duration of the 90° pulse, the dead time of the spectrometer, the dwell time, the contact time, the recycle delay time and the acquisition time were 2 $\mu$s, 6 $\mu$s, 4 $\mu$s, 1.5 ms, 7 s, and 49 ms, respectively. A typical number of 8192 scans were acquired for each spectrum. All experiments were conducted at 23 °C for PVA/LAP, which was either exhaustively dried or hydrated by D$_2$O.

### 3.3. Results and Discussions

**Strategy and Building Blocks and Structural Characterization**

The general strategy for the preparation of self-assembled artificial nacre is outlined in Fig. 1a. It is based on the concept that polymer-coated core/shell colloidal-scale nanoplatelets self-assemble into highly ordered lamellar films upon water removal due to excluded volume effects. These core/shell nanoplatelets are simply prepared by adsorption of specifically binding polymers onto fully exfoliated synthetic nanoclays in aqueous dispersion, followed by removal of excess polymer. This yields very well-defined core/shell particles without excess
of polymer and allows to approach highly ordered nacre-mimetics with fully exfoliated synthetic nanoclays at biomimetic compositions. We use polyvinylalcohol (PVA) due to its known affinity to nanoclays and also because a comparison can be made to earlier nacre-mimetics, either prepared by the layer-by-layer technique or via self-assembly.

Figure 1. Preparation of artificial nacre and AFM characterization of NTS nanoclay before and after coating with PVA. (a) Artificial nacre via concentration-induced self-assembly of polymer-coated nanoclay platelets with intrinsic hard/soft architecture. Perfect core/shell particles are isolated by centrifugation and redispersion. Different aspect ratios are indicated as diameter to thickness ($d/t$) and corresponding fracture modes are displayed to the right as influenced by the aspect ratio and polymer content. (b-c) AFM height image of (b) pristine NTS (scale bar 2 µm) and (c) PVA-coated core/shell NTS nanoplatelets on freshly cleaved mica (scale bar 2 µm), with (d) the corresponding section analysis.

Table 1 gives an overview of the used nanoclays. Since we focus on the effects of aspect ratio on structure formation and properties, it is of high importance to carefully assess the average size and its distribution. Much of the current understanding of the size distribution of nanoclays relies on scattering and laser diffraction techniques. Yet, these techniques only give an indirect measure and are complicated to apply due to the inherent size distribution, the anisometric/non-circular shape and possible bending of the particles. Commonly used atomic force microscopy (AFM) faces difficulties to provide a statistically valid analysis due
to the small scan area. Therefore, we invested considerable efforts to realize a statistically relevant real space analysis of the nanoclay dimensions via scanning and transmission electron microscopy (SEM/TEM) imaging. We refer to the Supplementary Information (SI) for representative SEM micrographs (Supplementary Fig. 1) and to Table 1 for the derived size distributions. In case of the ultrasmall Laponite (LAP), being one of the most thoroughly characterized nanoclays, neither TEM nor SEM led to sufficiently robust results and we confirmed the known value from literature with dynamic light scattering (DLS, Supplementary Fig. 2). Overall, the synthetic nanoclays display a wide range of aspect ratios from a few tens of nanometers (LAP) via several hundreds of nanometers (SUM, MTM, NHT) up to several micrometers (NTS). We emphasize that NTS even displays sheets in the range of more than tens of micrometers, thus being highly appealing for gas barrier materials, that crucially depend on having ultrahigh aspect ratio nanoplatelets. The imaging data of SUM and NHT reveal some differences with the literature values. We find that SUM is larger and NHT is smaller in size than the reported value.

We used AFM to directly visualize the successful coating of PVA in the core/shell nanoplatelets. The height profiles change from ca. 1 nm (pristine nanoclay, see also Supplementary Fig. 5) to 2 – 2.2 nm (PVA-coated nanoclay) in case of the exemplarily depicted NTS, thus confirming the presence of a thin adsorbed polymer layer (Fig. 1b-d). AFM also verifies the absence of unwanted aggregation and absence of excess free polymer.

### Table 1. Overview of used synthetic nanoclays

<table>
<thead>
<tr>
<th>Namea</th>
<th>Abbreviation</th>
<th>Type</th>
<th>Dimension (nm)</th>
<th>Aspect ratio (davg/tb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laponite</td>
<td>LAP</td>
<td>Na-Hectorite</td>
<td>25 ± 4c</td>
<td>20-31b</td>
</tr>
<tr>
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<td>SUM</td>
<td>Na-Saponite</td>
<td>140 ± 100d</td>
<td>35-600d</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>MTM</td>
<td>Natural Na-Bentonite</td>
<td>260 ± 200d</td>
<td>30-1000d</td>
</tr>
<tr>
<td>Sodium fluorohectorite</td>
<td>NHT</td>
<td>Fluorohectorite</td>
<td>750 ± 500d</td>
<td>121-3000d</td>
</tr>
<tr>
<td>Sodium tetrasilicic mica</td>
<td>NTS</td>
<td>Synthetic mica</td>
<td>3500 ± 2500d</td>
<td>650-14000d</td>
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</tbody>
</table>

a) Common names or trade name. b) An average thickness t of 1 nm is considered for all nanoclays as obtained from AFM (see Supplementary Fig. 5). c) Determined by DLS (Supplementary Fig. 2). d) Determined based on statistical image analysis of SEM micrographs counting more than 300 particles, and averaging over major and minor axis.
We initially compared two preparation methods for the nacre-mimetic films: (i) simple film casting via free water evaporation and (ii) water removal through a filtration membrane, a process similar to paper-making. Both procedures lead to macroscopic and self-standing films, typically prepared with thicknesses of 10 – 100 µm. Whereas both methods yield films with similar mesostructure for the small nanoclays (LAP and SUM), the films based on the larger nanoclay (NHT and NTS) exhibit a better order of the mesostructure with well aligned flat nanoplatelets after solution casting. Vacuum-filtrated films display a comparably wavy mesostructure (Supplementary Fig. 3). Such microscopic imperfections can lead to grain boundaries, unwanted light scattering and reduced transparency. Therefore, we focus exclusively on solution casting. The self-alignment of large aspect ratio polymer-coated nanoclays can be rationalized due to the formation of nematic liquid crystalline phases, whose critical concentration depends on the aspect ratio (Supplementary Fig. 4).\textsuperscript{56,57} For the ultrasmall PVA-coated LAP nanoclay, the behavior is however less self-evident, as the cationic rim regions can in principle interact with the anionic basal planes to form edge-on-plane structures, also known as “house of cards” structure.\textsuperscript{48,58} Therefore, we carefully analyzed the mesoscale order using SEM, TEM and 1D/2D X-ray diffraction (XRD).

SEM clearly reveals a layered arrangement of the nanoplatelets for all nacre-mimetics starting from PVA/SUM, confirming the successful hydrodynamic self-ordering of the polymer-coated nanoclays during water removal (Fig. 2). In case of ultrasmall LAP platelets, the SEM image shows assemblies of nanoclays protruding from the surface, as individual platelets cannot be identified due to their small size. Below, we will further evidence an in-plane ordering of PVA/LAP films using 2D XRD (Fig. 3c,d). For the larger nanoclays individual nanoclay layers are easily visible and the SEM images reflect the increasing platelet size in the following order SUM < NHT < NTS. TEM images of microtomed ultrathin cross-sections of selected nanocomposites confirm the presence of alternating hard/soft layers,
as quantified by grey scale and Fourier Transform analysis of the samples revealing the characteristic distances.

Figure 2. Electron microscopy characterization of the cross sections. SEM images of (a) PVA/LAP (scale bar 2 µm; inset at higher magnification and scale bar 250 nm), (b) PVA/SUM (scale bar 2 µm), (c) PVA/NHT (scale bar 5 µm), (d) PVA/NTS (scale bar 5 µm) showing a layered ordered arrangement of the nanoclays, embedded in a nanoconfined PVA matrix. SEM images clearly show the increase of platelet size from (a) to (d). TEM images of ultrathin cross sections of (e) PVA/SUM and (f) PVA/NTS (scale bars 10 nm) showing alternating hard and soft layers. The dark and grey lines correspond to nanoclay and polymer, respectively. Fourier transform analysis of the sample (e) or marked area of the sample (f) are shown as insets. (g-h) Grey scale analysis to quantify the distance between alternating layers.
Although the distances may be altered during the microtoming and imaging procedure, the variation between the nanoplatelets serves as an indication for the actual distribution of gallery spacings, which mostly scale between ± 0.15 nm around the average.

We used 1D XRD to quantify the interlayer spacing of the layered biomimetic nanocomposites (Fig. 3a,b). For better comparison, we first recorded the diffractograms of self-standing films of pristine nanoclays. LAP and SUM show rather broad peaks, indicating comparably small ordered domains formed by such nanoclays with low aspect ratios. The $d^*$-spacings of LAP and SUM are 1.29 nm$^{59}$ and 1.21 nm, respectively. On the contrary, sharp peaks can be obtained for the higher aspect ratio nanoclays, NHT and NTS, with $d^*$-spacings

![Figure 3. XRD characterization of the nanostructure of the layered nacre-mimetics. 1D XRD of (a) pure nanoclays and (b) nacre-mimetic materials. (c) Azimuthal intensity distribution profiles of the primary diffraction peak extracted from 2D XRD. Intensities are normalized to the peak maximum, (d) 2D XRD image of PVA/LAP at 10-15° beam inclination with respect to the plane of the film, (e) The degree of orientation calculated from the FWHM according to equation (1) for all nacre-mimetics. The value for nacre-mimetics based on natural MTM is shown in brackets, as it is clearly outside of the trend for the materials based on synthetic nanoclays, and neglected for the linear fit.](image-url)
MTM with an intermediate aspect ratio displays a broader peak corresponding to its hydrated $d^*$-spacing of 1.26 nm.\(^\text{45}\)

For the nacre-mimetics, we find an unexpected dependence of the primary diffraction peak with the aspect ratio of the nanoclay. The diffractograms (Fig. 3b, individual comparisons in Supplementary Fig. 6) clearly show a shift towards higher scattering vector $q$ with increasing aspect ratio. The corresponding $d^*$-spacings can be calculated to range between 3.7 to 1.7 nm when passing from the smallest LAP to the largest NTS. Weak and broad humps appear as integer multiples of the primary peak ($n\cdot q^*$) corresponding to the higher order peaks characteristic of a lamellar morphology. The XRD shows no peak for non-exfoliated synthetic nanoclays in the nanocomposites, thereby indicating a near quantitative activation of the nanoclay surface during the coating procedure. However in case of PVA/MTM, a small broad hump appears at $q \approx 5.3$ nm\(^{-1}\) indicating small traces of non-exfoliated MTM in the nanocomposite rooted from the difficulty of the exfoliation of natural clays and demonstrating the need for proper fractionation. Additional 2D XRD of PVA/LAP eliminates any ambiguity on the alignment of its mesostructure by demonstrating strongly confined diffraction arcs originating from a highly ordered structure, regardless of the small aspect ratio (Fig. 3d). The degree of orientation ($\Omega$) can be calculated from the full width half maximum (FWHM) according to equation (1) to be as high as 84% (see methods). The same analysis of the 2D XRD data for PVA/NTS containing nanoplatelets with a three order of magnitude larger aspect ratio reveals increased alignment with a very high degree of orientation close to 95%. In fact the degree of orientation follows a close to linear dependence in the semi-logarithmic plot when considering all synthetic nanoclays (Fig. 3e, Table 2). On the contrary, nacre-mimetics based on natural MTM show a lower degree of alignment, likely due to inhomogeneities hampering a perfect structure formation. The trend can be related to the increased propensity of larger aspect ratio nanoclays to form ordered nematic, liquid
crystalline phases and demonstrates a clear advantage for the structure formation process. Overall, it is important to realize that the values for all samples based on synthetic nanoclays scale within 10% and thus they are similarly aligned to a very high degree.

To further understand the observed differences in lamellar periodicities of the nacre-mimetics, we determined their elemental composition by elemental analysis. Here, a similar trend is observed, yielding the highest polymer content for the smallest nanoclay (ca. 58 wt% in PVA/LAP), while the highest aspect ratio nanoclays only contain less than half of this (ca. 24 wt% in PVA/NTS). PVA/MTM displays an intermediate polymer content of ca. 38 wt%. This trend is also fully reflected in thermogravimetric analysis (TGA), where degradation above 300 °C is observed (Table 2, Fig. 4c).

### Table 2. Structural characterization of various nacre-mimetics

<table>
<thead>
<tr>
<th>Name</th>
<th>Aspect ratio (d&lt;sub&gt;avg&lt;/sub&gt;/t)</th>
<th>Polymer content (wt%)</th>
<th>d&lt;sup&gt;′&lt;/sup&gt;-spacing (nm)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Degree of orientation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVA/LAP</td>
<td>25</td>
<td>57.5</td>
<td>52.7</td>
<td>3.70</td>
</tr>
<tr>
<td>PVA/SUM</td>
<td>140</td>
<td>49.5</td>
<td>47.3</td>
<td>3.03</td>
</tr>
<tr>
<td>PVA/MTM</td>
<td>260</td>
<td>37.8</td>
<td>n.d.</td>
<td>2.54</td>
</tr>
<tr>
<td>PVA/NHT</td>
<td>750</td>
<td>26.3</td>
<td>36.3</td>
<td>1.66</td>
</tr>
<tr>
<td>PVA/NTS</td>
<td>3500</td>
<td>23.5</td>
<td>23.6</td>
<td>1.68</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by XRD, n.d = not determined.

In principal these differences can either be attributed to different polymer/clay interactions (slightly different surface energies for the various nanoclays), or to geometrical reasons because higher rim-to-surface ratios for lower aspect ratio nanoclays lead to larger fractions of adsorbed polymer. Let us first rationalize the geometrical constraints using a simple model for disc-shaped nanoclays, taking into account the radius and height of the nanoclay, R and h, and the polymer volume, V<sub>bp</sub> and V<sub>rim</sub>, adsorbed at the two basal planes and around the rim, with the surface areas, A<sub>bp</sub> and A<sub>rim</sub>. A constant thickness, t, is assumed for the polymer coating.

Equation (2) describes the ratio of polymer volume adsorbed at the rim versus adsorbed on the two basal planes.
\[
\frac{V_{\text{rim}}}{V_{\text{bp}}} = \frac{A_{\text{rim}} \cdot t}{A_{\text{bp}} \cdot t} = \frac{2\pi Rht}{2\pi R^2 \cdot t} = \frac{h}{R}
\]

(2)

\[
V_{\text{rim}} = V_{\text{bp}} \cdot \frac{h}{R}
\]

(3)

This ratio scales with \(R^3\), meaning that the polymer volume adsorbed at the rims becomes progressively smaller at constant total surface area of the basal planes for increasing radius of the considered individual platelets (Fig. 4a). The total polymer volume \((V_{\text{pc}})\) on a single nanoclay platelet is the sum of the volume adsorbed at both basal planes and the rim and can be expressed as,

\[
V_{\text{pc}} = V_{\text{bp}} + V_{\text{rim}} = 2\pi R^2 \cdot t + 2\pi Rht = 2\pi R^2 \cdot t \left(1 + \frac{h}{R}\right)
\]

(4)

By combining the equations, we can express the ratio of polymer volume at rim to the total volume of polymer coating as follows,

\[
\frac{V_{\text{rim}}}{V_{\text{pc}}} = \frac{2\pi Rht}{2\pi R^2 \cdot t \left(1 + \frac{h}{R}\right)} = \frac{h}{R \left(1 + \frac{h}{R}\right)} = \frac{1}{R + \frac{h}{R}}
\]

(5)

Equation (5) similarly shows that smaller nanoplatelets have higher volume of polymer adsorbed at the rims. This ratio even enlarges when coverage at the rim area is favored over adsorption at the basal planes. Such a phenomenon is in fact reported for LAP, the best characterized synthetic clay, for which small angle neutron scattering demonstrated a higher thickness of the polymer coating at the rim areas versus the basal planes. Fig. 4a illustrates how the ratio of the surface area of the rim versus that of the basal plane decreases with increasing radius (nanoclay size). Interestingly, these scaling dependences are independent of the actually adsorbed thickness of the polymer layer, \(t\). Since the height of the used nanoclay platelets is nearly constant \((h \approx 1 \text{ nm})\), the scaling dependence is valid for different nanoclays.
Certainly, different surface energies due to the different chemical compositions of the nanoclays may also play a role in the adsorptive layer.

Figure 4. Polymer content and $d'$-spacing of the nacre-mimetics as a function of the aspect ratio. (a) Change in ratio of surface area of rim to basal planes with increasing size of the nanoclay platelets. The amount of polymer adsorbed at the rim becomes insignificant for increasingly larger nanoclays. (b) Dependence of polymer content and $d'$-spacing on the aspect ratio of all the nanoclays including fragmented NTS with smaller aspect ratios of 280 and 60 (dark cyan symbols). (c) Thermogravimetric analysis of pristine nanoclays and the corresponding nacre-mimetic hybrid films.

To investigate this effect, we used a high-shear microfluidizer to fragment the large NTS nanoclay and prepared nacre-mimetics from two smaller-sized NTS batches (PVA/NTS$_{280}$ and PVA/NTS$_{60}$; subscript indicates aspect ratio by SEM). Indeed we also find increasing polymer content for smaller nanoclay batches with the same surface energy as the parent nanoclay (NTS$_{3500}$). Hence, the geometrical model mostly explains the higher polymer content in PVA/LAP and PVA/SUM compared to the nacre-mimetics with larger nanoclays. Interestingly, for these differences in polymer content to translate into larger gallery spacings, the polymer content needs to be at least partly pushed into the gallery spacings during self-assembly process, possibly due to lateral contraction in the late stages of water evaporation. This becomes increasingly difficult for larger nanoclays, which can be seen in the near constant $d'$-spacing for the higher aspect ratio nanoclays (NHT and NTS). Fig. 4b compares the $d'$-spacing from XRD with the polymer content from elemental analysis and establishes a correlation between both characteristics.
Mechanical Properties

Next, we will discuss the mechanical properties as a function of aspect ratio, and viscoelastic properties of the polymer layer and its thickness (Fig. 5-6 and Supplementary Table 1). Previous experiments on clay-based nacre-mimetics almost exclusively focused on MTM as building block and hardly any data for mechanical properties is available for other aspect ratios or synthetic nanoclays. Establishing these relationships and understanding the fracture mechanisms for biomimetic materials, in particular involving polymers under nanoconfinement, are however vital to provide the foundation for future rational design and the ability to target performance maxima. Here, we focus mainly on a comparison of the properties of nacre-mimetics based on synthetic nanoclays and only relate at selected parts to previously investigated PVA/MTM materials. The influence of aspect ratio is intuitively anticipated owing to the fact that yielding of a composite material can more easily occur for lower aspect ratio nanoclays and higher fractions of polymer, while stiffness is favored for larger aspect ratio nanoclays and highest fraction of reinforcements. These relationships were successfully established for fiber reinforced composites and classical nanocomposites, but have not been shown to be applicable for highly reinforced nacre-mimetics that are controlled to large extent by interfaces and involve the nanoconfinement of the polymer layers. For simplicity, we have to make the reasonable assumption that the intrinsic stiffness of the various nanoclays and the interfacial stress transfer of the polymer onto the nanoclays are on a similar level. We believe this to be fair as we are dealing with the same material class with only small changes in the composition. To further support this assumption, we also later on discuss nacre-mimetics based on fragmented clay samples, thereby using exactly the same nanoclay but with different aspect ratios (PVA/NTS with \(d/t = 3500, 280, 60\)). We also discuss humidity-dependent studies to add crucial complementary information on the influence of the dynamics of the nanoconfined polymer on the macroscale mechanical.
properties. We refer to the Supplementary Table 1 for the list of all data on mechanical properties.

Focusing first mainly on the elastic properties (Fig. 5a,b), it is seen that nacre-mimetics based on the largest synthetic nanoclays (PVA/NTS) show drastically higher stiffness with a Young’s modulus close to 40 GPa at 20 %RH, which is approaching that of natural nacre (E = 40 – 60 GPa in wet and 70 GPa in dry conditions\(^3,4\)). At the same time this material reaches a tensile strength of 200 MPa, which is double or triple of that of natural nacre. Most importantly, the ultrahigh aspect ratio of NTS allows reaching stiffness values significantly higher than what can be achieved with natural MTM. PVA/NTS in fact realizes values that have previously only been achievable using covalent\(^36,62\) or supramolecular crosslinking.\(^15,40\)

Hence, there is a clear and profound advantage of exploiting larger aspect ratio nanoclays, giving a fresh impulse for the proper selection in future nacre-mimetics.

In general, a loss in stiffness is observed for decreasing the aspect ratio. This loss in stiffness can however not only be associated with the lower aspect ratio of the nanoclay, but also needs to take into account the lower weight fractions of inorganic reinforcements as found in elemental analysis, TGA and XRD (Fig. 4). To allow a better understanding, we calculated the Young’s moduli for selected aspect ratios and as a function of the reinforcement content (vol\%, Fig. 5c). These calculations are based on the Halpin–Tsai\(^63,64\) model developed for layered nanocomposites oriented in tension direction.\(^65\) We refer to the SI for the Jaeger–Fratzl model and the modified Halpin–Tsai model comparing systems with parallel and random orientation, respectively (Supplementary Fig. 7 and Supplementary Note 1).\(^64\) From this plot, we see that (i) increasing the volume fraction of nanoclay induces higher stiffness and (ii) larger aspect ratio nanoclays lead to higher stiffness at the same level of reinforcement. However, it also becomes evident that there is no further significant improvement in Young’s modulus upon increasing the aspect ratio once a critical aspect ratio
is reached at a particular volume fraction of nanoclay (vertical dependence). This is simply because stress transfer already fully activates the nanoplatelets after a critical size. In our nanocomposites, we find higher reinforcement contents when increasing the nanoclay aspect ratio. Therefore, the higher stiffness obtained for nacre-mimetics with larger nanoclays is not only due to increasing aspect ratio of the reinforcement but also due to containing higher fractions of it (see predicted values).

![Figure 5](image)

_Figure 5. Tensile mechanical properties of nacre-mimetics._ (a) Influence of the aspect ratio of nanoclays on tensile mechanical properties measured at 40 %RH for nacre-mimetics prepared from isolated core/shell particles. (b) Dependence of Young’s modulus of nacre-mimetics on the aspect ratio of nanoclay at different %RH (see also Fig. 6). (c) Variations of Young’s modulus with volume fraction of reinforcement are shown for different aspect ratios following the Halpin–Tsai model, considering $E_m = 2.3$ GPa at 40 %RH (see also Supplementary Note 1), $E_i = 270$ GPa and $t = 1$ nm (NC = nanoclay). The predicted values for our nacre-mimetics are added, considering the actual polymer content and the aspect ratio of the individual nanoclay. (d) Influence of polymer content on tensile mechanical properties for PVA/NTS and PVA/LAP (40 %RH, polymer content indicated in w/w within the panel). Dotted lines indicate stable crack propagation. (e) Dependence of Young’s modulus of PVA/LAP on polymer content. Photographs of PVA/LAP = 45/55 sample show the crack initiation and stable crack propagation. (f) Effect of platelet size of fluidized/fragmented NTS nanoclay on tensile mechanical properties of corresponding nacre-mimetics based on perfect core/shell particles.

Additionally, larger synthetic clays benefit from a slightly better in-plane orientation (Fig. 3e, Table 2). This can however only be considered as a minor contribution to enhancing
unidirectional stiffness as the degree of orientation for all synthetic nacre-mimetics scale within 10%, whereas the aspect ratios change by three orders of magnitude. The experimental stiffness values are lower than predicted by the Halpin–Tsai and Jaeger–Fratzl models (Fig. 5c, and Supplementary Fig. 7). This is yet a common phenomenon in nanocomposites and originates from the inefficient stress transfer from the matrix to the nanoclay, not allowing to realize the full potential of the nanoclay reinforcement.

