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Deoxyguanosine Phosphate Mediated Sacrificial Bonds Promote Synergistic Mechanical Properties in Nacre-Mimetic Nanocomposites

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Nacre, biomimetics, nanocomposite, self-assembly, montmorillonite, supramolecular

ABSTRACT

We show that functionalizing polymer-coated colloidal nanoplatelets with guanosine groups allows synergistic increase of mechanical properties in nacre-mimetic lamellar self-assemblies. Anionic montmorillonite (MTM) was first coated using cationic poly(diallyldimethylammonium chloride) (PDADMAC) to prepare core-shell colloidal platelets, and subsequently the remaining chloride counter-ions allowed exchange to functional anionic 2'-deoxyguanosine 5'-monophosphate (dGMP) counter-ions, containing hydrogen bonding donors and acceptors. The compositions were studied using elemental analysis, scanning and transmission electron microscopy, wide angle X-ray scattering, and tensile testing. The lamellar spacing between the clays increases from 1.85 nm to 2.14 nm upon addition of the dGMP. Adding dGMP increases the elastic modulus, tensile strength, and strain 33.0 %, 40.9 %, and 5.6 %, respectively, to 13.5 GPa, 67 MPa, and 1.24 %, at 50 % relative humidity. This leads to an improved toughness seen as a ca. 50 % increase of the work-to-failure. This is noteworthy, as previously it has been observed that connecting the core-shell nanoclay platelets covalently or ionically leads to increase of the stiffness, but to reduced strain. We suggest that the dynamic supramolecular bonds allow slippage and sacrificial bonds between the self-assembling nanoplatelets, thus promoting toughness, still providing dynamic interactions between the platelets.

Introduction

Biological nanocomposites, e.g. nacre, spider silk, bone, antler, teeth, and insect cuticle,¹ show synergistically high stiffness, strength, and toughness.² The excellent properties originate from the self-assembled structures of hard reinforcing and soft energy dissipating domains.^{3,4} But the natural materials can be difficult to scale up and to engineer from the first principles, and they are characteristically not economical. Biomimetics^{1,2,5,6} aims to reproduce some of the properties of natural structural materials, using rationally engineered and scalable components and processes.

Nacre is a biological composite composed of 95 vol% inorganic nanoscale platelets of aragonite, an orthorhombic polymorph of CaCO_3 , which are "glued" together by a small fraction of proteins and chitin.⁷ Nacre is stiff (tensile modulus = 60 – 90 GPa) and strong (tensile strength = 60 – 140 MPa), like ceramics in general, but it has also remarkably high toughness:⁷⁻¹⁰ Under wet conditions it has a toughness of ca. thousand times higher than pure aragonite.^{7,8} Several energy dissipation concepts have been identified.¹⁰⁻¹³ Frictional platelet sliding^{8,10,14} has been suggested as one of the key toughening mechanisms where the organic phase acts like a lubricant by allowing controlled mutual movement of the platelets, thus providing energy dissipation in deformation. Additionally nanoscale mechanisms, such as stiffening of biopolymer upon stretching limit the sliding of the aragonite platelets.^{8,15,16} Therein sacrificial bonds and hidden length scales are characteristic for biological composites.¹⁷⁻¹⁹

The nacre-like complexity is difficult to transfer into synthetic materials to reproduce the mechanical behavior, as the highly ordered self-assembled structure and supramolecular interactions need to be mimicked at several length scales. Nacre has been mimicked by sequential deposition processes,²⁰⁻²⁵ which are, however, not scalable and which are prohibitive