A discontinuity is observed when comparing PVA/MTM and PVA/SUM (Fig. 5a). Although natural MTM has a slightly higher aspect ratio, the resulting nacre-mimetic displays lower stiffness than PVA/SUM and also an onset of yielding. This is particularly interesting, considering that PVA/SUM contains almost 12 wt% more PVA. We associate the higher stiffness to the advantages of synthetic nanoclays, which display better exfoliation and a better adsorption of polymers due to a more homogeneous surface chemistry, therefore allowing better stress transfer and higher cohesive strength. In addition the degree of orientation is substantially lower for the PVA/MTM film, leading to a less efficient unidirectional reinforcement (see Fig. 3e). The lower stiffness of solution cast PVA/MTM in this paper as compared to previous PVA/MTM films prepared by vacuum filtration is attributed to the presence of 8 wt% more polymer in the cast film, different nanoclay fractionation and batch (natural product), and unlike structure formation processes associated with the different preparation methods. While vacuum filtration leads to a forced concentration increase at the surface of the filtration unit and an asymmetric structure development, free film casting mostly leads to a homogeneous increase of the concentration of the core/shell platelets. Upon passing a critical concentration, a liquid crystalline state develops, which then becomes arrested during final drying. Different lateral stress occurs during final stages of drying.
Concerning the tensile strength, a similar trend can be observed in the nacre-mimetics. Although tensile strength is governed by defects in case of linear elastic materials, we observe an increase in tensile strength as the size of the nanoclay (and concurrently the fraction of reinforcements, Table 2) enlarges, and reach a maximum of 200 MPa at 20 %RH for superlarge NTS nanoclay. We relate the observation of this consistent trend to similar amounts of detrimental defects due to analogous preparation conditions for all nacre-mimetics.

A direct comparison of all nacre-mimetics at 40 %RH (Fig. 5a) reveals a prominent transition in terms of the deformation modes when passing from highest to lowest aspect ratio nanoclays. We chose 40 %RH for this comparison, as the water uptake due to humidity is similar for all nacre-mimetics at this point (Fig. 6a). Interestingly, PVA/LAP shows a clear and pronounced onset of yielding. This preferential yielding is caused by the comparatively higher fraction of polymer, and more importantly, by the lower aspect ratio of the nanoclay allowing a transition of the deformation mode from platelet fracture to platelet pull-out, as also seen in SEM (Fig. 2a).

A more global understanding of the mechanical behavior depending on the size and type of synthetic nanoclay should also include (i) the influence of the polymer content on the yielding and mechanical properties for differently sized nanoclays and (ii) analyzing the effect of potentially different adsorption strength of polymers on nanoclays of different chemical composition.

We address the first objective by varying the polymer fraction in nacre-mimetics based on smallest (LAP) and largest (NTS) nanoclays from the values found in their corresponding materials based on “perfect” core/shell particles (PVA/LAP = 58 wt% PVA; PVA/NTS = 24 wt% PVA). This can be achieved by careful direct mixing and subsequent film casting. Let us first focus on PVA/LAP prepared at different polymer fractions. Structural characterization
by XRD shows lower gallery spacing for less polymer, hence confirming a smooth and adequately defect-free structure built-up also at lower fractions of polymer (Supplementary Fig. 8). The corresponding tensile testing curves for PVA/LAP show a similar yielding transition down to a polymer content of 35 wt% (Fig. 5d). For comparison, PVA/SUM \( (d/l = 140, 50 \text{ wt}\% \text{ polymer content}) \) does not show inelastic deformation under similar conditions, hence demonstrating a first clear influence of the nanoclay size on the transition to inelastic deformation. Upon further reduction of the polymer content down to the level of PVA/NTS (25%), the inelastic deformation is lost. This demonstrates that a minimum layer thickness of the nanoconfined polymer is necessary to allow inelastic deformation \( (d^* > 2.4 \text{ nm}, \text{ Supplementary Fig. 8}) \) for small LAP. To correlate this behavior from the other end, we also prepared PVA/NTS with a higher polymer content similar to PVA/LAP (labeled as PVA/NTS = 57/43). The corresponding tensile testing curve however still shows purely linear elastic behavior, and also some lower tensile strength, possibly due to a different level of defects. In summary, all of these comparisons demonstrate that the size of the nanoclay is crucial in deciding over the presence of inelastic deformation (at the same polymer content) and that toughness is favored for smaller nanoclays.

Interestingly enough we find stable crack propagation through the PVA/LAP materials down to a polymer content of ca. 45 wt\%, and one can observe a large process zone (stress whitening) around the propagating crack tip, even at only 40 %RH (Fig. 5e). This shows efficient distribution of fracture energy and is a clear indication of enhanced toughness. The polymer content of 45 wt\% can be considered as optimum for PVA/LAP as the higher amount of reinforcement also increases the stiffness to 14 GPa, without sacrificing inelastic deformation.

We study the second objective – effect of interfacial adsorption energy – for different sizes of the same nanoclay after fragmentation using a microfluidizer. We focus on two batches
with aspect ratios of 280 and 60, complementing the existing PVA/NTS\textsubscript{3500} material with aspect ratio 3500. The tensile curves of the corresponding nacre-mimetics show the same decrease of the elastic properties and an onset of yielding for the material containing the smallest batch of NTS (PVA/NTS\textsubscript{60}) (Fig. 5f). This behavior is very similar to what has been found earlier when varying the nanoclay aspect ratio by changing the type of nanoclay (Fig. 5a), and corroborates the relationships discussed above.

To better understand the deformation mechanisms as a function of the viscoelastic properties of the polymer, we further studied the effect of humidity on the mechanical properties of the nanocomposites based on the pure core/shell particles (Fig. 6). Fig. 6a quantifies the water uptake by water sorption experiments for the various nacre-mimetics. One observes a similar and rather low water uptake for all nacre-mimetics till around 40 %RH. Upon further increase of the relative humidity, the sorption curves start to deviate and the nacre-mimetics with smaller nanoclays contain more water due to higher polymer content. The overall differences range however in a narrow window of only 10%. The kinetics of water uptake for the increase from 80 – 92 %RH reveal a faster mass increase and an earlier equilibration for smaller nanoclays (Fig. 6b). This reflects the barrier properties of the materials, because water molecules have a larger tortuous pathway and hence slower migration perpendicular to the materials for largest aspect ratio nanoclays, while the diffusion of water molecules is comparably quick for smaller nanoclays.

In terms of mechanical properties, a softening in the elastic region is common to all materials due to the plasticizing effect of water (Fig. 6d-f; Fig. 5b). In strong contrast are however the differences in inelastic deformation. The tensile curves at different %RH clearly show that PVA/LAP and PVA/NTS serve as the two extremes, while PVA/SUM takes the intermediate position in demonstrating the switch over in behavior from elastic to plastic
deformation with increasing humidity (Fig. 6d-f, Supplementary Table 1). This trend clearly originates from the aspect ratio of the used nanoclay.

While humidity significantly increases the ductility of the materials with lower aspect ratio nanoclay (LAP and SUM) and leads to an increase of the elongation at break ($\varepsilon_b$) from below 1% (20 %RH) to 30% (100 %RH), inelastic deformation is almost absent for the largest aspect ratio nanoclays (NHT and NTS) up to 100 %RH. The pronounced yielding and inelastic deformation for PVA/LAP and PVA/SUM takes place by frictional sliding of small nanoclay platelets due to softening and lower internal cohesion of the polymer with increasing levels of internal hydration. This can be traced by solid state $^{13}$C cross-polarization magic-angle spinning nuclear magnetic resonance (13C-CPMAS NMR) for the nacre-mimetic with the highest polymer content (PVA/LAP) and for the two extreme cases of hydration, i.e. dehydrated and hydrated (Fig. 6c). The hydrated sample clearly shows the appearance of an

Figure 6. Influence of humidity on nacre-mimetics based on core/shell particles. (a) Moisture content of nacre-mimetics as a function of relative humidity at 28 °C. (b) Kinetics of moisture sorption from 80 to 92 %RH. (c) $^{13}$C-CPMAS NMR spectroscopy study of PVA/LAP at 23 °C in dry state and in hydrated state by soaking in D$_2$O. A characteristic rubbery peak (IV) at 66 ppm is obtained for hydrated PVA/LAP, while it remains absent in the dry materials. (d-f) Influence of humidity on tensile mechanical properties of PVA/LAP, PVA/SUM and PVA/NTS, respectively.
additional peak at 66 ppm in the region of the α-carbon (-CH$_2$\(-\text{CHOH}\)-; labeled as (IV)). This peak is associated with a rubbery character and enhanced chain dynamics of PVA, as opposed to pure glassy character found at low relative humidity.$^{66}$ PVA/LAP yields earlier and more than PVA/SUM owing to (i) the lower aspect ratio of the LAP nanoclay leading to less efficient reinforcement and easier platelet pull-out and (ii) its higher polymer content compared to PVA/SUM enhancing dynamics and interfacial slippage. Further differences can be seen in the slopes of the tensile testing curves in the plastic region. Contrary to PVA/SUM, PVA/LAP shows a drop in strength after the yield point for most humidities. This decrease derives from slight necking, which can exclusively be observed for PVA/LAP. Larger nanoclays in their corresponding nacre-mimetics (PVA/NHT and PVA/NTS) provide higher reinforcement and stiffness, leading to almost purely elastic deformation. This is due to the presence of minimal amounts of polymer, which is completely nanoconfined between stacked ultralarge nanoclays ($d^* \approx 1.7$ nm). Significant inelastic deformation can only be observed upon full plasticization when placed into water.

Correspondingly, the modulus of toughness or work-of-fracture (WOF), as measured by the area under the curves strongly depends on the deformation mechanisms and tendency for inelastic deformation. While the largest aspect ratio nanoclays show only minimum increase in WOF, the PVA/LAP and PVA/SUM materials show drastically enhanced toughness enabled by yielding at 40 and 80 %RH, respectively. As mentioned above, PVA/LAP also shows stable crack propagation. With respect to other known nacre-mimetics,$^{11,32,37,39,60,61,67}$ PVA/LAP based on pure core/shell platelets and its optimized variant with slightly less polymer (PVA/LAP = 45/55, see Fig. 5d) demonstrate good stiffness close to 10 GPa and 15 GPa, good tensile strength and at the same time realize a substantial WOF of $10 \pm 3.2$ MJ m$^{-3}$ and $15 \pm 6.5$ MJ m$^{-3}$ at 40 %RH, respectively. Owing to the more pronounced inelastic deformation this value increases up to $31 \pm 7.5$ MJ m$^{-3}$ at 80 %RH, albeit compromising
stiffness and strength. A similar trend and values are found for PVA/SUM, but with a transition at higher %RH, implying that depending on the application conditions the appropriate nanoclay needs to be selected.

**Transparency and Gas Barrier as Functional Properties**

In terms of developing multifunctional property profiles for functional biomimetic materials, synthetic nanoclays represent viable advantages, especially when aiming at fully transparent and highly flexible coatings and self-standing films with outstanding barrier properties. Such materials are intensely needed as flexible encapsulants or substrates for (printable) organic electronics, or for gas storage applications. The primary factors promoting gas barrier are increasing the nanoclay aspect ratio, as well as the nanoclay fraction, exfoliation and orientation in the nanocomposite, and diminishing free volume. Nacre-mimetics fulfill most criteria to the best possible extent, yet free volume remains difficult to predict and to experimentally access. For full transparency, grain boundaries and irregularities in the self-assembly must be prevented to reduce detrimental light scattering within the film. At the same time, the surface must be of high quality containing minimum roughness to avoid surface scattering.

First, let us focus on the transparency of our materials. The optical properties of the films are remarkable in terms of transparency, when properly treated (see below). Again, a clear size effect can be deduced, separating the smaller aspect ratio nanoclays from the ones with high aspect ratio. The photograph of PVA/LAP depicts a film with basically full, glass-like transparency and high optical clarity (Fig. 7a). PVA/LAP films transmit 95 - 97% of the spectrum of the visible light at a film thickness of ca. 25 µm and PVA/SUM films show 85 - 92% transmittance for the same film thickness. The best similar materials prepared from natural MTM and PVA only show a transmittance of 33 – 67% at normalized thickness of 25 µm.36 On the contrary, some unexpected difficulties are encountered for the nacre-mimetics
with higher aspect ratio nanoclays, NHT and NTS. Both materials do not reach the optical clarity of PVA/LAP and PVA/SUM, and typically only show translucent films. Careful SEM investigations reveal at least one origin by visualizing a ca. 1.5 - 2 µm thick heterogeneous skin layer, which forms during evaporation of the dispersion (see Fig. 7e, Supplementary Fig. 9). This layer causes surface scattering and leads to a certain opaqueness, while the interior and bottom of the film are perfectly structured as seen by SEM.

![Figure 7](image.png)

**Figure 7. Optical properties of nacre-mimetics based on synthetic nanoclays with various aspect ratios.** (a) Photographs of an almost fully transparent PVA/LAP film. (b) Transparency by UV-Visible spectroscopy (normalized to 25 µm thickness). (c-d) Nacre-mimetics with larger nanoclay (PVA/NTS) show translucency, but require a clear coat matching the refractive index of the nacre-mimetics closely to become almost transparent. (e) SEM depicting the skin formed during preparation of a PVA/NTS nacre-mimetic (scale bar 5 µm). (f) Schematic (not in scale) showing how a clear coat of matching refractive index diminishes surface scattering by providing a smooth top surface layer.

To overcome the detrimental surface scattering, we applied a very thin clear coat (ca. 3 µm, Supplementary Fig. 10) matching closely the refractive index of the nacre-mimetic to reduce interfacial scattering by providing a smooth top surface (Fig. 7c-f). This leads to a substantial increase of the transmittance as seen in the photographs and transmission measurement. Yet the transparency after applying the clear coat cannot reach the near perfect
optical quality of the films prepared from the lower aspect ratio nanoclays (PVA/LAP and PVA/SUM). This points to the need of even further refining the structure formation process, in particular diminishing the presence of the heterogeneous surface layer using highly tailored polymers and also understanding the contribution of scattering by individual superlarge nanoplatelets within the film. Overall, the synthetic nanoclays provide a substantial improvement, pushing the application areas of mechanically superior and thick nacre-mimetic films into fields where highest transparency is desirable.

We also studied the oxygen permeability being of pivotal importance for applications in barrier materials. Synthetic NTS nanoclay is among the nanoclays with the best ever reported aspect ratio, hence motivating above all to pursue gas barrier properties. In recent years, Ebina and Mizukami\textsuperscript{27} obtained a remarkably low oxygen permeability of 0.00074 cm\(^3\)·mm·m\(^{-2}\)·day\(^{-1}\)·atm\(^{-1}\) at dry conditions for a self-standing polymer/clay film. The film was prepared by coordination of 20 wt% poly(sodium acrylate) to the lateral rims of SUM as binder. Although being outstanding in terms of oxygen barrier properties, the films demonstrate poor mechanical properties exhibiting tensile strength of only around 25 MPa.\textsuperscript{27,28} In addition, sequential LbL of different nanoclays and polymers as ultrathin surface coatings revealed an extraordinary performance, and large hopes arise from new synthetic clays with highest aspect ratios.\textsuperscript{31,54} However, the LbL method ultimately faces clear limitations when aiming at higher coating thicknesses or even self-standing films. Main advantages of our films are the very good mechanical properties, simple and fast preparation of thick films, and the possibility to measure them directly as freestanding films, hence also eliminating any influence from supporting layers. Table 3 compares all materials at high relative humidity. High relative humidity poses challenging conditions for gas barriers based upon water-soluble polymers, as increased free volume and plasticization allow faster diffusion of gas molecules.\textsuperscript{32-34,37,68} Interestingly, the smaller synthetic nanoclays actually outperform previously investigated
PVA/MTM\textsuperscript{36}, despite the fact that the weight fraction of nanoclay is lower. In particular PVA/SUM containing the larger nanoclays compared to PVA/LAP shows a one order of magnitude better performance and reaches very low oxygen permeability of 0.056 cm\textsuperscript{3}·mm·m\textsuperscript{-2}·day\textsuperscript{-1}·atm\textsuperscript{-1}. A clear further increase of the gas barrier is possible by changing to PVA/NTS containing the largest synthetic clays, that allows to reach superbly low gas permeability of only 0.005 cm\textsuperscript{3}·mm·m\textsuperscript{-2}·day\textsuperscript{-1}·atm\textsuperscript{-1} (triple-checked for different films). Such permeability values are better than the commercially available barrier films based on synthetic polymers such as polyvinyl chloride, polyvinyl alcohol, polyethylene terephthalate\textsuperscript{69} and even highly oriented ethyl vinyl alcohol at similar humidity.\textsuperscript{70} In fact the gas barrier is amongst the best ever reported values for layered clay materials – found here in a self-standing material at 80 %RH.\textsuperscript{27,31,32,34,37,54} Therefore, the unique combination of transparency, gas barrier, and mechanical robustness make these rapidly prepared self-standing nanocomposite films a choice for food packaging, gas storage applications, and as sealants and advanced substrates for flexible organic electronics. The herein demonstrated high gas barrier and glass-like transparency complement our previously shown outstanding fire and heat barrier properties for self-assembled nacre-mimetics.\textsuperscript{44}

<table>
<thead>
<tr>
<th>Material</th>
<th>Aspect ratio</th>
<th>RH (%)</th>
<th>Oxygen permeability cm\textsuperscript{3}·mm·m\textsuperscript{-2}·day\textsuperscript{-1}·atm\textsuperscript{-1}</th>
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<tr>
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<td>80</td>
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<tr>
<td>PVA/SUM</td>
<td>140</td>
<td>80</td>
<td>0.056</td>
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<tr>
<td>PVA/MTM\textsuperscript{36}</td>
<td>260</td>
<td>80</td>
<td>0.325</td>
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<tr>
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<td>3500</td>
<td>80</td>
<td>0.005 (0.004)\textsuperscript{a}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Standard deviation based on 3 specimens is given in brackets.

### 3.4. Conclusions

We herein established the correlation among structure formation, nanostructuration, mechanical deformation modes and functional properties for self-assembled artificial nacre
using synthetic clays bridging three orders of magnitude in aspect ratio. We find that the mechanical properties can be crucially influenced by the size of the nanoclay, ranging from ultrastiff materials for the highest aspect ratio to extremely tough materials with pronounced inelastic deformation for the smallest. These differences are not only due to the different aspect ratios and changes in the failure mode from platelet fracture to platelet pull-out, but also relate to the fact that higher amounts of polymer are present for smaller nanoclay due to larger fractions of adsorbed polymers in the rim areas. Changing the viscoelastic properties via hydration-induced plasticization enables a further understanding of the changes in fracture behavior from linear elastic to plastic as a function of humidity and accelerated dynamics, following closely the nanoplatelet size.

True advantages of the synthetic nanoclay manifest in practically fully transparent, glass-like nacre-mimetics for the smaller aspect ratio nanoclays, while at the same time showing among the best gas barrier properties known for nacre-mimetics. Together with the advanced mechanical properties, a wide-ranging and advanced multifunctional property profile can be realized. The lower transparency for larger clays is in part due to the formation of a skin layer, which can be diminished using a suitable clear coat. Further improvements in this direction require to clearly characterize the free volume in these materials as a function of the aspect ratio, and that even better suited polymer systems need to be identified to reduce the remaining structural defects and the propensity for skin formation in nacre-mimetics based on largest-aspect ratio nanoclays.

This study establishes the needed foundation for future rational design of nacre-mimetics to tune material properties and target highest performance. The combination of advanced and tunable mechanical properties with excellently developed functionalities, allowed by feasible large-scale processing, extends the application prospects of nacre-mimetic materials beyond mechanical properties or the focus on singular functionalities. Advanced multifunctional
biomimetics are now in reach, such as high performance, mechanically robust, transparent barrier coatings and self-standing substrates for organic electronics.

3.5. **Acknowledgement**

The authors acknowledge financial support from the IGF 17502N grant agreement, and the BMBF in the framework of the NanoMatFutur Program. We thank Rockwood Industries, Kunimine Industires Co. Ltd., Topy Industries Ltd. For donating the nanoclay samples. This work was performed in part at the Center for Chemical Polymer Technology CPT, which is supported by the EU and the federal state of North Rhine-Westphalia (grant no. EFRE 30 00 883 02). This work made use of the Aalto University Nanomicroscopy Center (Aalto-NMC) premises. We thank Joby Kochumalayil for supporting oxygen barrier measurements of some samples. F.H.S. acknowledges support from the Thuringian Ministry for Education, Science, and Culture (TMBWK, grants #B514-09051, NanoConSens, and #B515-11028, SWAXS-JCSM). A.W. gratefully acknowledges continuous support by Martin Möller.

3.6. **References and Notes**


Nacre-mimetics with synthetic nanoclays up to ultrahigh aspect ratios


50. Topy industries product datasheet checked on 22/04/2014

http://www.topy.co.jp/english/dept/mica/industrial.html


3.7. Supplementary Information

Supplementary Figure 1: Size distributions of the used nanoclays. Scanning electron microscopic imaging and statistical analysis to derive the size distributions of the exfoliated and cleaned nanoclays used in the preparation of the nacre-mimetics. SEM images of (a) SUM (scale bar 1 µm), (b) MTM (scale bar 1 µm), (c) NHT (scale bar 2 µm) and (d) NTS (scale bar 10 µm). (e–h) Histograms of the size distribution of all nanoclays.
Supplementary Figure 2. Dynamic light scattering analysis of all nanoclays. (a) Intensity weighted apparent size distribution plots (CONTIN) measured at 23 °C and at 90°. Nanoclay concentration of 0.1 g/L is maintained by proper dilution with 18.7 mM of Na₄P₂O₇ salt solution. A slight shift of the maximum of the apparent hydrodynamic radius distribution can be observed with increasing true platelet size (as determined by imaging). Hence DLS reflects the size tendency, but cannot give quantitative information due to the fact that polydispersity in size and shape, non-circular shape, bending modes and rotational diffusion contribute to the scattering behavior. The dynamic light scattering form factor for discs is different to the ones for spherical particles, which is commonly used for the evaluation of DLS data. For a deeper discussion on DLS of disc like scatterers, we refer to our previous publication.¹ (b) Number weighted (black) and intensity weighted (blue) average size distribution plots of LAP. The plot shows that the majority of the clay nanoplatelets have hydrodynamic diameters around 20-31 nm. The intensity weighted size distribution grossly overestimates larger particles since intensity scales with $R^6$. 

¹
Supplementary Figure 3. Comparison between film casting and vacuum filtration for different nacre-mimetics. SEM images for comparing nacre-mimetics prepared by film casting (left column) and vacuum filtration (right column) of (a, b) PVA/LAP (scale bar 2 µm), (c, d) PVA/NHT (scale bar 5 µm), and (e, f) PVA/NTS (scale bar 5 µm). The PVA/LAP film shows almost similar appearance in both preparation methods but for larger nanoclays (NHT and NTS), the casted films display a better ordered mesostructure with well aligned flat nanoplatelets as compared to vacuum filtrated films with slightly curved and wavy mesostructure.
Supplementary Figure 4. Birefringence of dispersions containing large aspect ratio nanoclay. Observation of (a) an aqueous 0.5 wt% NHT dispersion and (b) an aqueous 0.5 wt% PVA/NHT dispersion after mixing overnight in glass tubes between crossed polarizers. Both NHT and PVA/NHT dispersion show shear-induced birefringence.