when macroscale sample thicknesses are aimed. Ice-templating and sintering allows tough nacre-mimics but suffer from a multistep process.^{26,27} Platelet-shaped nanoclay is a very promising choice for nanocomposites as when the scale is reduced, the platelets shows better enhancement efficiency than the fiber reinforcement at the same scale because of the interphase effects.²⁸ Recently a one-step scalable method of mimicking nacre by self-assembling nanoclay and polymers was shown^{29,30}, which allows high strength and stiffness, but requires further molecular engineering to implement dissipation mechanisms for promoted toughness. The key step in this approach is to bind a polymer layer on the surface of exfoliated clay platelets to yield core-shell platelets with intrinsic hard/soft character. Water removal after doctor-blading or filtering leads to packing into aligned self-assemblies of alternating montmorillonite (MTM) and polymer layers. In poly(vinyl alcohol) coated MTM system, the core-shell platelets were finally cross-linked using boric acid.²⁹ This increased strength and stiffness but it reduced strain-to-failure, as very little energy dissipation was allowed due to restricted mutual movement of the platelets in deformation. This suggested to incorporate weaker supramolecular interactions to allow dissipative deformations. It had been suggested that opening random ionic bonds would consume energy.³¹ However, ionic interlocking by multivalent ions in polyelectrolyte coated nanoclay self-assemblies essentially behaved similarly as the covalent case, thus hinting that the used ionic interaction is still too strong.³⁰ This raises the question whether even weaker hydrogen bonds would allow energy dissipation under deformations to increase the toughness.

Here we designed core-shell nanoplatelets of MTM coated by cationic poly(diallyldimethylammonium chloride) (PDADMAC), aiming to exchange the peripheral chloride counter-ions to 2'-deoxyguanosine 5'- monophosphates (dGMP). The latter moieties have several hydrogen bonding accepting and donating sites capable of several bonding

architectures³²⁻³⁴ thus promoting hydrogen bonding interactions between the colloidal platelets. In particular, the hypothesis was that the reversible hydrogen bonds allow sacrificial bonds and mutual sliding of the platelets for energy dissipation.

Experimental Section

Materials. The clay was a natural montmorillonite (MTM, Cloisite Na⁺, Southern Clay Products/ROCKWOOD Clay Additives GmbH, Moosburg, Germany), with an interlayer spacing of 1.17 nm and a cation-exchange capacity of 92.6 meq/100 g. An aqueous clay dispersion (0.5 wt%) was prepared. To guarantee delamination of hydrophilic clay platelets; the clay was added little by little into water, and stirred for 24 h under intense stirring. The dispersion was allowed to sediment for 24 h and the supernatant was used in the experiments.

Poly(diallyldimethylammonium chloride) (PDADMAC, $M_w = 200,000 - 350,000$ g/mol, 20 wt% aqueous solution, Sigma-Aldrich) and 2'-deoxyguanosine 5'-monophosphate sodium salt hydrate (dGMP, $\geq 99\%$, Sigma-Aldrich) were used as received. High purity deionized MilliQ water was used in all experiments.

Film Preparation. PDADMAC and dGMP were separately dissolved in water as 1.0 wt % and 3-4 wt % solutions, respectively. **Figure 1** shows the supramolecular preparation route for the present nacre-mimetic films. The clay suspension was added into the polymer solution dropwise under vigorous stirring. The polymer-clay platelet dispersion was then stirred at least for 24 hours to complete polymer adsorption and ensure exfoliation. The unbound polymer was twice removed by centrifuging and changing the water after which there was no clear positive reaction of chloride with silver nitrate (AgNO₃). The suspension was next divided into two aliquots. The first aliquot was modified with dGMP. The dGMP solution was mixed into the washed polymer-

clay dispersion and left in stirring at least 24 h, after which extra ions and dGMP were washed away. The second aliquot served us reference, i.e., no dGMP was added, yet the same washing was conducted as for the dGMP-modified aliquot. Finally, disc-shaped films were prepared from both aliquots by vacuum filtration through hydrophilic polytetrafluoroethylene membranes (LCR, FHL C04700, and Omnipore, JHWP04700, Membrane Filters, Millipore) with a pore size of 0.45 μm and subsequent drying at 40°C at least 48 h and then further dried in vacuum, while applying a slight weight to maintain planar shape.

Figure 1. The preparation of self-assembled nacre-mimetic structure involving hydrogen bonds: First the anionic nanoclay (MTM) platelets are coated with cationic polymer (PDADMAC) via adsorption. Excess polymer is removed by washing. Hydrogen bonding molecules, anionic dGMP, were introduced into structure resulting in polymer-coated clays, which were linked by hydrogen bondings due to recognition sites (D and A).