Supplementary Figure 5. Height profiles of several nanoclays by AFM. Average thickness of each clay is calculated from sectional analysis done on several platelets of the same nanoclay and then an average is taken over all the calculated thickness values. MTM: 1.04 ± 0.06 nm, NHT: 1.08 ± 0.05 nm, NTS: 1.02 ± 0.05 nm. The thickness of LAP has been evaluated by small angle neutron scattering to be 0.91 ± 0.01 nm. As the thickness is ca. 1 nm for all the nanoclays, we calculated the aspect ratio of nanoclays considering 1 nm as thickness.
Supplementary Figure 6. Individual comparisons of 1D XRD analysis of nacre-mimetic PVA/nanoclay films and pure nanoclay (a-e). Higher order peaks are indicated by arrows and the dotted line in (c) shows the peak position of non-exfoliated MTM. $d'$-spacing is calculated from the primary scattering peak ($q^*$) according to $2\pi/q^*$. 
Supplementary Figure 7. Calculation of the Young’s modulus according to the Jaeger-Fratzl and the modified Halpin–Tsai model. Variations of Young’s modulus with volume fraction of reinforcement are shown for different aspect ratios following (a) Jaeger–Fratzl model for nanocomposite having parallel orientation and (b) modified Halpin–Tsai model considering random orientation (triangles). Values calculated using classical Halpin–Tsai model (squares) are also shown for better comparison of Young’s modulus between parallel vs. random orientation. Predicted values based on the aspect ratio of the nanoclays used in this study are also shown using these models.

Supplementary Figure 8. 1D XRD of PVA/LAP with different polymer content. The influence of the polymer content on the nanostructure is obtained. Variation of $d'$-spacing with polymer content (inset).
Supplementary Figure 9. Skin formation during drying of PVA/NHT dispersion. (a) The top layer dries fast and forms a skin. The inset shows a close view of the skin attached to the wall of the petridish. (b) This skin can be easily peeled off with tweezers from the top surface of the remaining underlying dispersion during drying. The origin of the skin formation is related to the nanoclay size and only occurs for large clays. We hypothesize the origin as follows. The large particles tend to strongly segregate to the surface with low dynamics once adsorbed at the interface (Pickering effect). Additionally the large nanoclays provide a good barrier layer and prevent a faster evaporation from the underlying dispersion. Therefore the top layer dries comparatively quicker than the underlying dispersion. Macroscopically this is visible as a skin, which can be peeled off.

Supplementary Figure 10. SEM images of the cross-section of PVA/NTS before and after coating with a clear coat. (a) A skin is formed as top layer during film casting. The skin thickness is ca. 1.5 - 2 µm, (scale bar 20 µm). (b) The same film cross-section after applying a thin clear coat on top of PVA/NTS (scale bar 20 µm). The coating thickness is ca. 3 µm.

Supplementary Figure 11. Cleaning of NHT and NTS clay. (a) Three distinct phases of NHT and NTS nanoclays form after centrifugation at 12000 rpm for 90 minutes. (b) Viscous sol after collecting the middle phase. (c) 0.5 wt% dispersions of exfoliated NHT and NTS nanoclays in water.
Supplementary Table 1. Tensile mechanical properties as a function of aspect ratio and humidity

<table>
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<tr>
<th>Name</th>
<th>Young’s modulus $E$ (GPa)</th>
<th>Tensile strength, $\sigma$ (MPa)</th>
<th>Elongation at break $\varepsilon_b$ (%)</th>
<th>Work of fracture (WOF) (MJ m$^{-3}$)</th>
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<td>20 % Relative Humidity</td>
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Nacre-mimetics with synthetic nanoclays up to ultrahigh aspect ratios

Chapter 3
Supplementary Note 1

The Halpin–Tsai model and the Jaeger–Fratzl model are used for predicting the Young’s modulus of the nacre-mimetics considering parallel orientation (\(E_{\text{parallel}}\)), whereas, the modified Halpin-Tsai model is utilized to predict the Young’s modulus of the nacre-mimetics considering random orientation (\(E_{\text{random}}\)).

**Halpin–Tsai Model**

\[
E_{\text{parallel}} = E_m \left(\frac{1 + \frac{2d}{t} \cdot f_r \cdot \eta}{1 - f_r \cdot \eta}\right) \quad \text{with} \quad \eta = \frac{(\frac{E_r}{E_m}) - 1}{\frac{E_r}{E_m} + \frac{2d}{t}}
\]

**Modified Halpin–Tsai Model**

\[
E_{\text{random}} = E_m \left[ \frac{3}{8} \left(1 + \frac{2d}{t} \cdot f_r \cdot \eta_1\right) + \frac{5}{8} \left(1 + 2 \cdot f_r \cdot \eta_2\right) \right] \quad \text{with} \quad \eta_1 = \frac{(\frac{E_r}{E_m}) - 1}{\frac{E_r}{E_m} + \frac{2d}{t}} \quad \eta_2 = \frac{(\frac{E_r}{E_m}) - 1}{\frac{E_r}{E_m} + 2}
\]

**Jaeger–Fratzl Model**

\[
\frac{1}{E_{\text{parallel}}} = \frac{4(1 - f_r)}{G \cdot f_r^2 \cdot \left(\frac{d}{t}\right)^2} + \frac{1}{f_r \cdot E_r} \quad \text{with} \quad G = \frac{E_m}{2(1 + \nu)}
\]

where \(d\) = diameter, \(t\) = thickness and \(f_r\) = volume fraction of the reinforcement; \(E_m\) and \(E_r\) = Young’s modulus of matrix and reinforcement, respectively, \(E_{\text{parallel}}\) = Young’s modulus of the nanocomposite oriented in parallel direction, \(E_{\text{random}}\) = Young’s modulus of the nanocomposite oriented in random direction \(G\) = shear modulus of the polymer matrix, \(\nu\) = Poisson’s ratio. We consider \(E_m = 2.3\) GPa at 40 %RH, \(E_r = 270\) GPa and \(t = 1\) nm, for most polymers, \(\nu = 0.4-0.5\). To calculate the volume fraction, we use weight fraction of the reinforcement from elemental analysis and consider the density of polymer and nanoclay as 1.26 and 2.8 g/cm\(^3\), respectively.
Supplementary References


Facile access to large-scale, self-assembled, nacre-inspired high-performance materials with tunable nanoscale periodicities*

4.1. Introduction

Nature’s load-bearing materials are paradigms for lightweight engineering as they uniquely combine stiffness, strength and toughness with low density.\textsuperscript{1-2} Spider silk, wood, mother of pearl (nacre), crustacean cuticles and bone are some prime examples. Such biocomposites are characterized by ordered structures combining large fractions of hard, reinforcing segments with a minor amount of soft, energy-adsorbing and lubricating biopolymer. The interface between hard and soft is durable and well controlled. Nacre exhibits a brick-and-mortar architecture in which 95 \text{vol}\% of CaCO\textsubscript{3} microtablets are arranged in a minority phase of biopolymer. Due to its extraordinary mechanical properties nacre has inspired the fabrication of bioinspired, layered nanocomposite materials.\textsuperscript{3-5}

Some of the main lessons for nacre-inspired composites are the layered, highly oriented arrangement of the reinforcements, the alternating hard and soft layers, tailored interactions of the soft phase and the presence of a majority fraction of reinforcements. These aspects also fundamentally distinguish bioinspired nanocomposites from traditional ones, which only use low contents of reinforcements (< 10 \text{wt}\% nanoclay). Seashells are able to grow these complex materials in water in a lengthy process.\textsuperscript{6} However, for man-made structural materials manufacturing such slow growth strategies are not applicable and new time-efficient self-assembly strategies are needed to prepare similarly structured material. Finding access routes to such large-scale complex materials with high fractions of reinforcements and easily tunable nanoscale structures still remains a considerable scientific challenge.

Strategies for nacre-inspired materials often use sequential deposition strategies, such as
layer-by-layer (LbL) deposition of nanoclays and polymers or alternating spin-coating of thin polymer layers and monolayer deposition of platelets. These approaches led to remarkable properties, where for example high stiffness and strength, or good stiffness and high ductility were achieved. Although demonstrating interesting property profiles, these materials are tedious to prepare and restricted to finite dimensions with very small thickness. Other approaches to layered composite materials deal with ceramic-type of processing using ice-templating, sintering and infiltration of resins, deposition of platelets in electric fields or controlled sequential crystal growth of CaCO₃ in a layered fashion. Frequently, only structural control is demonstrated and mechanical or functional properties are not described, which in some cases relates to the too small material dimensions.

A simpler access route could be provided by direct co-casting of polymers and nanoclay, which can give rise to self-assembling lamellar films during water evaporation. For such an approach stable dispersions without coagulation and phase separation at high nanoclay contents are crucial and require the control of interactions. In fact much attention in concentrated polymer/clay systems was drawn to understanding the dispersion characteristics and structure formation processes. However, comparably little efforts were directed to using such self-ordering structures to realize mechanically excellent high-performance bulk materials, and to use the capabilities for a dedicated tuning of the nanostructures across the full composition range and up to high clay contents. One of the most notable co-casting approaches at high clay loadings was reported by Ebina et al. describing transparent, layered nanoclay/polymer films, which showed high thermal resistance and good gas barrier properties in presence of only 10 or 20 wt% of water-soluble polymer binder. Due to the small lateral size of the nanoclay the binder mostly localized at the cationic rims of the nanoplatelets. Although displaying attractive functionality, the material only had very low tensile strength around 25 MPa at strain to failure of 1.8%, thus falling short of nacre-mimetics targeting highest mechanical properties. Shikanaka et al reported
related transparent lamellar PEO/Laponite films with 57 wt% nanoclay, yet also with low stiffness and strength of 11 MPa and 28.7 MPa, respectively, at low elongation.\textsuperscript{35-37} In case of larger montmorillonite, Zhu et al. investigated the effect of salts on the structure and properties of layered PVA/MTM materials and discussed mechanical properties at 55 wt% nanoclay, yielding Young’s modulus and tensile strength between 6-11.5 GPa and 20-45 MPa, respectively, at elongations of 4-22%.\textsuperscript{38} Consequently, although there has been progress, success towards very strong and stiff nacre-inspired materials based on such a simple approach using widely available materials is limited and crucial advances need to be made.

We recently developed a water-based approach that allowed self-assemblies into nacre-inspired materials based on highly purified polymer-coated core-shell nanoclays.\textsuperscript{39-40} These core-shell platelets were prepared via adsorption of a single polymer layer on top of montmorillonite (MTM) nanoclays, by slow addition of a dilute nanoclay dispersion to excess synthetic polymer (e.g. polyvinylalcohol) and subsequent separation of excess polymer via centrifugation/redispersion cycles to maximize the fraction of reinforcements in the final material. Excess polymer was crucial to prevent coagulation due to the strong interactions of both components. After film formation, this has enabled high modulus (27 GPa) and high strength (165 MPa) at a majority fraction of 70 wt% reinforcements combined with low density and we could demonstrate covalent and supramolecular crosslinking to increase the properties. A similar approach was presented by Yao et al. for chitosan/MTM self-assemblies.\textsuperscript{41}

Although thick films could be prepared, this dedicated self-assembly approach suffers from a crucial bottleneck that is the need for an intermediate extensive purification step via centrifugation/redispersion cycles to isolate pure core/shell building blocks. Therefore, we were asking the question whether this purification step can be overcome by directly using optimized dispersions of nanoclay and polymer, and subsequent direct self-assembly into nacre-inspired films. The principal feasibility of such a strategy is indicated by the ability of
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nanoclay/polymer mixtures to form lamellar phases and well-ordered films (see discussion above), given the interactions are properly mediated and coagulation is prevented.

In addition, most of the present nacre-mimetic materials are based on polymers from petrochemical origin. In the light of finding sustainable alternatives for future materials, we also turned our attention to renewable polymers – with cellulose being the major relevant polymer due to its large-scale and global availability.

Herein, we will show how homogeneous dispersions of anionic sodium carboxymethylcellulose (CMC) and anionic montmorilonite (MTM) can be used to fabricate highly oriented, layered, thick and large-area nanocomposites with remarkable mechanical properties. Stiffness (25 GPa) and strength (320 MPa) are among and partly above the best ever reported properties for nacre-inspired materials. We will derive the influence of the nanoscale thickness of the soft, energy-dissipating, organic layer on the macroscopic mechanical properties by varying the nanoscale periodicity of the alternating hard/soft layers via adjusting the feed composition. Furthermore, we demonstrate that nanostructural control can also be maintained when the materials are adequately mixed in highly concentrated suspensions to allow for slurries that are directly suitable for doctor-blading into large area films. In addition to excellent mechanical performance and direct materials preparation from concentrated dispersions, we show functional benefits, such as transparency, the possibility to print on these materials and fire-blocking.

4.2. Experimental

Materials

Sodium carboxymethyl cellulose (CMC, degree of substitution = carboxymethyl groups per anhydroglucose unit = 0.9; M_w = 700 kg/mol, Aldrich), Na-Cloisite (MTM, Rockwood) and MilliQ water were used for all experiments.
Preparation of nacre-inspired films

Films cast at high dilution. MTM was dispersed as a 0.5 wt% dispersion over night and subsequently slowly added to a Philips HR2094/00 blender (750 W) containing a strongly agitated 0.25 wt% solution of CMC until the desired weight ratio was obtained. Thereafter the dispersions were homogenized for further 5 minutes, degassed to minimize voids in the final materials, poured into petri dishes to cast films and dried at ambient conditions. Accelerated drying can be performed at 50 °C providing fully dried films within a day, depending on the thickness.

Doctor-bladed films from high solid dispersions. MTM was slowly added as powder to a IKA HKD-T-0.6 high-performance kneader with two wide-bladed kneading elements, containing a 2.5 wt% CMC solution until the desired CMC/MTM ratios were obtained. After homogenization for 12 h and degassing within the kneader, the soft gels were doctor-bladed onto PET foils and dried at ambient conditions within one day. Accelerated drying can be performed at 50 °C providing fully dried films within a few hours, depending on the thickness.

Inkjet Printing

Inkjet Printing was performed using standard printer settings and commercial Canon inks on a Canon Pixma iP4950 inkjet printer.

Methods

Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission microscope (1.5 kV) after sputter-coating a thin gold layer.

Thermogravimetric analysis (TGA) was done using a NETZSCH TG 209C instrument under continuous flow of 25 mL/min of N₂ at a heating rate of 20 K/min.
Scanning force microscopy (SFM) was performed on a Veeco Multimode in tapping mode conditions using standard silicon cantilevers (PPP-SEIH-W from Nanosensors).

Transmission Electron Microscopy (TEM) was performed on a JEOL JEM-3200FSC Cryo-TEM, operating at liquid nitrogen temperature. Zero-loss filtered images were obtained at an acceleration voltage of 300kV. All images were registered digitally by a bottom mounted CCD camera system (Ultrascan 4000, Gatan) combined and processed with a digital imaging processing system (Gatan Digital Micrograph 3.9 for GMS 1.4). Microtomed ultrathin sections were obtained using a LEICA 125 Ultracut microtome. The samples were embedded into epoxy resin prior cutting.

Wide-angle X-ray scattering was performed at the small- and wide-angle x-ray scattering beamline MiNaXS beamline P03 at HASYLAB Hamburg, Germany. Scattering data was recorded using a 13keV (0.954 Å) x-ray beam with a beam size of 22.0 x 17.1 μm² and a Pilatus 300k detector at a sample to detector distance of 421 mm.

Mechanical tests were carried out on a DEBEN minitester equipped with a 20N load cell. All measurements were conducted at room temperature and an average humidity of 23%. The specimen sizes used were typically in the range of 2 cm x 2.25 mm x 30 – 50 μm. At least 5 (mostly 8) specimens were tested for each sample. A nominal strain rate of 0.1 mm/min was used. The slope of the linear region of the stress-strain curves was used to determine the Young’s modulus, E.

4.3. Results and Discussions

The herein used concept towards facile and large-scale nacre-inspired films based on natural building blocks is summarized in Scheme 1. First CMC/MTM hydrocolloid dispersions are prepared by high-shear mixing at different weight ratios with a focus on high ratios of nanoclay up to 90 wt%, followed by film casting. During film casting self-assembly into
lamellar dispersion phases takes place which upon drying leads to highly ordered bulk films. The stacking distance of the nanoclays in the final material, \( d \), is controlled, as will be shown below, by the feed ratio of the components as additional free polymer will contribute to an expansion of the organic phase.

Scheme 1. General strategy to self-assembled nacre-inspired films based on renewable sodium carboxymethyl cellulose (CMC, \( R=H \) or \( CH_2-COO\text{Na} \)) and naturally sourced montmorillonite (MTM). Core-shell platelets are formed at an intermediate state due to polymer adsorption on the nanoclay surface. The nanoscale periodicity, \( d \), of the nacre-mimetics can be tuned by adding additional free polymer in the feed.

One of the most important prerequisites to allow for the formation of ordered bioinspired polymer/nanoclay hybrid films from water is to prevent premature aggregation and coagulation of the components in the aqueous phase, which is especially problematic at low polymer content favouring bridging of nanoclays. Therefore, we chose anionic CMC to prevent flocculation in the presence of anionic MTM, as opposed to e.g. using strongly electrostatically interacting cationic polysaccharides such as chitosan. Some interaction was yet expected as MTMs have a cationically charged rim able to bind anionic CMC and because there is an entropic driving force to adsorb hydrophilic, only slightly charged polymers onto the basal planes of nanoclays.\(^\text{42}\) During water removal, additionally present hydrogen bonds between MTM and CMC can strengthen further and form a strong interfacial attachment needed for stress transfer.\(^\text{43-44}\)

Aside designing the system chemically, attention needs to be drawn to optimize physical mixing and addition protocols. We used a very high molecular weight CMC (700 kg/mol) to target best mechanical properties, yet this adds a challenge as it leads to very viscous solutions already at high dilution (ca. 4000 mPa·s at 1 wt%). Therefore, to prepare most
homogeneous dispersions, we slowly added a previously well homogenized 0.5 wt% dispersion of MTM (Na\textsuperscript{+}Cloisite) to a 0.25 wt% dispersion of Na\textsuperscript{+}CMC (700 kg/mol, 0.9 carboxymethyl groups per anhydroglucose unit) in a high shear mechanical blender until the desired ratio of organic to inorganic material was obtained. This method provides substantially higher shear than in standard lab equipment (magnetic stirrer). Note that MTM is already majorly exfoliated into single ca. 1 nm thick nanoplatelets in the utilized 0.5 wt% dispersion in water. The ratios were selected in a wide range of MTM/CMC (9/1, 8/2, 6/4, 4/6, 2/8, 1/9 w/w) to monitor the full behaviour of the system. Importantly, the addition of nanoclay to polymer minimizes potential bridging of several nanoclay particles by single polymer molecules, which can be observed as flocculation when small amounts of binding polymers are added to a nanoclay dispersion. In combination with the high shear mixing, all CMC/MTM dispersions were homogeneous to the naked eye, indicating efficient dispersion of both components.

To experimentally access the solution state, we conducted atomic force microscopy (AFM) investigations of dispersions containing CMC and MTM. Figure 1 displays an AFM image obtained after one centrifugation and redispersion cycle to remove excess polymer, which
would hinder clear imaging. It shows two flat and large nanoclay sheets with several hundred nanometers in diameter that are partly coated by a thin layer of CMC. The CMC coating is evident due to the increased height (see section analysis) and the rough surface on top of the nanoclay. Pristine nanoclay shows an extremely flat surface and an average height close to 1 nm. Note that the substrate surface is clean of polymer and thus the coating does not arise during drying of a solution. The driving force for binding on the basal surface is three fold. Elemental analysis of the MTM revealed the presence of Ca\(^ {2+} \) counterions within the Na\(^ + \)MTM (0.45 wt% of total MTM content). Due to their mutlivalency, they remain more tightly condensed to the highly charged MTM surfaces as compared to monovalent Na\(^ + \) counterions. Thus, the carboxylate groups of CMC can bind to them in addition to hydrogen bonding between alcohol and acid groups of the CMC and Si-O-Si units on the nanoclay surface, and the known entropic adsorption of polymers on the basal nanoclay planes. AFM thus confirms that well defined core-shell platelets are intermediately formed during the mixing, allowing for an efficient stress transfer in bulk. Their encoded order is transferred into layered hybrid films. Importantly, the stacking distances can be controlled by additional polymer in solution, as will be shown in wide-angle x-ray scattering below (Figure 3, Table 1).

The layered bulk nanocomposites were prepared by simple film casting of the various CMC/MTM dispersions. During the evaporation of the water, the concentration of the core-shell nanoclay platelets increases and they start to organize in a layered/lamellar structure due to hydrodynamic interactions. This process allows large-area and also thick films, typically prepared with thicknesses in the range of 30 – 200 \( \mu \)m. Accelerated drying at 50 °C can provide films within one day. Faster time scales may be achieved by increasing the temperature or concentration (see below), but are not in the main scope of this contribution. Figure 2 displays scanning and transmission electron microscopy (SEM and TEM) images of the resulting nanocomposites at different weight fractions (see also Figure S1, Supplementary
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Information). The SEM images clearly show the desired layered arrangement over large areas, independent of the ratio of CMC/MTM used. Due to the large size of the nanoclays tight interlocking can be formed by nanoclays branching from one layer into other ones (Scheme 1). We further recorded TEM images of a microtomed, ultrathin cross section of a selected nanocomposite to support the alternating hard/soft layers. Figure 2d depicts the TEM image of CMC/MTM = 20/80, in which well-spaced alternating dark (nanoclay) and grey (polymer) layers can be identified, as also further highlighted by a greyscale section analysis. The spacing is roughly 1.65 nm, which is larger compared to pristine MTM and indicates a thin polymer layer in-between. Due to distortions during microtoming of these stiff materials, the distances need to be treated with some care.

Figure 2. Electron microscopy characterization. (a-b) SEM images of layered nanocomposites at CMC/MTM = 20/80 and (c) CMC/MTM = 40/60. (d) TEM image of an ultrathin cross section of CMC/MTM = 20/80 with a cross section analysis highlighting the alternating hard and soft layers. Further SEM images of other compositions can be found in Figure S1 in the Supplementary Information.

Hence, to achieve a more quantitative understanding of the periodicities, we further performed wide-angle x-ray scattering (WAXS) at different beam inclinations with respect to
the observed orientation of the nanoclay layers using a high intensity synchrotron x-ray source. All WAXS curves were measured with the same time and intensity to allow for comparison.

Figure 3. Wide-angle x-ray scattering of the nanocomposites. (a) WAXS curves obtained for various nanocomposites and measured with the same intensity and time. The inset depicts the spacing calculated from the primary scattering peak (q*) according to \(2\pi/q^*\) as a function of the content of CMC. Both dehydrated (0.9 nm) and hydrated (1.2 nm) basal spacings of MTM are shown. The line serves to guide the eye. (b-c) Exemplary 2D scattering images obtained for CMC/MTM = 20/80 at different beam inclinations with respect to the plane of the film (b, 15° and c, 90°) as schematically shown in the bottom left corners.

The 2D detector images demonstrate the absence of scattering events for an x-ray beam irradiating perpendicular to the plane (Figure 3b) and in 40° (not shown). Diffraction peaks start to appear upon irradiation at shallow angles, here displayed for ca. 15° (Figure 3c). Most importantly, the diffraction peaks are strongly confined within two opposing arcs of small azimuthal width. Both effects confirm highly ordered systems. Integrations along the scattering vector in a window of ± 20° centered on the Bragg peak allow the quantification of the gallery spacing between the nanoclays (see Figure 3a). The scattering curves show a distinct shift of the primary scattering peak from the known distance of pure MTM in hydrated conditions (1.2 nm) to smaller q-values with increasing content of polymer (see Table 1). This confirms the successful intercalation of the MTM galleries during the
restacking in the drying procedure. The distance between the nanoclays consistently increases with rising polymer content (see inset Figure 3a), demonstrating the desired control of the nanostructure of the materials.

We emphasize that the system is near quantitatively exfoliated in solution and restacked in bulk, as a scattering peak for completely non-intercalated MTM can hardly be observed. Nonetheless, the only small increase of the gallery spacing at 10 wt% of CMC indicates that the polymer is not present as a continuous layer, but that MTM faces touch at certain points. From earlier investigations on the self-assembly of purified core-shell polymer-coated nanoclays, effectively covered with exactly one monolayer of polymer on each nanoclay, we know that the final materials contain roughly 20 – 30 wt% polymer and exhibit continuous polymer layers in-between the nanoclay stacks.\(^{39-40}\) In these systems, in fact a polymer double layer is formed in-between the stacks during the assembly of two polymer-coated nanoclays on top of each other. Consequently a continuous polymer layer can already be formed at slightly lower weight fractions, depending on the type of polymer used. Earlier investigations by Ebina et al. discussed adsorption of an anionic polymer in polyanion/nanoclay at the cationic rims of much smaller nanoclay, Na\(^+\)Saponite, with lateral dimension much smaller than 50 nm.\(^{17-18}\) In such systems using ultrasmall nanoclays edge effects are dominant, whereas this is not the case for the much larger MTM employed herein.

It can further be observed that the peak intensity diminishes for increasing polymer fractions, which originates from a wider distribution of stacking distances and loss of long-range correlation to allow for appearance of a Bragg peak. Large polymer contents above 60 wt% do not allow to identify any distinct stacking distance anymore, but the layered structure is unambiguously confirmed by SEM imaging (Figure 2 and Figure S1).

Consequently, both imaging and scattering data confirm that well-defined, highly ordered and near quantitatively exfoliated and restacked bionanocomposites can be obtained with this simple high-shear blending approach. Unwanted flocculation and ill-defined structure
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formation are absent due to the choice of polymer, addition sequence and high shear homogenization protocol. The nanoscale stacking periodicity is controlled by the amount of polymer within the nanoclay dispersion and allows tailoring the gallery spacing in the restacked nacre-inspired films with a high structural control. The mesostructures closely resemble the ones found in previous and more time-consuming nacre-mimetics based on LbL or self-assembly of purified core-shell nanoplatelets.\textsuperscript{7-9, 39-41} However, the precise tuning of the gallery spacing is a distinct advantage of this procedure and allows us to look in detail how mechanical properties change as a function of the hard/soft ratio from moderate to very high nanoclay content. The corresponding mechanical tensile testing data are summarized in Figure 4 and Table 1.

![Mechanical tensile tests of nanocomposites.](image)

**Figure 4. Mechanical tensile tests of nanocomposites.** (a) Mechanical tensile tests of CMC/MTM films of various compositions as indicated within the figure. The arrow serves to guide the eye from low to high fractions of MTM. (b) Stiffness (cyan, left column) and tensile strength (grey, right column) as a function of the composition.

Pure high molecular weight CMC (700 kg/mol) already displays good tensile properties (Young’s modulus \(E = 5.8\) GPa, tensile strength \(\sigma_{\text{UTS}} = 151\) MPa, elongation at break \(\varepsilon_{\text{max}} = 12.1\%\)). These values are better in terms of stiffness, strength and also in elongation at break, as compared to CMCs of lower molecular weight, which are easier to use in bulk material applications due to simpler handling in solution. Nonetheless, using this very high molecular weight CMC, although being more difficult to apply due to high viscosities, contributes to the
overall good mechanical performance. Starting from pure CMC, it is obvious that continuous addition of nanoclay leads to a stiffening and strengthening of the material up to a weight ratio of ca. 20 - 40 wt% (Figure 4b), originating from an efficient stress transfer from the CMC matrix to the MTM reinforcements. Upon reaching 40 wt% of nanoclay and further addition, a decrease of the tensile strength and for even larger fractions also a decrease of stiffness can be observed. Lower tensile strength can be explained by the increasing brittleness of the materials, which leads to early fracture based on cracks propagating from surface defects. Additionally, the WAXS measurements showed that the average stacking distances between the nanoclays becomes so small for low fractions of polymer (10 wt% CMC), that it is physically impossible for the nanoclays to have a fully continuous soft polymer layer in-between them throughout the full nanoclay interfaces. Therefore, some parts of the MTM platelets should be in direct contact and do not have any possibility to dissipate stress and fracture energy in a soft polymer phase intercalated between them. Incomplete activation of the nanoclay surface by CMC explains the observed lower stiffness at clay fractions larger 80%.

### Table 1. Structural and mechanical properties of nacre-inspired CMC/MTM films

<table>
<thead>
<tr>
<th>CMC/MTM</th>
<th>Nanoclay content (wt%)(^a)</th>
<th>d-spacing (nm)(^b)</th>
<th>Young’s modulus, (E) (GPa)</th>
<th>Tensile strength, (\sigma_{UTS}) (MPa)</th>
<th>Elongation, (\varepsilon_{\text{max}}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90/10</td>
<td>n.d.</td>
<td>-</td>
<td>14.1 ± 1.2</td>
<td>259 ± 9</td>
<td>5.6 ± 0.4</td>
</tr>
<tr>
<td>80/20</td>
<td>19.1</td>
<td>-</td>
<td>21.5 ± 2.5</td>
<td>319 ± 12</td>
<td>2.6 ± 0.2</td>
</tr>
<tr>
<td>60/40</td>
<td>40.5</td>
<td>2.71</td>
<td>24.6 ± 1.9</td>
<td>251 ± 20</td>
<td>1.5 ± 0.2</td>
</tr>
<tr>
<td>40/60</td>
<td>63.4</td>
<td>1.90</td>
<td>20.1 ± 3.9</td>
<td>217 ± 17</td>
<td>1.3 ± 0.6</td>
</tr>
<tr>
<td>20/80</td>
<td>83.4</td>
<td>1.43</td>
<td>16.6 ± 3.6</td>
<td>142 ± 10</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>10/90</td>
<td>90.8</td>
<td>1.34</td>
<td>6.8 ± 2.0</td>
<td>74 ± 5</td>
<td>1.5 ± 0.3</td>
</tr>
</tbody>
</table>

\(^a\) determined by TGA in the plateau area from 550 – 600 °C. n.d. = not determined. \(^b\) determined by WAXS. The basal spacing of pure MTM was determined to be 1.2 nm corresponding to the hydrated structure.

Overall we find an interesting optimum performance at 20 - 40 wt% of MTM considering the need to balance highest mechanical properties (Figure 4b) and functional properties for
instance in fire and gas barrier materials that benefit from large fractions of exfoliated nanoclay. Larger amounts of nanoclay may still be interesting for barrier applications, but in terms of mechanical properties fractions of MTM $\geq 60 \%$ correspond to an overloading in this material combination. All values are summarized in Table 1. Already at this point, it is important to emphasize that we achieve remarkable mechanical properties, combining high tensile strength, $\sigma_{UTS}$, close to 320 MPa with high stiffness (Young’s modulus, $E$) up to 21.5 GPa for CMC/MTM = 80/20. Importantly, we also still find 2.5% maximum strain, which is significantly above typical nacre-mimetics that break at strain close to or below 1%.\(^7\)-\(^9\), \(^39\)-\(^41\) The additional strain provides means for efficient fracture energy dissipation due to frictional platelet sliding. Next, we compare the mechanical properties to earlier nacre-inspired materials based on polymer/nanoclay nanocomposites. Since the lightweight character is one of the profound motivations to pursue biomimetic material concepts, we also report the specific material properties in a materials selector chart as introduced by Ashby and Wegst (Figure 5).\(^49\) In the field of polymer/nanoclay-based nacre-inspired materials Kotov et al. reported a range of systems prepared by LbL, also including post and sequential crosslinking procedures.\(^7\)-\(^9\) Notably the best system was produced by stepwise LbL deposition of PVA and MTM and intermediate crosslinking using glutaraldehyde, leading to stiff and strong nanocomposites at ca. 70 wt% of inorganic (light blue region).\(^7\) In general, the properties for very thin LbL films with ca. 70 wt% of nanoclay span a wide range. Non-crosslinked materials are typically in a range of Young’s modulus = 6 - 15 GPa and ultimate tensile strength of 75 - 150 MPa (cyan region 3).\(^8\)-\(^9\) Ionic crosslinking can be used to increase these properties to roughly double or triple these values (light blue region 1).\(^8\) The dark blue region (2) displays the area corresponding to the materials prepared by dedicated self-assembly of purified core-shell nanoclays. The best material is found at the top right and was prepared by post-crosslinking of PVA/MTM films with borates. We also include the best values so far reported for bionanocomposites with layered architectures, i.e. nanoclay/chitosan prepared via
either LbL\(^9\) or using the dedicated self-assembly of core/shell colloids\(^{41}\) (Young’s modulus = 6 - 10 GPa and ultimate tensile strength 75 - 100 MPa).

With respect to previous co-cast films, we also again refer to earlier work by Ebina, who used a small Na\(^+\)Saponite nanoclay (diameter < 50 nm) bound with small amounts of anionic polyelectrolytes including CMC. Despite demonstrating excellent gas barrier properties, the materials show brittle behavior and less than one tenth of the tensile strength achieved here (Na\(^+\)Saponite/poly(sodium acrylic acid) = 90/10 w/w: \(\sigma_{UTS} = 25\) MPa, \(\epsilon_{max} = 1.8\%\), Young’s modulus not reported).\(^{18, 50}\) This is clearly due to using excess reinforcements, as also confirmed in our studies when approaching such extreme nanoclay contents (Figure 3).

Further relevant previous co-cast polymer/nanoclay materials to compare to are: (i) PEO/Laponite (57 wt% Laponite, Laponite diameter < 30 nm; E = 11 MPa and \(\sigma_{UTS} = 28.7\) MPa) and (ii) PVA/MTM (55 wt% MTM; E = 6-11.5 GPa and \(\sigma_{UTS} = 20-45\) MPa). From this comparison, it becomes evident that our purposefully designed system exceeds previous co-cast self-assembling polymer/clay films considerably, partly by one order of magnitude.

Moreover, also with respect to nacre-mimetic materials\(^{7, 9, 39-41}\) in general, we report excellent and highly competitive properties (Young’s modulus up to 21.5 GPa and a tensile strength close to 320 MPa). This excellent performance can also be seen by adding them to the Ashby plot in Figure 5 (red region 4), notwithstanding the fact that Na\(^+\)CMC itself has a high density of 1.6 g/cm\(^3\). Although they cannot yet reach the specific stiffness of the ultrastiff and strong, crosslinked, sequentially prepared (PVA/MTM) LbL materials\(^7\), they exceed them already in terms of specific strength and occupy a previously unachieved property area. In fact, to the best of our knowledge the tensile strength is the highest ever reported one for non-crosslinked nacre-inspired materials and exceeds natural nacre considerably (tensile strength = 60 – 140 MPa).\(^{1, 2}\) It is also important to note that the best CMC/MTM-materials surpass the values for other biobased nacre-mimetics using chitosan up to three times in terms of stiffness.
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and strength, at comparable elongation at break.\textsuperscript{9, 41} Hence the present materials are also significantly tougher, considering the integral area under the stress/strain curves as an estimate for the work-of-fracture. We foresee that crosslinking procedures are able to further augment the present properties as it was seen for LbL based materials and the dedicated self-assembly approach using purified core/shell platelets. Overall, the present performance area places these nacre-inspired bionanocomposites in competition with glass fiber reinforced plastics and selected metals. They exceed classical polymer/nanoclay nanocomposites\textsuperscript{27} by one order of magnitude.

\textbf{Figure 5. Specific materials selector chart\textsuperscript{49} concerning lightweight engineering materials, highlighting different materials classes.} Best materials are top-right in this plot. Nacre-inspired polymer/nanoclay materials are shown according to their preparation pathways: 1/cyan: non-crosslinked LbL materials\textsuperscript{8-9}; 2/dark blue: dedicated self-assembly approach using purified core-shell nanoclays\textsuperscript{39-41}; 3/light blue: crosslinked LbL materials\textsuperscript{7-8}; 4/red: materials of the present study with the yellow mark denoting CMC/MTM=80/20. The mechanical performance of classical polymer/nanoclay composites is estimated based on a recent review.\textsuperscript{27} Densities of the material were estimated based on the known values for the components and the reported fractions of inorganic materials.

From a fundamental viewpoint, it is important to realize that the nanoclay loadings in any of the previous sophisticated approaches to nacre-mimetics using LbL or self-assembly of purified core/shell platelets (MTM \(\geq 70\) wt\%)\textsuperscript{7-9, 39-41} might in fact be too high to obtain sufficient dissipation of fracture energy in the soft phase to allow for high tensile strength and
optimum mechanical performance. This can be seen at the mechanical performance found at high nanoclay loadings for CMC/MTM = 20/80 - 40/60. Both samples correspond closely in terms of nanostructure and composition to earlier nacre-mimetics based on LbL or self-assembly of purified core-shell nanoplatelets, and also display similar mechanical properties. Yet, a slight increase of the polymer content in our materials promotes desirable inelastic deformations and frictional sliding of platelets and allows to double and triple the strength values and increase the toughness.

Hence, even if the closest polymer/nanoclay nacre-mimetic would require to have 95 vol% of inorganic material to match the content of the natural role model, the most relevant synthetic bioinspired layered polymer/nanoclay materials might be achieved with less nanoclay, at least at present design levels of the soft phase using commonplace polymers without tailored molecular energy dissipation mechanisms. This is an important factor to consider in the design for future bioinspired materials.

Figure 6. Thermal degradation profiles of the nanocomposites. (a) Thermogravimetric analysis of various nanocomposites and the two starting materials. (b) UV–VIS transmittance of various nanocomposite films at a thickness of 40-50 µm. The inset depicts a flexible and transparent foil of the composition CMC/MTM=60/40.

The relevance of these materials as functional coating or barrier foils is emphasized in the high optical transparency as compared for different nanoclay contents in Figure 6b. Lower translucencies for higher nanoclay contents relate to the natural origin of MTM, which contains some contaminants (iron ions) leading to a slightly yellowish color of the nanoclay
that translates into the layered nanocomposite. These problems can only be overcome by using synthetic nanoclays, for which there exists however still commercial limitations in the availability of high-aspect ratio materials required for good mechanical properties. Furthermore, the thermogravimetric analysis reveals an onset of decomposition for the various layered nanocomposites at just below 250 °C. This good thermal stability allows for a substantial application range in engineering materials and functional coatings (Figure 6a). Based on these promising results, we turned to the question whether it would be possible to prepare concentrated slurries of high nanoclay content that are directly suitable for doctor-blading, which is the technologically most relevant coating procedure for thick and infinitely large films. To provide homogenous dispersions, we used a high-performance kneader with two wide-bladed kneading elements, allowing efficient mixing of tough, non-flowing, highly viscous media. We added solid MTM directly into an agitated 2.5 wt% CMC solution to yield a ca. 3.6 wt% dispersions of MTM/CMC = 40/60 and homogenized it under significant shear of the kneader. Note that we chose one of the optimum compositions, identified in the tensile tests, yet with high content of nanoclay as relevant for functional barrier coatings. We emphasize that such a mixture is impossible to homogenize with a standard magnetic stirrer. Although it seems feasible to prepare higher concentrated gels with kneading, they are not suitable anymore for doctor-blading due to too high gel strength if the concentration is above 4 - 4.5 wt%. Subsequent doctor blading of the resulting softer, homogenous gel allowed thick and translucent self-standing foils, typically prepared in thicknesses from 30 – 150 μm. Drying at elevated temperature obviously proceeds quicker than when cast from dilute dispersion at comparable film thickness (ca. 50 °C). Further optimization to accelerate the drying in the future is feasible by using CMC of lower molecular weight, which would allow to prepare slurries of higher concentration, yet still at suitable viscosities for doctor-blading. Figure 7a displays a translucent film of roughly a DIN A4 page in size at 50 μm thickness. The microscopic observation of the film shows a preserved highly ordered mesoscale
structure of the nanoclay/polymer nanocomposite, despite using such a fast macroscopic processing technique (Figure 7 b,c).

**Figure 7.** Large-area films prepared by doctor-blading of a CMC/MTM = 60/40 dispersion of high solid content (~3.6 wt%). (a) Nacre-inspired foil being roughly of a DIN A4 page in size and a thickness of 50 μm. (b-c) Overview and higher resolution SEM images, depicting constant film thickness and the layered arrangement of the nanoclays. (d) Comparison of the mechanical tensile properties of the doctor-bladed film and a film cast from dilute dispersions. (e) Institute logo printed on a nacre-inspired bionanocomposite using a commercial deskjet printer. (f) Time-laps series of photographs depicting the fire-blocking properties of the bioinspired films (thickness 120 μm) upon exposure to a butane gas torch (temperature ca. 1300 °C). Note that the material is still translucent and fully self-standing. Flames cannot be observed.

Additional mechanical tensile tests reveal equally good mechanical properties for doctor-bladed films prepared from high concentrations and films cast from dilute dispersions (Figure
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7d), thereby validating this direct approach to be applied for continuous roll-to-roll processing.

In terms of functional benefits of these large-scale nacre-inspired films, we also conducted preliminary experiments on fire-blocking properties and the ability to print on these materials. The time-laps series of photographs in Figure 7f demonstrates intriguing fire-shielding properties during exposure to the flame of a gas torch. Already at a nanoclay content of only 40% the material hardly burns and is instantly self-extinguishing. Furthermore, it is shape persistent and chars into a solid barrier material resisting longer term exposure to flames. During exposure to flames, the material expands due to gas evolution while burning the intercalated polymer, and a porous foam-like structure develops that provides a heat barrier. Further condensation of silanol groups at the nanoclay surface contributes to self-cooling and also mechanical integrity due to covalent bond formation between adjacent nanoclays.

Importantly, the material does not contain halogen atoms or heavy metals, often needed in present-day fire-barrier materials, and can be processed from water using sustainable building blocks. Taking into account that the preparation can be easily scaled to large quantities and coatings and films of high optical quality can be made, we expect that this effort contributes to finding viable, environmentally friendly alternatives for future fire-barrier materials.

Already earlier, we and other demonstrated in a range of studies that such highly loaded and ordered bioinspired nanoclay/polymer nanocomposites are excellent gas barrier materials.17, 39, 51-52 We will comprehensively address the barrier properties also with respect to oil and water vapor in future. Herein, we show that large-area self-standing films can be used directly for simple ink-jet printing. This is relevant in the context of finding flexible, transparent and oxygen-impermeable substrates for the cost-effective fabrication of printable, oxygen-sensitive organic electronic devices. The photograph displayed in Figure 7e was obtained using a commercial inkjet printer and inks and demonstrates that already standard inkjet printing settings can be applicable to pattern and structure these nacre-inspired
bionanocomposites. Refined and also functional inks and optimized printing procedures can lead to useful devices with enhanced protection against oxygen.

4.4. Conclusions

We demonstrated a facile, large-scale pathway to high-performance nacre-inspired films with tunable nanoscale periodicity using naturally available building blocks and simple, scalable procedures in water. In terms of applicability it contrasts earlier, more sophisticated and time-consuming preparation strategies for nacre-mimetic materials due to the combination of simplest and fast preparation with excellent mechanical and functional properties.

The additional advantage to tune the hard/soft ratio and the spacing of the nanoscale periodicity between the nanoclays allowed to deduce that very high fractions of nanoclay (≥ 70 wt%), as previously considered optimized in nacre-inspired nanoclay/polymer materials, might in fact not be the ideal composition. Slightly higher polymer contents promote beneficial ductility, inelastic deformation and fracture energy dissipation to allow reaching higher strain-to-failure, toughness and tensile strength. Overall this dedicated tuning of the thickness of the soft phase enabled mechanical properties that are among the best ever reported ones for layered polymer/nanoclay nanocomposites and nacre-inspired materials. We foresee that ionic and covalent crosslinking will allow to further augment the mechanical properties.

Concerning a successful water-borne preparation of nacre-inspired films by co-casting at high nanoclay loading from viscous media, the consideration of chemical interactions, correct mixing protocols and high-shear homogenization are the important parameters to prepare suitable, high quality hydrocolloid dispersions for subsequent ordered structure formations. High shear even allows highly homogeneous and concentrated dispersions, suitable to directly prepare films and large-area coatings with essentially the same properties as films cast from dilute dispersions. An extension to higher solid content is feasible by changing to polymers of
lower molecular weight, which will be beneficial for transfer to roll-to-roll applications. The developed procedures can be adapted to other systems to access well-ordered films, e.g. synthetic nanoclays for fully transparent materials, or also for (reduced) graphene oxides and other functional nanoplatelets (e.g. BN, MoS$_2$) which are difficult to prepare as high-quality, concentrated aqueous dispersions.

The excellent mechanical properties and simple preparation are combined with functional benefits – translucency, fire blocking and ability to pattern the surfaces via inkjet printing – and will help to develop bioinspired materials combining mechanical and functional properties as needed for future applications.

Overall we expect this approach, using naturally occurring components, to promote sustainable alternatives for present-day high-performance materials combining mechanical and functional properties and push nacre-inspired materials closer to real-life applications.

4.5. Acknowledgments

The authors thank Lars Berglund (KTH Stockholm) for helpful discussions and Felix Schacher (FSU Jena, Germany) for initial XRD measurements. The authors acknowledge financial support from the IGF 17502N grant agreement, the “ERANET WoodWisdom Program”, the “Fonds der Chemischen Industrie” and HASYLAB. This work made use of the Aalto University Nanomicroscopy Center (Aalto-NMC) premises. We also thank Franz-Josef Steffens for experimental help. Andreas Walther gratefully acknowledges continuous support by Martin Möller.

4.6. References and Notes


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4.7. Supplementary Information

Figure S1: SEM images displaying highly ordered layered composites for CMC/MTM = 60/40 (right) and CMC/MTM = 80/20 (left).
5.1. Introduction

The nacreous layer in mollusc shells sets a paradigm for lightweight engineering by providing a stiff, strong and at the same time tough protective layer – a combination of material properties rarely found in synthetic material classes.\textsuperscript{1, 2} Nacre is composed of a brick-and-mortar architecture, in which micron-sized aragonite platelets (95 vol\%) are laminated by a biopolymer matrix. The complex interplay of sophisticatedly structured organic matrix and proper dimensions of the micron-sized tablets allows synergetic mechanical properties and in particular a high work-of-fracture, being 3000 times higher than the constituent aragonite monolith. In nacre, higher toughness is only found at high relative humidity (RH), where yielding of the biopolymer matrix and inelastic deformations are enabled due to increased dynamics based on hydration-induced weakening of secondary bonds.\textsuperscript{3-9}

The inspiration taken from nacre continues to change our view on polymer/clay nanocomposites. After their inauguration by Toyota more than two decades ago, a tremendous amount of effort has been focused on enhancing mechanical properties of predominantly petro-chemically based polymers by using the classical nanocomposite approach of dispersing small amounts of reinforcing nanoclay into a matrix polymer. Such materials are optimized for established polymer processing methods and the main challenges are to achieve an efficient dispersion, tight interfacial adhesion, and percolation. Despite undoubted success, it has remained extraordinarily difficult to obtain synergetic improvements of stiffness, strength
Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics. This has motivated for biomimetic nanocomposites, in which the relevant structural aspects of selected biological materials are mimicked using technically more feasible constituent materials and processes, aiming at the superior property profiles of their biological models, and potentially incorporating new functions relevant for the engineering world.