Mechanical Testing. The samples were conditioned and measured under controlled humidity, as listed in **Table S1** (see SI). The samples denoted as “dry” were vacuum dried at least 36 h. The conditioning and all the measurements were done at 21 - 24 °C. Tensile testing was carried out on a DEBEN Microtest 200 N tensile tester equipped with MT 10250 controller (Deben UK Ltd, Suffolk, UK). A nominal strain rate of 0.1 mm/min, 200 N load cell and gauge length of 10 mm were used. The strain was determined optically by Digital Speckle Photography (DSP) system. Aramis 6.2 (GOM GmbH, Germany) or Vic 2D (Limes Messtechnik and Software GmbH) was used for digital image correlation. The images of the specimen were recorded by two (with the Aramis 6.2) or one (with the Vic 2D) high-resolution cameras (5 MB) with same time step as the tensile tester (2 images/s). If just one camera was used, the camera was aligned carefully perpendicular to the surface of the samples.

The thickness and width of each specimen was measured. The width was measured with digital slide gauge (Digimatic, Mitutoyo) and thickness with linear gage (LGF-01100L-B transmission-type photoelectric linear encoder, Mitutoyo) three times before the speckle patterning and conditioning. The speckle pattern for DSP was sprayed on the samples by airbrush and then ribbons (average size of 18 mm x 2.1 mm x 80 μ m) were glued on sandpaper from their ends to facilitate the clamping.

The thickness, width, load and strain values were imported into MATLAB for further processing. The engineering stress (i.e. load/initial cross-sectional area), Young's modulus and work-to-failure (area under the curve) were calculated. The Young's modulus was usually determined up to 0.04 strain% where the samples behaved linearly. At least 5 specimens of each composite film were measured and used in the calculations (exact number of specimens listed in **SI Table S1**). The average curves shown in **Figure 4** were obtained by linear interpolation and

extrapolation till the average maximum strain of the specimens. The error bars are the standard deviation.

WAXS Characterization. Wide-angle x-ray scattering (WAXS) measurements were performed in vacuum with a rotating anode Bruker Microstar microfocus X-ray source (Cu K α radiation, $\lambda = 1.54 \text{ \AA}$) equipped with Montel focusing optics (Incoatec). The distance between the sample and the Bruker V α ntec 2D area detector was 80 mm. The magnitude of the scattering vector is given by $q = (4\pi/\lambda) \sin\theta$, where 2θ is the scattering angle. Positions of reflections have been obtained by fitting Gaussian peaks together with an appropriate background to Lorentz corrected data.

Cryo-TEM Characterization. Transmission Electron Microscopy (TEM) of microtomed sections was performed on a JEOL JEM-3200FSC Cryo-TEM, operating at liquid nitrogen temperature. Freeze-dried composite samples were sectioned at $-40 \text{ }^{\circ}\text{C}$ using a Leica UC7 ultramicrotome. The thin ($\sim 70 \text{ nm}$) sections were deposited on lacey carbon grids and re-hydrated with water for 5 min. The samples were then blotted and subsequently vitrified in a mixture of liquid ethane and propane ($-180 \text{ }^{\circ}\text{C}$). Zero-loss imaging of vitrified samples was carried out with JEOL JEM-3200FSC 300 keV TEM operated at liquid nitrogen temperature.

SEM Characterization. Scanning Electron Microscopy (SEM) was carried out on a JEOL JSM7500FA field emission microscope with acceleration voltage of 1.5 - 2 keV. The cross-sections were obtained as a result of tensile test or prior to mechanical testing simply by bending by hand until a specimen ruptured. A thin platinum, Pt, layer was sputtered onto the samples (Emitech K950X/K350, Quorum Technologies Ltd, Kent, UK).

Elemental analyses, EA, were performed by Mikroanalytisches Labor Pascher (Remagen-Bandorf, Germany). Hydrogen, carbon, nitrogen, chlorine and phosphorus were determined (see **SI Table S2**) at least two parallel samples were used.