The biomimetic nanocomposite approach differs profoundly from the classical one: the latter relies on pure mixing of the components with a proper compatibilization. By contrast, in biomimetic nanocomposites, ordered structures are pursued by typically using high fractions of reinforcements e.g. nanoclay\textsuperscript{13-20}, flattened double-walled carbon nanotubes\textsuperscript{21}, 2D graphene oxide\textsuperscript{22} or graphene nanoplatelets\textsuperscript{23} etc. in presence of a soft matrix, able to balance sufficient binding and dynamic fracture energy dissipation by control of (supra)molecular interactions. For clay based nacre-mimetic nanocomposites, Tang et al. reported a first approach using Layer-by-Layer (LbL) deposition of polymers and nanoclays to obtain highly reinforced layered nanocomposites (ca. 70 wt\% clay).\textsuperscript{13} This sequential strategy was further extended to a range of polymers and notably the best stiffness and strength values were obtained for Polyvinylalcohol/montmorillonite (PVA/MTM) materials, sequentially covalently crosslinked with glutaraldehyde. However, the process is tedious and time-consuming (LbL growth rate ca. 1-2 µm/day) and faces obstacles to reach beyond laboratory scale.\textsuperscript{15-17, 20, 24, 25}

We recently introduced a colloidal route for self-assembled nacre-mimetic materials using concentration-induced self-ordering of polymer-coated montmorillonite (MTM) platelets with intrinsic hard/soft core-shell character.\textsuperscript{18, 19} This procedure represents a major advance over the classical LbL technique as core-shell colloids are accessible on a large scale and layered materials with high fractions of reinforcements (ca. 70 wt\%) can be prepared fast by simple vacuum filtration, similar to paper-making, or by doctor-blading, and even via spray coating. Covalent crosslinking can increase the stiffness and strength and the procedure was later extended to chitosan/MTM by Yao et al.\textsuperscript{26} As a functional benefit relevant for technological
Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics. Despite such progress, these water-borne polymer/clay nacre-mimetics are typically limited by two aspects. Firstly, the materials display a linear elastic fracture behaviour (high stiffness and strength), but do not undergo yielding and inelastic deformation needed to achieve high toughness. In this context it is important to realize that nacre itself is only very tough in wet conditions, in which balanced dynamics in the soft phase allow for yielding, inelastic deformation and strain up to roughly 1%. Secondly, due to the selection of waterborne components, which is very attractive to achieve full exfoliation and activation of nanoclay and moreover for environmental reasons, the high stiffness and strength typically decay much at high humidity. We address the origin of such hydration-induced changes for PVA/MTM nacre-mimetics in a dedicated publication, in which we find that humidity leads to a decrease of the glass transition temperature of the nanoconfined polymer layer and a macroscopic softening of the material.

We recently presented an approach to overcome the first problem and to promote ductility and tensile strength while preserving the stiffness. We found that enlarging the stacking distance between the nanoclays in carboxymethylcellulose/montmorillonite (CMC/MTM) nacre-mimetics by adding slightly more polymer allows some inelastic deformation and higher toughness even at very low humidity. The stiffness was preserved at a similarly high level as compared to self-assembly of pure core-shell platelets, yet the ability for better dissipation of the fracture energy allowed much higher ultimate tensile strength (above 300 MPa). Changes of the mechanical properties as a function of the nanoclay content was afterwards also discussed by Cheng and co-workers for PVA/MTM system. Although this approach leads to lower contents of nanoclay unlike in perfect biomimetic approach (nacre: 95 vol% inorganic platelets), the better mechanical properties justify the approach. Liu and Berglund found in a related CMC/MTM system that the addition of some anionically charged
crystalline cellulose nanofibrils can further enhance the mechanical properties.\textsuperscript{29}

Stabilization against humidity requires either tight, covalent crosslinking or a more dynamic, supramolecular crosslinking. While covalent crosslinking of the matrix can only lead to a stiffening of the nanocomposite, mastering dynamic interactions can in principle allow for a synergetic improvement of stiffness, strength and toughness by controlling the dynamic exchanges of bonding sites. In fact, earlier simulations demonstrated that randomly distributed supramolecular binding sites between layers can induce synergetic properties by dynamic rebinding of transient interactions in a stick/slip fashion.\textsuperscript{30} Importantly, yielding and inelastic deformation can take place and frictional sliding of platelets can occur on high stress levels. A validation of this concept requires tailored polymer dynamics and supramolecular interactions. In case of spider silks, Lee et al for instance demonstrated that infiltration of metal ions can lead to a simultaneous enhancement of stiffness, strength and toughness by replacing hydrogen-bonding sites in the protein matrix by metal/ligand interactions.\textsuperscript{31} This demonstrates that ionic interactions are feasible tools to target synergetic material properties.

Herein, we will for the first time show and quantify how ionic bonds, introduced by infiltration of divalent Cu\textsuperscript{2+} ions, allow stabilization of the mechanical properties of self-assembled water-borne nacre-mimetics based on CMC/MTM at high RH (95\%). Moreover, we will demonstrate a synergetic, simultaneous improvement of stiffness, strength and work-of-fracture at this high RH owing to the dynamic state of crosslinking.

5.2. Experimental

Materials

Sodium carboxymethylcellulose (CMC, $M_w = 700$ kg/mol, degree of substitution (DS) = 0.9, Aldrich), Na-Cloisite (MTM, Rockwood) and MilliQ water were used for all experiments.
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Preparation of nacre-inspired films

MTM was dispersed as a 0.5 wt% dispersion overnight and subsequently slowly added to a Philips HR2094/00 blender (750 W) containing a strongly agitated 0.25 wt% solution of CMC until the desired weight ratio was obtained. Thereafter the dispersions were homogenized for further 5 minutes, degassed to minimize voids in the final materials, poured into petri dishes to cast films and dried at ambient conditions.

Counterion exchange from Na\(^+\) of Cu\(^{2+}\).

Films with thicknesses of ca. 30 µm and dimensions of 3 x 3 cm were placed onto some supporting sticks into a petri dish, so that the subsequently added liquid can also infuse from the bottom side. Afterwards ca. 50 mL of a 50 – 200 mM CuSO\(_4\) solution was added and the film was allowed to rest for 7 days. During this time, the film turned bluish. Afterwards the film was given into pure water for 24 h to remove excess CuSO\(_4\) and dried.

Methods

Scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission microscope (1.5 kV) after sputter-coating a thin gold layer.

Fourier Transform Infrared (FTIR) spectra were recorded using Thermo Nicolet Nexus 470 spectrometer with a smart split pea ATR single reflection Si crystal over a frequency range from 1800 to 1250 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\).

Mechanical tests were carried out on a DEBEN minitester equipped with a 20N load cell. All measurements were conducted at room temperature and the samples were conditioned at the respective relative humidities for at least 2 days. The specimen sizes used were typically in the range of 2 cm x 2 mm x 30 µm. At least 5 (mostly 8) specimens were tested for each sample. A nominal strain rate of 0.1 mm/min was used. The slope of the linear region of the stress-strain curves was used to determine the Young’s modulus, E.
Estimation of the exchange efficiency from \( \text{Na}^+ \) to \( \text{Cu}^{2+} \) during counterion exchange.

The estimation can be done by comparing the mol/g concentration of counterions found in the materials: Before counterion exchange the dominant ion is \( \text{Na}^+ \), with minor contents of \( \text{Ca}^{2+} \) originating from some contamination of the \( \text{Na}^+ \)MTM. After counterion exchange both \( \text{Na}^+ \) and \( \text{Ca}^{2+} \) ions are almost quantitatively replaced by \( \text{Cu}^{2+} \) and their concentration is close or below the detection limit of the instrument. The detailed values can be found in Table 1. From ICP-AES (Inductively coupled plasma atomic emission spectroscopy), the concentrations in mol/g can be calculated based on the atomic weight of the elements yield: \( c_{(\text{Na})} \), \( c_{(\text{Cu})} \), \( c_{(\text{Ca})} \) in [mol/g]. An almost complete quantitative exchange would occur for \( \frac{c_{(\text{Na})} + c_{(\text{Ca})}}{2c_{(\text{Cu})}} = 1 \), assuming only insignificant changes of the total mass of the material due to different atomic weights of the counterions.

5.3. Results and Discussion

The starting point for the investigations is layered, nacre-mimetic nanocomposites of CMC/MTM at weight ratios of 6/4 and 8/2. These are prepared by simple high shear mixing of exfoliated MTM nanoclay into high molecular weight CMC solutions (CMC = 700 kDa) and subsequent evaporation. CMC/MTM core-shell colloids form during this procedure in the hydrocolloid mixture and self-order into layered nacre-mimetic nanocomposites during water removal. Additional CMC expands the spacing between the nanoclay platelets and promotes inelastic deformation and best combination of mechanical properties as found in our preceding work. The experimental strategy is sketched in Scheme 1.

Those materials perform extremely well in comparison to other bioinspired polymer/clay nacre-mimetics nanocomposites and display remarkable stiffness and strength above 20 GPa and 300 MPa, respectively, in dry state. The higher polymer content in CMC/MTM = 80/20 promotes higher strain. The material properties are summarized in Table 2. It is important to
emphasize that the Na\textsuperscript{+}CMC used has a high DS (degree of substitution) of 0.9, meaning that 90% of the repeating units are charged and available for non-covalent linkages.

Scheme 1. Preparation of nacre-mimetic brick-and-mortar type of layered nanocomposites by concentration-induced self-ordering of polymer-coated nanoclay and subsequent infiltration of divalent ions. The polymer-coated nanoclays form due to adsorption of Na\textsuperscript{+}CMC onto Na\textsuperscript{+}MTM. Additional polymer widens the spacing between the nanoclay. Subsequent exposure to CuSO\textsubscript{4} solutions leads to replacement of monovalent Na\textsuperscript{+} ions by divalent Cu\textsuperscript{2+} ions and the introduction of supramolecular ionic bonds between the acid groups and the acid groups with the negatively charged MTM surface as sketched in the lower part.

The structural characterization of these layered nanocomposites is presented in Figure 1. A well-aligned layered structure is visible in all four cases and from earlier wide-angle x-ray scattering the stacking distance of the lamellar nanoclays was derived to 2.7 nm for CMC/MTM = 6/4.\textsuperscript{14} The interlayer correlation was not defined enough to be detected for CMC/MTM = 8/2, even when using a synchrotron radiation source. Nonetheless, scanning electron microscopy unambiguously confirms the nacre-inspired, layered brick-and-mortar architecture (Figure 1c).

Upon exposure to high RH the pristine materials soften, as will be quantified below. To prevent softening and decay of mechanical properties, we chose to control ionic interactions found at the carboxylic acid groups within the Na\textsuperscript{+}CMC and at the Na\textsuperscript{+}MTM via the counterions. Ionic interactions are a versatile tool as they allow changing interactions by the
valency and size of the ion and a large range of dynamic binding situations are accessible. As a major difference to covalent bonds, these can also be changed by photo-induced valency changes or via electrochemistry, thus opening considerable avenues to tailor macroscopic mechanical properties by mediating nanoscale interactions.\textsuperscript{32-35}

**Figure 1.** SEM images depicting the layered arrangement of CMC/MTM nanocomposites. (a-d) CMC/MTM nanocomposites with weight fractions of (a, b) 6/4 and (c, d) 8/2, and (a, c) before and (b, d) after infiltration with Cu\textsuperscript{2+} ions. The insets show photographs of specimens (ca. 3 x 3 cm) before and after counterion exchange. The blue color clearly indicates the uptake of Cu\textsuperscript{2+} ions.

Sodium counterions are found as major species in the as-prepared CMC/MTM material due to the utilization of Na\textsuperscript{+} CMC and Na\textsuperscript{+} MTM. To induce ionic supramolecular interactions, we infiltrated the CMC/MTM materials with Cu\textsuperscript{2+} ions by exposure to excess CuSO\textsubscript{4} solutions. The effect of strengthening can be seen directly in a macroscopic fashion. While exposure of pristine (Na\textsuperscript{+}) CMC/MTM nanocomposites to pure water leads to swelling and dispersion of the materials, the treatment with CuSO\textsubscript{4} solutions leaves the film intact and strengthens it, as observed by a macroscopic hardening. After swelling, excess Cu\textsuperscript{2+} ions are removed by placing the film in pure water, leaving behind a bluish film that confirms the
remaining of Cu$^{2+}$ ions (Figure 1b, inset).

In fact polyelectrolyte research tells us that monovalent ions can be exchanged to multivalent ions quite easily, because multivalent ones are more tightly condensed to the polyacid backbones.\cite{36-39} We used FT-IR spectroscopy to monitor changes in structure upon counterion exchange. Figure 2 displays the FT-IR spectra in the characteristic range of the carbonyl region. A comparison of Na$^+$CMC and Na$^+$CMC/MTM shows little difference in the nature and position of the bands, which is due to the fact that only one kind of coordination can take place between carboxylate ion and monovalent Na$^+$ as shown in Figure 2b.

![Figure 2. Fourier Transform Infrared analysis of the nanocomposites.](image)

(a) FT-IR spectra of Na$^+$CMC, Na$^+$CMC/MTM= 60/40 and Cu$^{2+}$ infiltrated CMC/MTM= 60/40. (b-e) Schematic representation of the coordination of carboxylate ligands to metal ions (b-c) chelating bidentate, (d) bridging bidentate, (e) coordination through vicinal diol of CMC. Charges are omitted in the structures for more clarity.

For Na$^+$CMC and Na$^+$CMC/MTM a broad band corresponding to asymmetrical stretching mode ($v_{\text{asym}}$) and a band corresponding to symmetrical stretching mode ($v_{\text{sym}}$) for COO$^-$ appear at 1591 cm$^{-1}$ and 1414 cm$^{-1}$, respectively. After complexation with Cu$^{2+}$ ions, the asymmetric stretching band broadens slightly while the peak maximum stays near constant (1590 cm$^{-1}$). The symmetrical stretching mode ($v_{\text{sym}}$) for COO$^-$ shifts to 1420 cm$^{-1}$ and a stronger shoulder is visible at 1455 cm$^{-1}$. Following earlier literature on polyacrylic acid(PAA)/Cu(II) complexes, the most probable coordination types with Cu$^{2+}$ ions are shown...
in Figure 2 (c-d) including (i) chelating bidentate, (ii) bridging bidentate. In principle a third type of complexation (e) with the vicinal diols of the sugars might appear for low degree of substitution and low charge density. Separate peaks can be identified in pure PAA/Cu(II) model complexes at $v_{\text{asym}}$ (COO$^-$) = 1558 cm$^{-1}$ for chelating bidentate and $v_{\text{asym}}$ (COO$^-$) = 1611 cm$^{-1}$ for bridging bidentate. Herein, the $v_{\text{asym}}$ (COO$^-$) band is so broad that it covers the full region of 1558-1611 cm$^{-1}$. This indicates that both coordination geometries (c and d) coexist in the material. Additionally, the CMC chains are also linked to the MTM surface via Cu(II) ions, which leads to additional asymmetrical stretching modes, resulting in an overall, single and broad peak. The additional peak in the symmetric stretching area (1455 cm$^{-1}$) implies additional type of complexation compared to Na$^+$CMC/MTM. Importantly, we see that very little conversion of Na$^+$CMC to its acid form takes place during ion exchange. Only a small shoulder is observed at ca. 1733 cm$^{-1}$, which is shifted compared to pure acidified CMC (1726 cm$^{-1}$) and thus suggests some interaction of the carbonyl group with the Cu$^{2+}$ species. Overall, these data confirm that indeed the ionic groups are the major structural supramolecular links in the CMC matrix.

Table 1. Counterion composition determined by ICP-AES

<table>
<thead>
<tr>
<th>Nacre-mimetic Composition</th>
<th>Counterion</th>
<th>mass fraction [%]</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Na$^+$</td>
<td>Cu$^{2+}$</td>
</tr>
<tr>
<td>CMC/MTM = 60/40</td>
<td>pristine Na$^+$</td>
<td>4.5 ± 0.2</td>
<td>≈ 0</td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$ treated</td>
<td>&lt; 0.1</td>
<td>7.0 ± 0.1</td>
</tr>
<tr>
<td>CMC/MTM = 80/20</td>
<td>pristine Na$^+$</td>
<td>4.8 ± 0.2</td>
<td>≈ 0</td>
</tr>
<tr>
<td></td>
<td>Cu$^{2+}$ treated</td>
<td>&lt; 0.1</td>
<td>8.1 ± 0.7</td>
</tr>
</tbody>
</table>

Elemental analysis via inductively coupled-atomic emission spectroscopy (ICP-AES) quantifies the exchange of the counterions (Table 1). The weight fractions of sodium diminish from 4.5 ± 0.2 wt% and 4.8 ± 0.2 wt% to below 0.1 wt% in CMC/MTM = 6/4 and 8/2, respectively. At the same time, copper is detected in concentrations of 7.0 ± 0.1 and 8.1 ± 0.7
 Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics

wt% for the respective materials. In addition, trace amounts of Ca\(^{2+}\) counterions present as contaminating counterions in the Na\(^{+}\)MTM (0.26 ± 0.02 and 0.22 ± 0.02 wt% for CMC/MTM = 6/4 and 8/2) are also exchanged. A calculation of the molar exchange efficiency of the mono- and divalent Na\(^{+}\) and Ca\(^{2+}\) ions with the divalent Cu\(^{2+}\) ions reveals that all counterions were successfully exchanged during this procedure (see Experimental Section) and that a slight excess of Cu\(^{2+}\) is present. We attribute deviations to the perfect ratio of 100% to the possible coordination of some Cu\(^{2+}\) ions to hydroxyl groups of the CMC and tight entrapment of those during exchange of the counterions (Table 1). A possible coordination is depicted in Figure 2e.

In contrast to earlier investigations, simply focusing on the potential effect of supramolecular stiffening at low RH\(^{13, 15, 17, 19, 24}\), we put the emphasis on understanding the effect across the full range of RH to deduce the hydration-induced changes in internal polymer cohesion and dynamics. Therefore, the tensile mechanical properties were measured after conditioning the samples before and after counterion exchange to 25, 55 and 95 %RH. Figure 3 depicts the influence of humidity on the stress/strain curves for both compositions before (left) and after (right) counterion exchange. All values including the standard deviations are also summarized in Table 2.

A first comparison of the pristine materials shows a decay of the stiffness and strength for both pristine Na\(^{+}\)-CMC/MTM nacre-mimetics with increasing percentage of RH (Figure 3a,c; left-hand side). Stiffness and strength fall to roughly 50% at 55 %RH and to 10% at 95 %RH, as compared to the dry state (25 %RH, see Table 1). This decay is expected and caused by the water molecules, which diminish the hydrogen bonding within the CMC matrix and the interactions between CMC and MTM. At intermediate 55 %RH a slightly higher elongation to break and larger inelastic deformation can be observed; especially for CMC/MTM= 80/20. At this point the hydrogen bonds are not completely diminished by water molecules and are still strong enough to provide sufficient cohesion and frictional sliding of the platelets and enable
some inelastic deformations within the polymer matrix at higher polymer content (CMC/MTM = 80/20). In essence, the material is plasticized by water.\textsuperscript{44, 45} Interestingly, when further increasing the RH to 95\%, higher tensile elongation is absent and cracks are initiated at roughly the same elongation as compared to the material at lowest humidity (ca. 1.5\% strain). This point defines maximum tensile strength and also elongation as listed in Table 2.

### Table 2. Overview of tensile mechanical properties

<table>
<thead>
<tr>
<th>Counter-ion</th>
<th>Relative humidity (%)</th>
<th>Young’s modulus, E (GPa)</th>
<th>Tensile strength, $\sigma_{UTS}$ (MPa)</th>
<th>Elongation, $e_{\text{max}}$ (%)</th>
<th>WOF [MJ/m$^3$]\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>CMC/MTM = 60/40</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pristine Na\textsuperscript{+}</td>
<td>25</td>
<td>24.2 ± 2.0</td>
<td>245 ± 20</td>
<td>1.5 ± 0.2</td>
<td>2.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>55</td>
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\textsuperscript{a}Values at/till crack initiation. \textsuperscript{b}Modulus of toughness, also termed work-of-fracture, as determined by integration of the stress/strain curve.

The material still exhibits a good stiffness of 1.5 GPa, but crack initiation is poorly inhibited and cracks propagate stably through the soft material. Exemplary stress/strain curves after crack initiation are continued as dotted line. In addition to less efficient hydrogen bonding, the loss of cohesion in the matrix can be related to the polyelectrolyte character of the CMC, because some ionization and repulsion can occur in presence of larger amounts of water. This is also clear from the fact that CMC freely dissolves in water.

The situation is drastically different upon exchange of the counterions with Cu\textsuperscript{2+} ions. These divalent counterions lead to a remarkable wet stabilization of the mechanical properties.
and limit the loss of mechanical properties as compared to the pristine CMC/MTM material (Figure 3b,d; right-hand side). Stiffness and tensile strength undergo only small reductions from low to intermediate RH. A further increase to 95 %RH demonstrates that the material with larger polymer content (CMC/MTM = 80/20) is more susceptible to changes, which is due to larger contents of polymer and breakage of more number of hydrogen bonding sites within excess polymer (compare blue and red curves in Figure 3b,d).

Figure 3. Overview of mechanical properties as a function of counterion and humidity. Top row: (a-d) Stress/strain curves for (a) pristine CMC/MTM = 60/40 and (b) Cu²⁺ infiltrated CMC/MTM = 60/40 obtained at different RH. Bottom row: Stress/strain curves for (c) pristine CMC/MTM = 80/20 and (d) Cu²⁺ infiltrated CMC/MTM = 80/20 obtained at different RH.

SEM images of the fracture cross-sections of pristine and Cu²⁺-infiltrated CMC/MTM = 60/40 composites after stretching at 95 %RH are shown in Figure S1 (Supplementary Information). No significant differences in the fracture surfaces can be identified, indicating yet similar fracture modes.

Next, let us inspect the changes originating from the counterion exchange in greater precision for the individual specimens at a given humidity (Figure 4). Comparing the
performance of pristine and Cu$^{2+}$-treated samples in the dry state (Figure 4a,d, 25 %RH), one can only observe minor differences upon changing the ionic interactions from Na$^{+}$ to Cu$^{2+}$. The similar behaviour is due to the fact that the large amount of hydrogen bonding within the matrix dominates and provides tight cohesion. A slight stiffening can be observed in CMC/MTM = 80/20 which points to some enhanced cohesion. Related to this, we also find lower elongation at break and tensile strength for the Cu$^{2+}$ treated materials, originating from the tight and non-dynamic ("frozen") binding state of the ionic crosslinks when dehydrated. It is important to emphasize again that a DS of 0.9 provides a very high density of crosslinks in the material. Here, the addition of "frozen" ionic crosslinks promotes the brittleness of the matrix. Earlier failure can also be understood by the fact that fracture in such strongly linear elastic materials is dominated by surface defects imparted during sample preparation, which leads to sites for crack initiation and failure, and consequently limited maximum elongation and tensile strength.

![Graphs showing mechanical properties at different relative humidities](image)

**Figure 4.** Detailed comparison of mechanical properties of pristine and Cu$^{2+}$ infiltrated samples at the respective relative humidities. Mechanical properties (a-c) for CMC/MTM = 60/40, and (d-f) for CMC/MTM = 80/20. The relative humidities are indicated on top.

However, upon exposure to higher humidity, the effectiveness of hydrogen bonding to provide tight cohesion in the CMC matrix diminishes rapidly and the ionic interactions take
the lead in defining the mechanical cohesion. At 55 %RH both pristine materials undergo significant inelastic deformation, considering the highly reinforced state (Figure 4b,e). An exchange to Cu$^{2+}$ counterions leads to tight supramolecular crosslinks, as seen in much higher stiffness and shorter elongation at break. This is particularly well visible for CMC/MTM = 80/20 (Figure 4e). The behaviour is still reminiscent of a rather non-dynamic crosslinking.

Upon further increase to 95 %RH, the situation is again different (Figure 4c,f). In fact, a large loss of cohesion can be observed for the pristine materials due to electrostatic repulsion of carboxylic groups in the CMC and diminished hydrogen bonds. In large contrast, the mechanical properties of the Cu$^{2+}$-treated materials decay much less and show that inelastic deformation zones develop that are much larger compared to lower humidities. This is again nicely visible for the CMC/MTM = 80/20 sample (Figure 4f), which shows doubled elongation at break compared to the dried state. Due to the high crosslinking density (DS = 0.9), almost every repeating unit of the CMC is ionically bonded, and we therefore suggest that this inelastic zone is partly caused by sacrificial breaking and rebinding of Cu$^{2+}$ ionic supramolecular bonds, i.e. dynamic and transient bonds.

Importantly, at 95 %RH, the elongations at maximum tensile stress are similar for the pristine and the Cu$^{2+}$ infiltrated material, yet stiffness and strength are one order of magnitude higher for the supramolecularly bonded nacre-mimetics. In consequence, the work-to-fracture or the modulus of toughness, which can be calculated from the integral area under the stress-strain curve, is 5 – 10 times of that of the pristine material. Consequently, we observe a synergetic improvement of mechanical properties. This synergetic improvement is further evidenced in Figure 5, which compares the relative mechanical performance of the pristine materials to the Cu$^{2+}$ infiltrated ones.

Here it becomes more obvious that up to 55 %RH, stiffness is increased on the expense of toughness. Yet at high relative humidity, all three relevant material parameters are found to be much greater than unity – by factors of 3 to 9 – thus clearly confirming a synergetic
improvement (Figure 5). In comparison with other nacre-mimetics, it is interesting to realize that the ionically bonded materials presented here in this study perform very well, even in wet conditions.

![Figure 5. Comparison of the mechanical property characteristics (Young’s modulus, tensile strength and modulus of toughness) as a function of the composition. (a) for CMC/MTM = 60/40, and (b) CMC/MTM = 80/20, obtained by dividing the respective material property of the Cu²⁺-infiltrated nacre-mimetic by the pristine (Na⁺) one. Synergetic improvements are visible at 95 %RH, where all three ratios are substantially larger than unity.](image)

In particular the higher reinforced sample CMC/MTM = 60/40 displays excellent properties in the hydrated state at 95 %RH (E = 13.5 GPa, σ_{UTS} = 125 MPa) with values that are actually comparable to a range of uncrosslinked LbL-based polymer/clay nacre-mimetics, which were measured at much lower RH.\(^{13, 15, 17, 24, 26}\) Hence, this corresponds to a truly remarkable wet strength stability of the nacre-mimetics. In contrast to covalently crosslinked materials, which could also lead to water-stable materials,\(^{15}\) the dynamic nature of the supramolecular ionic bonds still allows inelastic deformation in the range of 1 – 1.5% up to a maximum elongation of 1.5 – 2.5%. This substantially contributes to achieving toughness.

Although the manifestation of the effect of synergetic material performance requires tailored conditions at high humidity at this point of time, it is conceptually relevant to develop and understand non-covalent crosslinking in highly reinforced bioinspired composites to, in the end, develop synergetic material combinations with tailored properties independent of humidity. To this end ionic interactions are particularly useful as wide range of interactions
Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics

are accessible by simple means. Herein, we deliberately chose Cu$^{2+}$ ions due to its tight binding with polyacids. However, from polyacrylic acid/ionic complexes, it is already known that other bivalent ions (e.g. Ca$^{2+}$) display different dynamics of complex formation.\textsuperscript{41-43, 46, 47} Thus, specific complexation effects may be used to further change dynamics and supramolecular strength. Additionally, by changing the valence of the counterions further to trivalent or even tetravalent ions, we expect to foster and further tailor interactions and mechanical properties in the hydrated state.

5.4. Conclusions

We have shown for the first time that understanding and mediating supramolecular ionic interactions in highly reinforced bioinspired layered nanocomposites composed of alternating layers of CMC and MTM can be used to drastically increase the wet-strength of water-borne nacre-mimetic materials. It was found that the occurring loss of internal cohesion of the CMC matrix (the “mortar”) due to loss of hydrogen bonding ability upon exposure to higher RH can be compensated by implementing ionic supramolecular interactions via an exchange of the pristine monovalent counterion Na$^+$ by divalent Cu$^{2+}$. The latter ones form supramolecular ionic linkages between carboxylic acid groups within the CMC matrix and link carboxylates to the nanoclay surface.

In addition to preserved mechanical strength, we find the onset of synergetic, simultaneous improvements of stiffness, strength and work-of-fracture/modulus of toughness at high RH. All three relevant material characteristics exceed considerably the mechanical properties of the pristine CMC/MTM materials at high dynamics, i.e. in the hydrated state. We attribute this favourable behaviour to the dynamic state of crosslinking, which may allow for a breakage and rebinding of anionic species with the Cu$^{2+}$ counterions.

Although responsive and adaptive mechanical properties can be achieved by altering the counterion charge via external stimuli e.g. light and electrochemically-induced changes of
counter-ion charges$^{32-36}$ yet it will be a challenge to implement them in highly reinforced and stiff bioinspired bulk materials with lower dynamics in future.

One of the main challenges to master synergetic properties in bulk materials will be to further understand how to regulate the dynamic state of the crosslinking points and the polymeric material, which might be accessible by using a range of counterions with different binding strength and going to low-$T_g$ polymers with intrinsically higher dynamics.

We further expect to apply similar counterion manipulations in other bioinspired materials, e.g. nanocellulose papers and peptide-based materials.

5.5. Acknowledgments

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5.6. References and Notes


Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics

Chapter 5

Ionic supramolecular bonds preserve mechanical properties and enable synergetic performance at high humidity in water-borne, self-assembled nacre-mimetics.

5.7. Supplementary Information

Figure S1: SEM images of (a) pristine CMC/MTM = 60/40 and (b) Cu$^{2+}$ infiltrated CMC/MTM = 60/40 composites after stretching at 95 %RH.
Self-assembled, bioinspired, hybrid brick-walls as fire barrier coatings on textiles with amphiphobic and self-cleaning features

6.1. Introduction

Fire remains one of the largest reasons for non-natural fatalities and causes dramatic loss of property and gross national product in the range of billion euros every year. Most effective present-day fire retardant materials use heavy metals\(^1\)\(^-\)\(^4\) or bromine\(^5\)\(^,\)\(^6\) containing species to efficiently arrest fires. In the light of environmental and health concerns, and upcoming legislation restrictions regarding brominated fire retardants,\(^6\)\(^,\)\(^7\) it is thus very important to develop new procedures for intrinsically fire retardant bulk materials, as well as, for fire-retardant and fire-blocking coatings, at best using environmentally benign materials and processes.\(^8\)\(^,\)\(^9\) The combination of tailored polymers with inorganic nanoparticles, e.g. nanoclays\(^10\)\(^-\)\(^17\) or carbon nanotubes,\(^18\)\(^-\)\(^21\) polyhedral silsesquioxanes (POSS),\(^22\)\(^,\)\(^23\) layered double hydroxides,\(^24\)\(^-\)\(^26\) providing oxygen barrier properties and strength, preventing dripping of hot, molten plastics, and enabling an intumescent, self-expanding foam-like heat barrier behavior is a most promising approach for fire-retardant coating materials.\(^27\) Aiming at a quantitative understanding in such materials greatly requires approaches towards structurally well-defined surface coatings, in which benefits in the fire behavior can explicitly be linked to defined composition and architecture. Interesting progress towards nanostructured fire-resistant coatings has been reported for ultrathin coatings based on step-wise, layer-by-layer deposition of different polymers and nanoclay,\(^28\)\(^-\)\(^33\) in which substrates are alternatingly dipped into polymer and nanoclay to build up multilayers of organic and inorganic phases. Even though attractive fire barrier properties could be shown, the process remains sequential, and laborious, and it is difficult to reach thicknesses beyond one micrometer (e.g. hundreds of
double layers). Hence, there is still a tremendous need to develop simple, fast and scalable procedures to prepare thick coatings with tailored nanostructure based on readily available constituents and presenting excellent fire barrier properties.

Here, we show a one-pot, single-step self-assembly approach to prepare thick, bioinspired, layered, hybrid, brickwall coatings with well-defined nanostructure on cotton textiles, as formed through self-assembly of tailored mixtures of sodium carboxymethylcellulose (CMC) and montmorillonite (MTM) nanoclay at high fractions of the inorganic component. The coating thickness on the textile can be tailored using different CMC/MTM concentrations in the coating bath. We study the fire barrier and fire retardancy properties as a function of coating thickness by thermogravimetric analysis (TGA), fire break-through test, vertical flame test (VFT), thermal imaging using forward looking infra-red (FLIR) camera, and cone calorimetry. We also modify the surface of the fire retardant coating to impart amphiphobic and self-cleaning features. Hence, this study demonstrates a process which is scalable and can be introduced into existing coating technologies to provide bioinspired, multifunctional, fire barrier nanocomposite coatings on textile.

6.2. Experimental

Materials

Sodium carboxymethyl cellulose (CMC, degree of substitution = carboxymethyl groups per anhydroglucose unit = 0.7, $M_w = 90$ kg/mol, Aldrich), Na-Cloisite (MTM, Rockwood), Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (97%, Aldrich), MilliQ water, and pure cotton textile (ISO 105-F, 150 mm width) were used for all experiments.

Preparation of bioinspired hybrid fire-retardant nanocomposite coating on textile. CMC and MTM were added as premixed (60/40 w/w) powder into a IKA HKD-T-0.6 high-performance kneader with two wide-bladed kneading elements containing the appropriate
amout of water to reach a total concentration of ca. 8 wt%. After homogenization for 12 h, the slurry was diluted to different concentrations (1, 1.75, 2.5 and 5 wt%), and degassed. Then a custom-made continuous coating machine was used to guide the cotton textile (width 150 mm) from a roll through the coating bath at 10 mm/min for each slurry concentration. Afterwards, the wet coated fabrics were dried at ambient conditions. We use the following nomenclature for the coating compositions. Textile coated with CMC/MTM = 60/40 w/w at various concentrations are abbreviated as CMC$_{60}$MTM$_{40}$-x% where x = 1, 1.75, 2.5 or 5 wt%.

**Surface modification of nacre-mimetic coating on cotton textile.** A CMC$_{60}$MTM$_{40}$-2.5% coated textile was dipped into a 5 mM solution of trichloro(1H,1H,2H,2H-perfluorooctyl)silane in heptane, and left for 15 min. After that the coated textile was rinsed with heptane and water few times and dried.

**Methods**

Field emission-scanning electron microscopy (SEM) was performed on a Hitachi S-4800 field emission microscope using 1.5 kV acceleration voltages.

Thermogravimetric analysis (TGA) was done using a NETZSCH TG 209C instrument in both air and N$_2$ atmosphere from 25 to 850 °C at a heating rate of 10 °C/min.

Wide-angle x-ray diffraction (WAXD) was performed using an Empyrean setup from PANalytical using the Bragg Brentano parallel-beam geometry. An Empyrean Cu x-ray tube LFF HR (line source of 12×0.04 mm$^2$) provided CuK$_{α}$ radiation with $λ = 1.542$ Å at 40 kV voltage and 40 mA current.

Fire break-through tests were performed on the coated fabrics and the control using a Soudogaz® X 2000 PZ gas torch with maximum flame temperature of 1750 °C. All samples were cut into circular shape having ca. 7 cm in diameter and fixed in a circular metal holder.
keeping a 130 mm distance between the samples and the direct flame. Finally the samples were exposed to the direct flame at an angle close to 90° and the fire break-through process was monitored using a standard video camera.

Bench-scale vertical flame tests (VFT) were performed on the coated fabrics and the control with dimensions of 160 mm × 12.5 mm (L × W). A yellow flame was kept at the bottom of the sample for 5 s. The burning was monitored using a forward looking infrared camera A655sc camera (FLIR) in the temperature range of 20 – 660 °C, and standard video.

Cone calorimeter experiments were conducted on a FTT cone calorimeter at 50 kW/m² heat flux, with an exhaust flow of 24 L/s, according to ISO 5660, on sample dimensions of 100 mm × 100 mm (L × W). The heat release rate was determined by the measurement of the oxygen consumption derived from the oxygen concentration and the flow rate in the combustion product stream. Parameters such as time to ignition (TTI), peak heat release rate (pkHRR), total heat release (THR), and total smoke release (TSR) were evaluated.

6.3. Results and Discussion

In our previous work⁴,⁵, we demonstrated that the fine control of the molecular interactions between anionic CMC and anionic MTM nanoclay allows the formation of homogeneous, concentrated slurries of both components – even at high solid content. Those could be used to prepare highly ordered nacre-mimetic, layered nanocomposites with tailored nanostructure (e.g. adjustable d-spacing between the nanoclay) and we found a near optimum combination of mechanical properties at a composition of CMC/MTM = 60/40. Given this unusual, large-scale access to nacre-mimetics, and the fact that preliminary investigations showed interesting fire retardancy, we were motivated to investigate in detail, how such materials could be applied as coating, and quantitatively understood as fire barrier materials.
The general strategy for the preparation of self-assembled, layered, bioinspired nanocomposite coatings on cotton textiles is shown in Figure 1a. We start with the preparation of CMC/MTM dispersions by kneading a paste at CMC/MTM = 60/40 (w/w) at ca. 8 wt% solid content in water. Well-defined core/shell nanoplatelets are formed by adsorption of CMC onto MTM nanoplatelets due to hydrogen bonding and hydrophobic effect. Those are decisive to predefine the length scales of the final nanocomposite and reach well-ordered alternating hard and soft layers during evaporation-induced self-assembly. For applying the coating, the cotton textiles are passed through a bath containing different concentrations of the CMC/MTM (60/40 w/w) hydrocolloid dispersion (1, 1.75, 2.5, 5 wt%, after dilution from the initial paste) at 10 mm/min. A nanocomposite coating forms during drying of the dispersions on the cotton textiles. We denote the specimens as CMC$_{60}$MTM$_{40}$-x%, where the subscripts denote the weight fractions of both components and ‘x%’ denotes the concentration of the coating dispersion in wt%. Reasonably we can expect that the coating weight/thickness depends on the concentration of the bath and that a morphological transition may occur starting from coating of individual fibers at low concentration/viscosity to the presence of a fully coated film at high concentration/viscosity. For comparison, we also casted a nacre-mimetic nanocomposite film by evaporation in a petri dish. This allows characterizing the nanocomposite structure in a straightforward manner and serves as a comparison to structures created on textiles.

The structural characterizations of the nanocomposite film, as well as, CMC$_{60}$MTM$_{40}$-1%, and CMC$_{60}$MTM$_{40}$-5% coated fabrics are displayed in Figure 1b-f. X-ray diffraction (XRD) of the nanocomposite film shows a primary diffraction peak (q*) in the range of 1.7 – 2.3 nm$^{-1}$, corresponding to gallery spacings in the range of 3.7 – 2.7 nm. Although the diffractogram of the coated fabric does not present very sharp peaks due to the undulated surface of the textile, it still clearly shows a hump (arrow in Figure 1b) in the same range, thus confirming
the successful formation of nacre-mimetic structures on the fabric. Weak and broad humps in both diffractograms appear around 3.5 – 5.3 nm\(^{-1}\), which is the 2q* peak corresponding to the higher-order peaks characteristic of a lamellar morphology. The dominant peak of pure MTM is strongly diminished, indicating the achievement of high levels of delamination in the kneading process.

![Image of Figure 1](image)

**Figure 1. Preparation of bioinspired nanocomposite coatings and structural characterization.** (a) Schematic of the self-assembled nanocomposite films based on CMC, (R = H or CH\(_2\)-COONa) and natural montmorillonite (MTM) via concentration-induced self-assembly of polymer-coated nanoclay platelets with intrinsic hard/soft architecture, and coating of textiles from different concentrations of CMC/MTM = 60/40 w/w dispersions at 10 mm/min. (b) XRD of the pure MTM and CMC\(_{60}\)MTM\(_{40}\) films, and CMC\(_{60}\)MTM\(_{40}\)-5% coated fabric. The arrow shows the appearance of diffraction hump for the coated textile. (c-g) SEM images of the cross-sections of (c) CMC\(_{60}\)MTM\(_{40}\) film, (d) CMC\(_{60}\)MTM\(_{40}\)-1%, (e) CMC\(_{60}\)MTM\(_{40}\)-5%, and (f) high magnification image of the CMC\(_{60}\)MTM\(_{40}\)-5%. CMC\(_{60}\)MTM\(_{40}\)-1% exhibits only a conformal coating of the fiber (d, inset, and SI 1), and CMC\(_{60}\)MTM\(_{40}\)-5% shows the ordered layered structure of nacre-mimetic coating (f, inset).
Further investigation of the morphology by SEM confirms the desired well-aligned layered structure in the films and coatings. Notably, the high magnification SEM image of CMC$_{60}$MTM$_{40}$-5% (Figure 1f, inset) clearly shows that in addition to coating of individual fibers, a continuous film with 8.5 ± 3 µm thickness remains on the surface of the whole fabric (see Figure 7e). Such a film is absent for lower slurry concentrations in the coating bath (e.g. 1 wt%), where only a conformal coating of the fibers exists (Figure 1d and inset). Formation of such a film is related to the high viscosity of the slurry and to the coating procedure. It is an important difference to polymer/nanoclay multilayers formed by LbL, which could form only conformal coatings on fibers.$^{30, 36, 37}$

The thermal and thermo-oxidative stability of the coated fabrics and control are examined by thermogravimetric analysis (TGA) in both N$_2$ and air atmosphere from 25 to 850 °C at 10 °C/min as shown in Figure 2.

![Figure 2: Thermal and thermo-oxidative stability of CMC$_{60}$MTM$_{40}$-coated fabrics and the control. (a) TGA plot of the control and CMC$_{60}$MTM$_{40}$-1%, 1.75%, 2.5%, and 5% coated fabrics in N$_2$. (b) DTGA plots (top) in N$_2$ and (bottom) in air. (c) The average coating weight added on the textile from different slurry concentrations, and the residual mass calculated at 500 and 800 °C in N$_2$ atmosphere for all the samples.](image-url)

The coated fabrics exhibit similar decomposition curves like the control, but they undergo a slightly earlier onset of degradation (Figure 2a,b). Differential thermogravimetric analysis (DTGA) plots in Figure 2b show that pure cotton (control) begins to degrade around 280 and 275 °C in N$_2$ and air, respectively. The initial minute weight loss at ca. 110 °C is due to the removal of moisture. The major weight loss occurs between 280 to 400 °C in both
Self-assembled, bioinspired, hybrid brick-walls as fire barrier coatings on textiles with amphiphobic and self-cleaning features

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atmospheres resulting from the decomposition and dehydration of the cellulose leading to thermally stable residues. The second weight loss between 400 to 530 °C in air corresponds to the further oxidation of the char to produce CO and CO$_2$.\textsuperscript{38} Despite having an earlier onset, CMC$_{60}$MTM$_{40}$-coated fabrics undergo slower degradation with increasing the slurry concentration as seen from the smaller and wider peak in the DTGA plots when going from CMC$_{60}$MTM$_{40}$-1% to CMC$_{60}$MTM$_{40}$-5% (Figure 2b).\textsuperscript{39} This slower rate of thermal degradation arises from the highly ordered, layered arrangement of the large MTM nanoplatelets (aspect ratio = 260\textsuperscript{40}) inside the CMC/MTM coating. On one hand, this layered nanocomposite structure provides thermal insulation and reduces the heat transfer into the cotton fabric, and on the other hand, it lowers oxygen diffusion due to the tortuous pathway (oxygen barrier property = 0.022 cm$^3$·mm·m$^{-2}$·day$^{-1}$·atm$^{-1}$ at 50 %RH and 0.115 cm$^3$·mm·m$^{-2}$·day$^{-1}$·atm$^{-1}$ at 80 %RH).\textsuperscript{38, 41} The residual mass of the coated fabrics at 500 °C (after the first step of degradation), and at 800 °C (almost at the final stages of degradation) in N$_2$ increases with increasing slurry concentrations indicating higher inorganic content originating from thicker coatings (Figure 2c). We determine the average weight added to the fabric from each coating concentration which ranges between 0.6 and 3.8 mg/cm$^2$ with increasing the concentration from 1 to 5 wt% in the bath. The values reflect the tendency found in SEM, where thinner conformal coatings on individual fiber are observed at lower slurry concentrations, while a continuous film forms in addition to coating of individual fibers at higher concentrations (Figure 1d-f).

Next, we study the ability of the textiles to withstand direct high intensity flames from a short distance (130 mm) for longer time using a fire break-through test. All samples were fixed in a circular holder with ca. 7 cm diameter and then exposed to a high temperature torch at nearly 90° angle. Figure 3 shows photographic snap shots series during the test. The control catches fire within 3 s, and is consumed completely after 18 s without leaving any residue in
the holder. In contrast, all coated fabrics char into a solid barrier material resisting long term exposure to direct flames. Most coated fabrics undergo shrinkage during charring in the direct flame, and get loose from the sample holder (see inset of Figure 3b,c,d). We believe that this behavior should be less relevant for larger specimens. Increasing the coating thickness limits this behavior, and CMC$_{60}$MTM$_{40}$-5% chars into a shape persistent solid barrier material which completely restricts the fire from breaking through it (Figure 3e). Figure 3 further shows that the time to catch fire gradually increases with increasing slurry concentration, and the best fire barrier is observed for CMC$_{60}$MTM$_{40}$-5%, which chars but does not support any flame even after direct flame exposure for 60 s.

Figure 3: Fire breakthrough test. Photographs of (a) the control, (b) CMC$_{60}$MTM$_{40}$-1%, (c) CMC$_{60}$MTM$_{40}$-1.75%, (d) CMC$_{60}$MTM$_{40}$-2.5% and (e) CMC$_{60}$MTM$_{40}$-5% at times indicated during exposure to a high temperature torch flame (1750 °C) at nearly 90° angle and 130 mm away from the sample. (inset of b,c,d) Shrinkage of the coated fabrics during charring in the direct flame. Sample edges are marked in dotted white line.

To study flame retardancy and self-extinguishing behavior, we performed bench-scale vertical flame test (VFT) on specimens with dimensions of 160 mm × 12.5 mm (L × W) in
analogy to EN ISO 11925-2. The flame was kept at the bottom of the sample and ignited for 5 s. A forward looking infrared camera (FLIR) allows monitoring the spatiotemporal temperature profiles and standard video monitors the general behavior. Figure 4 shows the photographs and FLIR images after 5 s of ignition, and photographs at the end of burning. The photographs after 5 s of ignition show that the flame is much brighter and stronger in case of the control, but becomes less vigorous for fabrics coated in higher slurry concentration and thus having higher thickness.

![Figure 4: Optical photographs from the bench-scale vertical flame test (VFT) and the corresponding FLIR images of the CMC_{60}MTM_{40}-coated fabrics and the control. (a) VFT photographs of CMC_{60}MTM_{40}-coated fabrics and the control after 5 s of burning. (b) FLIR images after 5 s with a color scale from 20 to 660 °C. (c) VFT photographs of all the samples at the end of burning.](image)

The control burns immediately and is totally consumed within 19 s after ignition. CMC_{60}MTM_{40}-1% still allows flame propagation and complete burning, yet it shows a
significant amount of coherent char with some slits at the end. The behavior of CMC_{60}MTM_{40}-1.75\% and CMC_{60}MTM_{40}-2.5\% is different. Those are not consumed completely, but burn up to half of the sample height (ca. 85 mm) in 8–9 s after ignition leaving behind a broken solid char due to the presence of higher coating thickness. Although they self-extinguish right after removal of the direct flame, a glowing frontier appears later, which propagates very slowly within the burning height (ca. 50 mm, Figure 5e) and vanishes completely at 50 and 90 s after ignition for CMC_{60}MTM_{40}-1.75\%, and CMC_{60}MTM_{40}-2.5\%, respectively. CMC_{60}MTM_{40}-5\% performs extremely well in terms of fire retardancy. It self-extinguishes once the direct flame is removed, and does not support either flame or glow propagation. It forms a continuous and intact solid charred residue due to the highest coating thickness.

Figure 5: Temperature vs time plot of the CMC_{60}MTM_{40}-coated fabrics and the control at different sample height during bench-scale VFT. (a-c) Temperature profiles of the control, CMC_{60}MTM_{40}-1.75\%, and CMC_{60}MTM_{40}-2.5\% at 10, 50, 100, 120 and 150 mm. (d,f) Comparative study of the temperature profiles of all CMC_{60}MTM_{40}-coated fabrics at (d) 50 and (f) 100 mm sample height. (e) FLIR images of CMC_{60}MTM_{40}-1.75\% and CMC_{60}MTM_{40}-2.5\% corresponding to the first temperature peak at ca. 5 s (left, hot gas) and second temperature peak at 50 s and 65 s (right, glowing frontier).

The spatiotemporal FLIR imaging allows deeper insights into the thermal behavior and flame propagation. While stills from the FLIR videos after 5 s of ignition are shown in Figure
4b, the complete temperature vs. time profiles of the samples are shown in Figure 5. First, we discuss the temperature profiles at different sample heights (from 10 to 150 mm) of the control and the CMC$_{60}$MTM$_{40}$-coated fabrics from two intermediate slurry concentrations, serving as the most instructive examples (CMC$_{60}$MTM$_{40}$-1.75% and CMC$_{60}$MTM$_{40}$-2.5%; Figure 5a-c). Afterwards, we focus on the comparison of the temperature profiles at sample heights of 50 and 100 mm for all samples (Figure 5d-f). The temperature profiles of the control in Figure 5a reveal a consistent shift of the traces with increasing sample height. They exhibit temperatures around 400 ± 500 °C during passage of the flame front. The behavior is different for exemplary CMC$_{60}$MTM$_{40}$-1.75% and CMC$_{60}$MTM$_{40}$-2.5% samples. Here the flame stops before reaching 100 mm, and therefore, the temperature profiles at 100, 120 and 150 mm are essentially flat, except for the initial 5 – 15 s, where some hot gases from the flame and the sample pass the markings. At 10 mm, both samples show the initial burning process initiated by the exposure to the direct flame. Most interesting is the observation of the profiles at the 50 mm marking, where two maxima can be identified. The first maximum corresponds to the initial flame exposure and burning of the sample, and originates from the ascent of hot gases. Yet, the second maximum indicates the delayed, glow frontier which smoulders across the sample with a delay until the glow vanishes. The temperature of this glow frontier is significantly lower. The glow frontier in CMC$_{60}$MTM$_{40}$-1.75% stops just below the 50 mm marking (lower temperature increase), while it stops just on or above the marking in CMC$_{60}$MTM$_{40}$-2.5%, causing higher temperature rise in the second maxima as compared to CMC$_{60}$MTM$_{40}$-1.75%. The photographs in Figure 5e serve to illustrate the two maxima at different times. At higher sample height (100 mm, Figure 5f) the two maxima disappear for intermediate coating weight because the glowing frontiers do not reach this height. While all coated fabrics show a significant drop in temperature at a sample height 100 mm or higher, the temperature profile of CMC$_{60}$MTM$_{40}$-1% does not differ much from the
control, as similar to the control, CMC_{60}MTM_{40}-1% is consumed completely, due to the lower coating thickness.

We further quantify the maximum burning height reached by either flame propagation or smouldering, and the time to reach this height during bench-scale VFT. Figure 6a shows that the flame reaches 160 mm height in just 10 s in case of the control and CMC_{60}MTM_{40}-1%, while CMC_{60}MTM_{40}-1.75%, CMC_{60}MTM_{40}-2.5%, and CMC_{60}MTM_{40}-5% arrest the burning within half of their height showing resistance to flame/glow propagation. Self-extinguishing behavior and arrested flame propagation is observed starting from CMC_{60}MTM_{40}-1.75%, where it burns initially in the direct flame and then smoulders after removal of the direct flame up to burning height of only 85 ± 5 mm in 8 s after ignition. The best result is obtained for CMC_{60}MTM_{40}-5%, where it self-extinguishes once the direct flame is removed and smoulders up to only 30 mm height in 9 s after ignition. Dripping is not observed in any samples.

Figure 6: Vertical flame test analysis and cone calorimetry measurements of the CMC_{60}MTM_{40}-coated fabrics and the control. (a) Maximum burning height and the time needed to reach that height for CMC_{60}MTM_{40}-coated fabrics and the control. Burning does not even reach half of the total sample height (160 mm) for fabrics coated from slurry concentration as low as 1.75%. (b) Heat release rate of the CMC_{60}MTM_{40}-
coated fabrics for all the slurry concentrations and the control. (c-g) Photos of the residues of the coated fabric and the control after burning in cone calorimetry, (c) control, and (d-g) CMC_{60}MTM_{40}-1%, 1.75%, 2.5% and 5%, respectively.

To predict the combustion behavior of the materials in real fire situation, we further estimate the heat release rate (HRR) and flammability of the coated fabrics and the control using cone calorimetry under a constant heat flux of 50 kW/m² (Table 1 and Figure 6b-g).^{42}

Table 1. Overview from cone calorimetry measurement

<table>
<thead>
<tr>
<th>Sample</th>
<th>TTI (s)</th>
<th>pkHRR (kW/m²)</th>
<th>avg. HRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>TSR (m²/m²)</th>
</tr>
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<tbody>
<tr>
<td>control</td>
<td>8 ± 2</td>
<td>88 ± 1</td>
<td>28 ± 2.5</td>
<td>1.8 ± 1</td>
<td>4.5 ± 1</td>
</tr>
<tr>
<td>CMC_{60}MTM_{40} (\times 1)%</td>
<td>8 ± 2</td>
<td>73 ± 3</td>
<td>28 ± 1.5</td>
<td>1.7 ± 0.1</td>
<td>3.6 ± 0</td>
</tr>
<tr>
<td>CMC_{60}MTM_{40} (\times 1.75)%</td>
<td>9 ± 3</td>
<td>70 ± 2</td>
<td>25 ± 2.1</td>
<td>1.6 ± 0.1</td>
<td>3.8 ± 0.6</td>
</tr>
<tr>
<td>CMC_{60}MTM_{40} (\times 2.5)%</td>
<td>5 ± 1</td>
<td>69 ± 3</td>
<td>27 ± 0.6</td>
<td>1.7 ± 0.1</td>
<td>1.0 ± 0.5</td>
</tr>
<tr>
<td>CMC_{60}MTM_{40} (\times 5)%</td>
<td>7 ± 2</td>
<td>55 ± 7</td>
<td>17 ± 2.2</td>
<td>1 ± 0.1</td>
<td>2.1 ± 1.1</td>
</tr>
</tbody>
</table>

TTI = time to ignition, pkHRR = peak heat release rate, avg. HRR = average heat release rate, THR = total heat release rate, TSR = total smoke release.

Although the time to ignition (TTI) remains almost the same for all CMC_{60}MTM_{40}-coated fabrics and the control, increasing the slurry concentration for the coated fabrics results in continuous reduction in peak heat release rate (pkHRR), total heat release (THR), and total smoke release (TSR). Furthermore, the heat profiles are more extended in the time axis for increasing coatings thickness. This demonstrates that all CMC_{60}MTM_{40}-coated fabrics exhibit significantly higher fire-retardancy as compared to the control.^{39} The CMC_{60}MTM_{40}-5% reduces the pkHRR and THR to 37% and, 44%, respectively, compared to the control. This improved fire-retardancy for CMC_{60}MTM_{40}-5% stems from the thicker MTM-containing nanocomposite coating, which increases the protective char formation on the coated textile surface (Figure 6c-g).^{38} This thick protective solid char acts as a thermal barrier and lowers the formation of flammable volatiles, therefore, leading to the reduction in pkHRR and
Lower pkHRR is a desired parameter to exhibit efficient fire-retardancy in real fire situation as it retards or diminishes the self-propagation or spreading of the flame to other materials when the external flame or ignition source is removed. Similarly, reduction in TSR is also a very important factor for evaluating fire retardancy in real fire situation as smoke can cause serious problems like choking, unconsciousness, lack of breathing during evacuation. A 53% reduction in TSR for CMC$_{60}$MTM$_{40}$-5% as compared to the control is noteworthy, indicating that not much dense smoke is released during burning of the coated fabric. Therefore, CMC$_{60}$MTM$_{40}$-5% appears as a very effective fire retardant nanocomposite coating.

To evaluate the surface morphology before and after burning, we further characterized selected samples by SEM (Figure 7). The SEM images show that CMC$_{60}$MTM$_{40}$ coating on textile retain a similar weave structure as in the control (Figure 7a,b, and SI 1a). Under high magnification, the individual fibers of the control show smooth and clean surfaces (Figure 7g) but become rougher after applying the coating (Figure 7h, and SI 1b). Moreover, for CMC$_{60}$MTM$_{40}$-5%, the individual fibers are linked together, and the gap between them which may serve as sites for the penetration of heat, are diminished due to a thicker coating (Figure 7h). The SEM images after burning shows that thinner conformal coating of CMC$_{60}$MTM$_{40}$-1% is enough to preserve the fabric wave structure, although significant shrinkage is observed, creating gaps between yarns (Figure SI 1c,d). In contrast, due to thicker coating, CMC$_{60}$MTM$_{40}$-5% shows an intumescent effect by forming an expanded foam-like char with a lot of bubbles on its surface (Figure 7c,f). These bubbles are formed due to evolution of gas while burning the intercalated polymer during exposure to flames. As a result, a nanoporous foam-like structure develops that provides good heat insulation to the underlying materials. A significant expansion from the initial 8.5 ± 3 µm to 25-50 µm enables CMC$_{60}$MTM$_{40}$-5% to self-extinguish quickly once the direct flame is removed and to
Self-assembled, bioinspired, hybrid brick-walls as fire barrier coatings on textiles with amphiphobic and self-cleaning features

stop the flame propagation (Figure 7i). Further dehydroxylation of the aluminosilicates results in self-cooling via water formation and also improves mechanical integrity due to char formation.\textsuperscript{34} Interestingly, after burning, we also observe some hollow fibers with diameters between 7-15 µm which are similar to the average diameters of the fibers before burning. This confirms that the CMC/MTM dispersion penetrates through the textile during the coating procedure and coats the individual fibers.

![Figure 7: SEM images of the CMC\textsubscript{60}MTM\textsubscript{40-5%} coated fabric and the control.](image)

(a,d,g) Microscopic images of the surface and cross-section of the control, and (b,e,h) that of CMC\textsubscript{60}MTM\textsubscript{40-5%}, before burning. (c,f,i) Microscopic images of CMC\textsubscript{60}MTM\textsubscript{40-5%} after burning in VFT showing (c) the surface, and (f,i) the cross-section. (i) Individual hollow fibers are seen after burning of CMC\textsubscript{60}MTM\textsubscript{40-5%}, encircled in red. The control was completely consumed during burning, so no image can be shown after burning.

Given the diverse requirements of materials in general, especially in a real application context, it is important to develop multifunctional property profiles. One of the major bottlenecks in the application of water-borne polymer/clay nanocomposite coatings, no matter
whether prepared by LbL strategy or by the faster self-assembly approach herein, is the inherent susceptibility to water. To promote the durability, and functionality of the coatings when exposed to humid environment or water, we sought to impart them with an amphiphobic coating, providing repellency of water (and oil) and combining it with self-cleaning features. The latter is generally obtained by coatings of low surface energy and hierarchical roughness.

We choose a coated fabric from intermediate slurry concentration (CMC$_{60}$MTM$_{40}$-2.5\%) and performed a surface modification with trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Figure 8a), which binds to the hydroxyl groups available at the CMC. Due to the high polarity of the CMC, the unmodified coated fabric rapidly absorbs water and bends under the weight of the absorbed water. Yet, once modified with the low surface energy fluorosilane, the fabric shows hydrophobic behavior with high repellency and high contact angles towards water (Figure 8b,d).

Figure 8: Surface modification and photographs showing amphiphobicity, water roll off and self-cleaning of the coated fabrics. (a) Schematic representation of surface modification of CMC$_{60}$MTM$_{40}$-coated fabrics with
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trichloro(1H,1H,2H,2H–perfluoroctyl)silane, (not in scale). (b) Photographs of water droplets, and (c) salad oil droplets on both unmodified and modified coated fabrics. (d) Water droplet is soaked on the surface of the unmodified coated fabric whereas it can easily roll off and bounce off from the modified coated fabric. (e) Self-cleaning behavior of modified coated fabric.

At the same time, the modification also provides protection against non-polar liquids such as salad oil, a clear advantage of using fluorinated coatings over only hydrophobic coatings (Figure 8c).

The snap shot series in Figure 8d further shows that the water droplets bounce on the surface of the modified coated fabric, and easily roll down with a low sliding angle (< 25°). This is due to the low adhesiveness resulting from the cooperation of the surface hierarchical structure of the fabric and the low surface energy of fluorosilane. This is a beneficial feature for self-cleaning surfaces, and prompted us to also investigate the potential for self-cleaning. Using deposited activated carbon, we find that a series of water droplets easily removes the deposited dirt and recovers the pristine clean surface (Figure 8e). Overall this demonstrates that simple fluorinated surface coatings can be applied to the nacre-mimetics CMC/MTM fire barrier coatings and amphiphobic and self-cleaning features can be imparted as desirable for application needs.

6.4. Conclusion

We demonstrated a single step, large-scale, self-assembly approach to prepare thick, bioinspired, well-defined, hybrid, brickwalls as fire-retardant coatings on textiles. The coating weight/thickness is tuned by changing the slurry concentrations. While lower slurry concentration imparts conformal coating of the individual fibers, CMC60MTM40-5% forms a thicker continuous film on the textile (ca. 8.5 µm). Formation of such a film is related to the high viscosity of the slurry. Hence, this process makes a starking difference to polymer/nanoclay multilayers formed by LbL, which could provide only conformal and ultrathin coatings (< 1µm) on fibers in alternating deposition from dilute suspensions.
We found that the fire barrier properties of the coated fabrics increases with increasing slurry concentration making CMC$_{60}$MTM$_{40}$-5% as the best fire barrier coated fabric. It not only withstands long-term high temperature direct flame exposure, but also prevents the penetration of flame through it by forming a shape persistent solid char during fire breakthrough test. It exhibits notably lower temperature build up during vertical fire tests, and significantly decreases the pkHRR (37%), THR (44%), and TSR (53%) as compared to the control as seen from cone calorimetry. Furthermore, SEM images showed that the CMC$_{60}$MTM$_{40}$-coated fabrics exhibit an intumescent effect by forming a thick and expanded foam-like char with lot of bubbles on its surface due to evolution of gas. This nanoporous char provides good heat insulation to the underlying materials and improves fire retardancy.

In terms of functional benefits of these nacre-mimetics CMC/MTM fire barrier coatings, we imparted amphiphobic and self-cleaning features by surface modification with a fluorosilane. This furnishes a water- and oil-resistant surface based on water-borne CMC/MTM coatings, and imparts self-cleaning, thereby increasing the durability and usefulness for applications in harsher conditions.

Importantly, the presented strategy opens a generic platform towards sustainable high-performance green and non-flammable thick nanocomposite coatings. As a major advantage, these fire-retardant coatings are devoid of any halogen atoms or heavy metals, often required in present day fire-barrier materials, and processed from water using sustainable building blocks. We expect that this continuous roll-to-roll coating process can be scaled to large quantities and implemented into existing coating technology. While we showcased the applicability on textiles, we believe it to be applicable on diverse substrates, and that further tuning of type of polymer system will allow an optimization of the properties and increased intumescent behavior. Further studies on these systems are currently under way.
6.5. Acknowledgement

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6.6. References and Notes


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6.7. Supplimentary Information

Figure SI 1: SEM images of the CMC$_{60}$MTM$_{40}$-1% coated fabric. (a-d) Microscopic images of the surface of CMC$_{60}$MTM$_{40}$-1%, (a,b) before burning, and (c,d,inset) after burning. The arrows guide the eye to locate the conformal coating of individual fibers.
Tough and catalytically active hybrid bio-fibers wet-spun from nanochitin hydrogels

A.1. Introduction

The activation of biomass and its processing into high-performance materials with advanced functionalities is decisive in developing sustainable alternatives for present-day functional materials based on increasingly depleted primary fossil resources. In the context of biobased polymer materials, it has been the general approach to, on the one hand, either degrade or ferment existing biopolymers into monomer units and then reutilize these building blocks for the synthesis of polymers, or, on the other hand, to fully dissolve the biomaterials into molecular polymer chains. The latter was extensively used to produce cellulose or chitosan from plants or crustaceans, respectively. However, despite long-term developments of materials based on these polymers, the resulting properties mostly fall drastically short of the ones found in the biological parent materials, which is due to disruption of higher order of the hierarchical natural structures.¹

For instance, there exists a long history on cellulose in polymer technology to use dissolution and recrystallization in the regeneration. This does not lead to the recovery of the same strong native crystalline structure, resulting in inferior mechanical properties. This even holds for fiber spinning, certainly one of the most advanced processing techniques able to induce a large-scale alignment of polymeric chains for the production of highest performance synthetic fibers.

Consequently, the shortcomings in mechanical properties suggest a different approach, in which the high-performance natural crystalline bionanomaterial is directly isolated and utilized instead of full dissolution and recrystallization procedures.
In the past decade there has been a great interest in nanocellulose,\textsuperscript{2-6} which can be divided into short cellulose nanowhiskers and long and entangled nanofibrillated cellulose. So far the main attention in nanocellulose was focused generating strong and tough nanopapers, biomimetic nanocomposites, and classical nanocomposites upon adding small contents to polymeric matrices, as well as in the fabrication of robust foams and aerogels.\textsuperscript{7-19} Toward functionalities, flexible magnetic and electroactive aerogels, homogeneous catalysis, and magnetic nanopapers were recently shown.\textsuperscript{8, 9, 20} Flexible and transparent sheets with low thermal expansion based on nanofibrillated cellulose were used as substrates for OLED displays.\textsuperscript{21} We and others recently demonstrated that nanofibrillated cellulose can be spun into high-performance fibers with excellent mechanical properties.\textsuperscript{22, 23}

In recent years, nanochitin whisker and nanofibril emerged as a second class of highly crystalline, renewable polysaccharide bionanoparticles.\textsuperscript{24, 25} Chitin is based on aligned chains of (1-4)-linked 2-acetamido-2-deoxy-\(\beta\)-D-glucopyranose units able to form strong intermolecular hydrogen bonds and can be isolated from a vast range of biomass sources. The isolation of nanochitin is particularly relevant for promoting sustainability as it activates a ton-scale waste product of the food industry (shrimp, crab, lobster) and allows transforming it into a potential high value added bionano-building block. This also contrasts earlier utilization of chitin as source for polymeric chitosan or for use as nonfunctional \(\mu\)m- and mm-sized filler particles in composites. Other conventional approaches deal with molecular dissolution of chitin in strongly solvating and partly hazardous solvents such as concentrated organic and aqueous LiCl solutions, hexafluoroisopropanol, or ionic liquids that are able to break the strong hydrogen bonds, and the use of these solutions for wet-spinning or film formation.\textsuperscript{26-28} Both chitin and chitosan are valuable polymers and materials for medical applications, for example, as tissue scaffolds and for wound dressings, as well as for antibacterial coatings.\textsuperscript{29-32} In general, research in the field of nanochitin is much more at its infancy compared to
nanocellulose and focused so far mostly on the controlled preparation of nanowhiskers and nanofibrils. Only a few reports exist on advanced characterization of the properties of these bionanoparticles, their chemical hybridization, and their use in standard nanocomposites or functional materials deriving thereof. Transparent and flexible films with low thermal expansion were recently reported.

Herein we will first show how to prepare strong and tough macrofibers by extrusion of hydrogels containing surface-deacetylated chitin nanofibrils into a coagulation bath. This is the first step toward implementing a full-scale wet-spinning. We will further reveal how to add functionality to these macrofibers by using the amine functions to host catalytically active noble metal nanoparticles, furnishing biobased, and renewable hybrid materials. These hybrid macrofibers can be used repeatedly for catalytic reductions without loss of activity, rendering them interesting as novel bioderived supports for nanoparticle catalysts. Thereby we demonstrate an integrative approach merging a simple low-energy preparation route to robust macrofibers based on a sustainable bionanomaterial with advanced functionalities deriving from the hybrid formation with inorganic synthetic nanoparticles.

A.2. Experimental

Materials. Ethanol (p.a. grade), THF (p.a. grade) and $\text{H}_2\text{PtCl}_6$ (99.9 %), $\text{NaBH}_4$ (99 %), p-nitrophenol (> 99 %) were purchased from Merck or Aldrich and used without further purification. Chitin powder was purchased from Nakalai Tesque.

Preparation of Surface-Deacetylated Chitin Nanofibrils (ChNF). Surface-deacetylated chitin nanofibrils were prepared based on a previously reported method. For partial deacetylation of chitin, commercial chitin powder was suspended in aqueous NaOH (20 wt%) and refluxed for 6 h. The deacetylated chitin was collected by centrifugation, and washed thoroughly with distilled water. The wet sample was dispersed in water at 1.35 wt%, and
acetic acid was added to adjust the pH value to 4 to facilitate nano-fibrillation. The dispersion was passed through a grinder (MKCA6-3; Masuko Sangyo Co., Ltd.) with the rotation speed of 1500 rpm. Grinder treatment was performed with a clearance gauge of -1.5 (corresponding to a 0.15 mm shift) from the zero position. The position was determined as the point of slight contact between the two grinding stones.

Fiber preparation. Macrofibers were prepared by extrusion of hydrogels containing surface-deacetylated chitin nanofibrils (ChNF, 1.35 wt%) through a syringe needle (typical diameter 1.9 mm) into a coagulation bath (e.g. ethanol, THF). After a certain aging time (typically 30 min) the wet fibers were removed from the bath and dried at ambient conditions.

Platinum nanoparticle loaded fibers. Fibers were prepared in various starting quantities according to the following general example. H₂PtCl₆ was added to the ChNF hydrogels in a weight ratio of 1/10 – 1/100 regarding the dry weight of the hydrogel. Thereafter, the suspensions were strongly mixed with a spatula and shortly ultrasonicated. After fiber extrusion in THF, the macrofibers were dried in the dark and subsequently swollen in 10 mM NaBH₄ solution overnight to reduce the PtCl₆²⁻ ions into Pt nanoparticles. The reduction resulted in dark fibers.

Catalysis. Catalytic reduction of p-nitrophenol with NaBH₄ in the presence of Pt nanoparticles immobilized on the macrofibers was performed at room temperature by adding a macrofiber (5 cm in length), previously rehydrated and conditioned in 10 mM NaBH₄ solution for 30 h, to a solution containing 3 mL p-nitrophenol solution (0.2 mM) and 3 mL of NaBH₄ solution (10 mM). The extent of reduction was monitored by UV-VIS spectroscopy of small samples (40 μL) diluted in water in a ratio of 1/20.
Methods

**Scanning electron microscopy (SEM)** was performed on a Hitachi S-4800 field emission microscope, typically operating at 1 – 1.5 kV. A thin gold coating was sputtered onto the fibers prior to imaging.

**Thermogravimetric analysis (TGA)** was done on both plain ChNF macrofiber and one modified with H$_2$PtCl$_6$ using NETZCH TG 209C instrument under continuous flow of 25 mL/min of N$_2$ over a temperature range of 25 - 800 °C at a heating rate of 20 K/min to find out the thermal behavior as well as the actual metal loading in the fiber. Both samples were approximately 6 mg in mass.

**Atomic force microscopy (AFM)** was performed on a Veeco Multimode in tapping mode conditions using standard silicon cantilevers (PPP-SEIH-W from Nanosensors) with a spring constant of 4 N/m and an oscillation frequency of 75 kHz.

**Cryogenic transmission electron microscopy (cryo-TEM)** was done by placing a drop of the sample on a plasma-treated lacey carbon-coated copper grid, from which most of the liquid was removed with blotting paper, leaving a thin film stretched over the lace. The specimens were instantly vitrified by rapid immersion into liquid ethane and cooled to approximately 90 K by liquid nitrogen in a temperature controlled freezing unit (Zeiss Cryobox, Zeiss NTS GmbH, Oberkochen, Germany). The temperature was monitored and kept constant in the chamber during all of the sample preparation steps. After freezing, the specimen was inserted into a cryo-transfer holder (CT3500, Gatan, München, Germany) and transferred to the Zeiss LEO 922 OMEGA TEM, operating at 200 kV. Zero-loss filtered images were recorded at temperatures around 90 K.

**X-ray Diffraction (XRD)** analysis was obtained with Ni-filtered Cu Kα from an X-ray generator (Shimadzu XRD-6000) operating at 40 kV and 30 mA.
**Solid-State** $^{13}$C NMR experiments were performed on a Bruker AV700 NMR spectrometer operating at a proton frequency of 700.02 MHz and a $^{13}$C frequency of 176.08 MHz. $^{13}$C NMR data were recorded for spinning samples that were placed in a 3.2 mm rotor under cross-polarization magic-angle spinning (CPMAS) condition and were spinning at 5 kHz. The duration of the 90° pulse, the dead time of the spectrometer, the dwell time, the contact time, the recycle delay time and the acquisition time were 2 μs, 6 μs, 4 μs, 1.5 ms, 7 s, and 49 ms, respectively. A typical number of 8192 scans were acquired for each spectrum. All experiments were conducted at 23 °C.

**Elemental Analysis** was performed to calculate the degree of substitution values of amino group of the chitin nanofibers from the C and N contents in the elemental analysis data by using elemental analyzer (Elementar Vario EL III, Elementar).

**Calculation of the shell thickness containing the hydrolyzed chitosan units.** We used a simple geometrical model to estimate the potential thickness of the shell containing the hydrolyzed chitosan units. The model is based on assuming infinitely long cylinders and a constant density for chitin and chitosan units. For an infinitesimally thin slice of these cylinders, the cross sectional area of the nanofibril ($R_{\text{cryo-TEM}} \approx 4.5$ nm) can be calculated to $A_{\text{total}} = 63.6 \text{ nm}^2$. Assuming equal densities for chitin and chitosan units, one can calculate the fractional area occupied by chitosan units ($A_{\text{chitosan}} = 6.7 \text{ nm}^2$, 10.6 % of hydrolyzed chitosan as derived from elemental analysis). Considering that the deacetylation occurs concentrically at the surface, $A_{\text{chitosan}}$ can be subtracted from the total area, $A_{\text{total}}$, as a shell, furnishing the residual area of non-hydrolyzed chitin of $A_{\text{chitin}} = 56.9 \text{ nm}^2$. This yields a radius of the residual area of crystalline chitin of 4.25 nm surrounded by a thin shell of only 0.25 nm. Since the cross section of one chitosan unit is however closer to 0.5 nm and the interchain distance perpendicular to the sheet-like arrangement of the aligned polysaccharide chains in the [---]
chitin crystal (a-axis) is ca. 0.47 nm\(^\text{37}\), it can be concluded that only around 50 % of all surface units are in fact hydrolyzed.

**Mechanical tests** in tension were carried out on a Zwick Universal tensile testing machine with a 100N load cell. All measurements were conducted at room temperature and an average humidity of 65%. As the ChNF-based macrofibers exhibit an uneven cross section along the fiber, we calculated the average acting fiber diameter by weighing a fiber of certain length and recalculating the volume and diameter via a small density for nanocrystalline polysaccharide materials (1.5 g/mL). This is a very conservative approach and the obtained values are above the smallest diameters observed by SEM. Five samples were considered to calculate the average values.

**A.3. Results and Discussion**

The chitin nanofibrils (ChNFs) were prepared by a two step process, employing first an alkaline hydrolysis of commercial chitin powder in 20 wt% NaOH, and subsequently a wet disintegration by a high-shear grinder equipment having specially designed pair of grinding stones at a pH value of 4. The acidification leads to a charge-up of the amine groups of the partly deacetylated chitin and causes electrostatic repulsion between nanofibrils. Consequently, the acidic condition aids both in an eased nano-fibrillation, as well as in an enhanced stabilization of ChNFs. The X-ray diffraction analysis (XRD, Figure 1a) of the starting material exhibits four diffraction peaks at \(2\theta \approx 9.5^\circ, 19.5^\circ, 20.9^\circ, \) and \(23.4^\circ\), which are characteristic for the 020, 110, 120, and 130 planes of \(\alpha\)-chitin, respectively. The XRD analysis of the ChNFs shows peaks that closely coincide with the original diffraction peaks of \(\alpha\)-chitin and present an overall similar shape concerning peak intensity, width and distribution. This allows to conclude a near constant relative crystallinity index and crystalline size and shows that deacetylation mainly takes place on the nanofibril surface while the original crystalline structure is maintained in the core part.
Figure 1. (a) X-ray diffraction analysis of surface-deacetylated ChNFs and the starting material α-chitin. (b) $^{13}$C CP-MAS solid-state NMR spectra of surface-deacetylated ChNF. Spinning sidebands, marked by stars, are separated from the centerbands by ± 28.4 ppm.

$^{13}$C CP-MAS solid state NMR of dried ChNFs further underscores the predominant structural integrity of the α-chitin. The peaks closely resemble those of pure α-chitin. The comparably small peak of the carbonyl group at 173 ppm is caused by lower polarization transfer due to the absence of directly attached hydrogen atoms and the appearance of pronounced spinning sidebands. The absence of doublets for the C-4 signal around 86 ppm and for the C-6 signal around 59 ppm, characteristic of fully hydrolyzed chitosan, confirms a low degree of deacetylation (Figure 1b). From earlier investigations, it is however also known that the peaks for C3 and C5 continuously merge from a peak with two well separated maxima for pure α-chitin into a single peak at a degree of deacetylation of 20 mol%. The near merger of these two peaks found in our chitin nanofibrils hence strongly indicates some hydrolysis, which can be estimated between 5 – 20 mol%. A precise value for the degree of deacetylation can be obtained by elemental analysis comparing the C and N content, which yields a molar fraction of hydrolyzed units of 10.6 mol%. In conclusion, the combination of analytical techniques allows concluding that the resulting nanofibrils maintain their α-chitin structure in the core and are slightly deacetylated on the surface. A schematic drawing of the
resulting core-shell structure of these surface-deacetylated chitin nanofibrils is also presented in Scheme 1.

The resulting dispersion forms strong hydrogels in water at the utilized concentration of 1.35 wt%. We used cryogenic transmission electron microscopy (cryo-TEM) to characterize the particle shape of the nanofibrils. In cryo-TEM, a thin ($\leq 150$ nm) film of an aqueous dispersion spanning over the holes of a TEM grid is rapidly vitrified and then transferred into a TEM instrument under cryogenic conditions while maintaining the vitrified, noncrystalline state of water. This allows examining the dispersed particles in a near unperturbed quasi in-situ state in water and drying artifacts, as possibly encountered in atomic force microscopy or scanning electron microscopy, can be excluded.

![Cryo-TEM images](image)

*Figure 2. Cryo-TEM images obtained from concentrated (a, ca. 0.5 wt%) and dilute dispersions (b, ca. 0.05 wt%)*

Figure 2 depicts cryo-TEM images obtained from high concentrations ($c \approx 0.5$ wt%, a), in which a hydrogel is formed, and at low concentrations ($c \approx 0.05$ wt%, b) of a freely flowing dispersion. The image at higher concentration clearly depicts several micrometer long and entangled nanofibrils, whose mechanical interlocking and hydrogen-bonding association leads to gel formation. At higher dilution, individual nanofibrils with high intrinsic stiffness can be observed more easily and an analysis of the cross sections reveals the diameters to be in the range of $7 - 15$ nm with a majority fraction centered around 9 nm. A slight longitudinal
aggregation of individual nanofibrils into loose bundles can be observed, which can be attributed to some incomplete fibrillization or secondary aggregation in dispersion due to insufficient repellency and strong hydrogen bonding. Assuming a similar density for the α-chitin inside the core and the deacetylated chitosan on the outside of the nanofibrils, the thickness of the shell containing the deacetylated groups can be calculated to ca. 0.25 nm at an average diameter of 9 nm and a degree of deacetylation of 10.6 mol% (details can be found in the experimental section). Because the cross section of one chitosan unit is however closer to 0.5 nm and the interchain distance perpendicular to the sheet-like arrangement of the aligned polysaccharide chains in the α-chitin crystal (a-axis) is ca. 0.47 nm it can be concluded that only around 50% of all surface units are in fact hydrolyzed. This small value for the thin shell is therefore in good agreement with the persisting shape of the XRD patterns, which indicated a similar degree of crystallinity and crystalline size before and after the fibrillization, as discussed above (Figure 1a).

The macrofibers were prepared by simple wet-extrusion of a hydrogel containing surface-deacetylated chitin nanofibrils at a concentration of 1.35 wt% into coagulation solvents, e.g. ethanol or tetrahydrofuran (Scheme 1). The prerequisites for the coagulants are miscibility with water and moderate polarity and hydrogen bonding ability. During solvent exchange, the infiltrated organic solvent reinforces interfibrillar hydrogen bonding and leads to the formation of stable macrofibers. The resulting organogel macrofibers can thereafter be removed, typically after 30 min inside the coagulation bath, and are dried at ambient conditions. Importantly, the process is cost-effective, energy efficient, and straightforward. The simplified water removal from the highly hygroscopic ChNF macrofibers is also central for large-scale applications. The overall process presents a versatile platform technology, and allows for the entrapment of functional materials by co-dispersion of additives into the
precursor hydrogel matrix. We will demonstrate this below for the fabrication of catalytically active inorganic/organic hybrid macrofibers.

Scheme 1. Preparation of ChNF-based macrofibers based on extrusion of ChNF hydrogels into a coagulation bath and drying. The top right side depicts the repeating units of chitin, dominantly found in the core, and of chitosan that can be found on the surface due to soft hydrolysis.

On a macroscopic level, the ChNF-based macrofibers exhibit a whitish appearance, which originates from certain porosity and light scattering at internal ChNF/air void interfaces (Figure 3b). The cross sections of the as far prepared macrofibers are not perfectly circular and vary slightly along the length. This can be attributed to some flattening during the aging in the coagulation bath and to some imperfections already present within the ChNF hydrogel because of the strong interfibrillar attraction. However, considering that the nanochitin material has been extracted from a natural resource without breaking down the crystalline secondary structure and only using water-based treatments combined with a mechanical homogenization procedure, and not prepared synthetically from well controlled low-molecular weight petrochemical components and their polymers, we find the macroscopic quality of the final material promising.

We used scanning electron microscopy (SEM) and atomic force microscopy (AFM) to examine the surface morphology and nanoscopic order of the individual nanofibrils (Figure 3
a, c-f). A longitudinal structuring of the macrofiber on the micrometer scale can be observed as imposed from the shearing process during the extrusion. However, only a random network of ChNF can be observed at higher magnification as both depicted in AFM and SEM images. The shear forces created during the extrusion are yet insufficient to allow for a global alignment of the nanofibrils and realization of their full mechanical reinforcement effect. The observation of intact nanofibrils at the surface confirms their structural integrity during the coagulation procedure in ethanol.

![Figure 3. SEM images of the macrofibers.](image)

Figure 3. SEM images of the macrofibers. (a,c,d) SEM images of a macrofiber prepared via wet extrusion of a ChNF hydrogel at various magnifications. Digital photograph (b) of an as-prepared macrofiber of ca. 12 cm length. Shaded topography (e) and height (f) AFM images with a z-scale of 47 nm.

The tensile mechanical properties reveal a good combination of tensile strength, ductility and stiffness with lightweight material character (Figure 4). We determined the Young’s modulus to be $3.0 \pm 0.2$ GPa with a tensile strength of $91 \pm 5$ MPa at a maximum elongation of about $14 \pm 3\%$. This yields a large work-of-fracture, as estimated via the integral area under the stress-strain curve, of $9.8 \pm 0.3$ MJ/m$^3$. In comparison to macrofibers based on nanofibrillated cellulose, these ChNF-based macrofibers are less stiff and less strong but undergo substantially larger inelastic deformation and require a higher work to fracture.$^{22, 23}$ The macrofibers display a large plastic, ductile strain regime in the range of $2 - 14\%$ strain,
in which frictional sliding and reorientation of the nanofibrils takes place allowing efficient dissipation of fracture energy.

![Stress-strain curve](image)

**Figure 4.** Stress-strain curve of a surface-deacetylated chitin nanofibril-based macrofiber measured at 65% relative humidity and at 23 °C.

Stiffness and ultimate strength are three times higher compared to a typical, molecularly dissolved and recrystallized chitosan film. Furthermore, the ChNF macrofibers are in range with fibers based on molecular chitosan, which recrystallize during the preparation. Typical values for those range in stiffness from 2.5 to 10 GPa and tensile strength from 80 to 200 MPa for unstretched and stretched fibers, respectively, at elongations from 3 – 8%. Forced spinning of different grades of molecularly dissolved chitins from ionic liquids yet leads to better properties, depending on the chitin source and pretreatments, as compared to the unstretched fibers here. Qin et al. reported wet-spun chitin fibers with Young’s moduli in the range of 4.7 – 10 GPa, tensile strength of 80 - 237 MPa at maximum elongation of 3.3 – 13 %. In terms of eco-friendliness, our waterborne process does however not necessitate the use of ionic liquids, fluorinated solvents or large salt concentration (e.g. LiCl) to break the hydrogen-bonding of pristine chitin typically used in its wet-spinning process.

We expect that substantially higher values are in reach upon more efficient alignment of the surface-deacetylated chitin nanofibrils by using additional wet-drawing procedures in an up-scaled wet-spinning process. However, this requires mastering the challenge of an all-
colloid wet-spinning and wet-drawing procedure, which is considerably different to the wet-spinning of molecularly dissolved polymers. Further results on the influence of the extrusion rate and wet-drawing on the mechanical properties will be reported in due course.

The good mechanical performance is accompanied by an excellent thermal stability. Thermogravimetric analysis reveals an onset of degradation above a temperature of 280 °C. This allows for a substantial application range in functional fiber technology (Figure 5).

![Thermogravimetric analysis of a ChNF-based macrofiber.](image)

Figure 5. Thermogravimetric analysis of a ChNF-based macrofiber.

Next, we will demonstrate how to functionalize these ChNF macrofibers with a focus on hybrid inorganic/organic conjugates with metallic nanoparticles (NPs) to prepare catalytically active macrofibers as recyclable catalyst carriers. The available amine functionality of the partly hydrolyzed chitin repeating units at the surface of the ChNF is particularly beneficial as it allows for ionic interaction and tight coordination to metals salts (or molecules) to prepare metal, semiconducting and metal oxide particles.

We used H$_2$PtCl$_6$ as precursor salt to generate catalytically active platinum (Pt) NPs attached to the ChNFS (Figure 6a). The acidic H$_2$PtCl$_6$ is able to form strong ionic complexes with the hydrolyzed chitosan surface groups and potentially also chelate-type coordination bonds with vicinal diols found in the saccharide motifs, leading to a tight binding between the
inorganic salt and biobased nanofibrils. Similarly, both types of chemical affinities stabilize and bind the resulting Pt-NPs to the ChNF. The precursor salt was mixed with the ChNF hydrogels in weight ratios of metal salt/ChNF = 1/10 - 1/100, corresponding to the dry weight of the hydrogel. After wet-extrusion into a THF coagulation bath, drying and subsequent reduction in an excess aqueous 10 mM NaBH₄ solution, intensely colored fibers were obtained, indicating the successful preparation of Pt-NPs on the ChNF-based macrofibers. Figure 6b depicts a dark brownish macrofiber loaded with Pt-NPs at an initial weight ratio of H₂PtCl₆ to ChNF of 1/10. Interestingly, the fiber formation process and the macroscopic fiber stability are similar compared to pristine ChNF despite incorporating up to 10 wt% dry weight of salt during the fiber formation process.

Figure 6. Hybrid inorganic/organic nanoparticle-loaded nanochitin macrofibers. (a) Schematic preparation by coextrusion of metals salts and subsequent reduction with NaBH₄ solution. (b) Photograph of an intensely colored macrofiber loaded with Pt-NPs (after reduction). (c) Cryo-TEM image of Pt-NPs bound to fibrillar aggregates of ChNF in the gel state. Dry weight ratio of ChNF to H₂PtCl₆ is 10/1.

Due to the strong interfibrillar hydrogen bonding interactions, the macrofibers only swell in water once dried, thereby providing a beneficial larger surface area due to possible diffusion within the gel network, yet they do not undergo disintegration. In fact the macrofibers remain intact during moderate stirring with a magnetic stirrer and a loss of NP cannot macroscopically be detected by the naked eye. The strong binding to the nanofibrils can be visualized by cryo-TEM of Pt-NPs generated within ChNF-based hydrogel (Figure 6c). The images clearly depict a fibrillar arrangement and strong attachment of the NPs to the nanofibrils and bundles of nanofibrils. The main fraction of the diameter of the NPs is in the
range of 4–5 nm. Importantly, free NPs can hardly be observed. Some inhomogeneous
distribution of the NPs among the nanofibrils can be attributed to an efficient binding and
kinetic trapping of the metal salt to those nanofibrils present in the top volume of the
hydrogel, to which the salt solution (H₂PtCl₆) is added. A full redistribution of metal salt,
prior reduction, into a fully homogeneous material may require longer aging and high shear
treatment.

The macroscopically and microscopically observed good binding prompted us to explore
these NP-loaded composite fibers as recyclable, biobased catalyst carriers. We selected the Pt-
catalyzed reduction of p-nitrophenol by NaBH₄ as model reaction to investigate the catalytic
properties of the Pt-NP loaded macrofibers.⁵¹,⁵² The total Pt loading of the fiber was 2 wt% as
deduced from TGA analysis of the hybrid fiber (see Figure S1, Supplementary Information).

![Figure 7. Catalytic reduction of p-nitrophenol (c = 0.1 mM) with NaBH₄ (5 mM) using Pt-NP loaded macrofiber. (a) Absorption spectra at different reaction times for the third consecutive run. Samples of less than 1 % of the total volume were withdrawn from the mixture to minimize concentration changes between immobilized Pt NPs and reactants. The samples were diluted 1/20 v/v before measurement. Double-linear (b) and semi-logarithmic (c) plot of the relative decrease in concentration of reactant for five consecutive catalytic reaction cycles as a function of time.](image)

The reaction was simply started by adding a piece of well swollen Pt-ChNF macrofiber to
a small reaction vessel, containing the substrate and reducing agent. The occurring reaction
can be conveniently followed by UV-VIS spectroscopy by analyzing small aliquots. Figure 7a
depicts the time-dependent changes and shows the disappearance of the characteristic
absorption peak of p-nitrophenol at 400 nm and the appearance of a new peak at 290 nm,
corresponding to the product, p-aminophenol. The observation of two isosbestic points at 278 nm and 312 nm confirms a smooth and clean conversion, free of side reactions, and a constant total molar concentration of educt plus product.

To investigate the repeatability of the reaction and stability of the catalytic particles, we transferred the Pt-NP loaded macrofiber after completion of one given run to a new vessel containing fresh reactants and repeated the reaction several times. Figure 7b displays a comparison of five consecutive reaction runs, all of which show near constant reaction speeds, confirming no loss of activity during repeated catalytic cycles and an excellent stability of the Pt-NPs entrapped on the macrofibers. The utilization of intermediately dried fibers as macroscopic catalyst scaffold represents a major advantage over, for example, Pt-NP coordinated to nanofibrils in hydrogels, as the swollen macrofiber can simply be handled and moved from one reaction vessel to another. This were not the case for Pt-NP loaded nanofibrils in the initial hydrogel state or for freely flowing dispersion at higher dilution, which would require centrifugation to separate the product from the Pt-NP/nanofibril hybrids and redispersion of the latter to start another reaction. Overall the reactions run to completion within 30 – 40 min, which is fast considering the partly heterogeneous character of the reaction taking place at and partly within the swollen macrofibers and the moderate Pt-loading. Since the NaBH₄ concentration is in large excess compared to the substrate concentration, the reaction can be treated as quasi-first order reaction following equation 1.

$$-\frac{dc_t}{dt} = k_{app}c_t$$  

(1)

Based on the semi-logarithmic plot (Figure 7c), the average apparent rate constants can be calculated to be centered around $9.3 \pm 0.5 \times 10^{-4}$ s⁻¹. All values are in a rather narrow window, which further underscores that no loss of potentially loosely bound NPs occurs, thereby
validating the concept of using biobased surface-deacetylated chitin nanofibril scaffolds as recyclable carriers to tightly host functional inorganic materials.

A.4. Conclusions

We demonstrated that hydrogels consisting of pure highly crystalline surface-deacetylated chitin nanofibrils can be wet-extruded into mechanically robust macrofibers, suited to host inorganic nanoparticles as functional materials. The direct quasi in situ imaging with cryogenic TEM confirms the ChNF hydrogels to be constituted of micrometer-long nanofibrils with diameters centered around 9 nm. A further comparison with $^{13}$C CP-MAS solid state NMR, XRD and elemental analysis allows assigning a core-shell structure to these nanofibrils, in which the highly crystalline chitin core is surrounded by a thin, partly hydrolyzed shell. Approximately 50% of the chitin surface units are deacetylated and contribute to electrostatic stabilization. The facile water-borne fiber generation process is the first step toward implementing a full scale colloid wet-spinning procedure. The mechanical properties of the resulting macrofibers are substantially different to the ones obtained from nanofibrillar cellulose by presenting much larger strain to failure and work-to-fracture, yet lower stiffness and strength. The resulting macrofibers, although produced in a waterborne processing scheme, do not undergo redispersion in water once dried, which is due to strongly enforced interfibrillar hydrogen bonding once dried. We exploited this effect by using the macrofibers in water-based applications as recyclable catalyst carriers.

The macrofibers can simply be loaded with platinum nanoparticles by facile coextrusion of salt precursor and subsequent reduction to furnish inorganic/organic hybrid macrofibers. These swollen gel-like fibers showed high activity in the catalytic reduction of p-nitrophenol with NaBH$_4$. More importantly, the catalytic model reactions could be repeated with similar efficiency during several runs, thereby confirming no or only insignificant loss and high stability of metal NPs. Due to the remaining structural integrity, the fibers can simply be
handled with hands or tweezers. This represents a feasible combination of catalytic reactivity and eases of separation, in-between the benefits of homogeneous and heterogeneous catalysis, and renders the hybrid materials interesting as robust and recyclable green catalyst supports. Using the same immobilization concept, we foresee that further advancements are possible by improving the porosity of the supports, for example, by employing rehydrated aerogels that retain their porous structure during reswelling and extending it to different nanomaterials. Such simple recyclable catalyst systems can also become suitable as simple water-purification systems upon incorporation of photocatalytic NP (TiO$_2$) as needed in developing countries with large chitin wastes. Overall, the presented procedure demonstrates a simple platform technology of how to create highly functional and mechanically robust macroscopic fibers and materials deriving thereof, based on a sustainable resource, as directly relevant for past-oil technologies.

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A.6. References and Notes


Appendix A


A.7. Supplementary Information

Thermogravimetric Analysis of ChNF and ChNF/Pt-based macrofibers:

Thermal analysis shows that both the macrofibers are thermally stable up to 280 °C and then follow a sharp degradation in between 280° and 450 °C and after that the weight loss is remained more or less constant. Nearly 2.05 wt% of Pt metal has been successfully incorporated in ChNF/Pt macrofiber as estimated from TGA. This value is very close to the theoretical value of metal loading, 3.8 wt%. So, ca. 53% metal loading efficiency has been achieved in this case. Small loss in metal loading may be attributed due to incomplete reduction of metal precursor to metal NPs in macrofiber.

Figure S1: Thermal stability of the ChNF and ChNF/Pt-based macrofibers and estimation of Pt metal loading in Pt ChNF macrofiber.
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