Results and Discussion

Structure and composition. The amount of nitrogen, based on elemental analysis (see **SI Table S2**), indicates that the MTM/PDADMAC composites (i.e. without dGMP) contain 23 ± 2 wt% of PDADMAC. The molar ratio of chlorine to nitrogen showed that 39 ± 2 % of the amino groups of PDADMAC still have the chloride counter-ions. These amino groups are not electrostatically bound to the MTM surface, as they are in the center of the PDADMAC layers or in the peripheral surface of the core-shell MTM/PDADMAC platelets, and especially the latter ones are available for further complexation. After modification with dGMP there was only 12 ± 5 % chloride containing amino groups available and phosphorous (0.72 ± 0.05 wt%) was observed, which confirms that most of the chlorine ions were exchanged to dGMP. The dGMP modified films contain 8 ± 1 wt% of dGMP and 18 ± 2 wt% of PDADMAC. The two types of compositions are denoted as MTM/PDADMAC and MTM/PDADMAC/dGMP.

SEM micrographs of the film cross-sections (**Figure 2 A-B**) show layered nacre-mimetic structures highly aligned at macroscale for both MTM/PDADMAC and MTM/PDADMAC/dGMP. High-resolution TEM electron micrographs (**Figure 2 C-D**) reveal in more detail the well-ordered stacks of alternating hard clay and soft polymer layers. The darker parts are nanoclay platelets as even the internal crystalline structure of MTM is visible in the high magnification TEM images. The layered structure is further confirmed by WAXS (**Figure 3**), which shows the first (q^*) and second ($2q^*$) order diffraction peaks. The characteristic

spacing of the self-assembled nanoclay platelets can be calculated from the maximum of the q^* via $d = 2\pi/q^*$. The corresponding characteristic spacings for MTM/PDADMAC and MTM/PDADMAC/dGMP are 1.85 and 2.14 nm, respectively. Expansion can be understood as in the first case, the individual clay platelets are covered with thin layer of polymers and in the latter case there is an additional layer of dGMP. As the nominal length dGMP molecules is ca. 12 Å, the observed periodicities suggest that the dGMPs are, in fact, highly tilted or even lying flat between the core-shell nanoplatelets as suggested in **Figure S1** (See SI).

Figure 2. SEM micrographs of fracture surfaces for A) MTM/PDADMAC and B) MTM/PDADMAC/dGMP. High-resolution TEM micrographs for C) MTM/PDADMAC and D) MTM/PDADMAC/dGMP.

Figure 3. Wide angle X-ray scattering curves confirm the lamellar structure showing the first (q^*) and second ($2q^*$) order diffraction peaks for MTM/PDADMAC (black) and MTM/PDADMAC/dGMP (red).

Mechanical properties. The stress-strain curves were measured for MTM/PDADMAC and MTM/PDADMAC/dGMP at different relative humidities (RH), and Figure 4 shows their averages and scatter using at least 5 samples (see **SI Table S1** for the exact number of specimens used in calculations). At all humidities, the strength and stiffness increase upon addition of dGMP. This is at first sight surprising, as one could a priori have expected that adding additional low molecular weight molecules (here dGMP) between the layers would lead to reduced strength due to potential plasticization. That adding dGMP, by contrast, increases the strength and modulus suggests that dGMP takes active part in binding of the layers. This is also an indirect proof that hydrogen bonding takes place between the layers, as hydrogen bonding is the characteristic supramolecular interaction of dGMPs. Unfortunately, a direct verification of hydrogen bondings between dGMPs by FTIR seemed challenging due to the complex compositions and overlapping peaks. **Figure 5** presents the tensile strength, maximum strain,

Young's modulus and work-to-failure based on the integral of the stress-strain curve. The values with standard errors, the number of specimens used in calculations, and temperature- and relative humidity ranges are collected in **Table S1** (see SI).

Figure 4. Effect of humidity on tensile stress-strain curves for MTM/PDADMAC (black) and MTM/PDADMAC/dGMP (red) at various humidities: A) Vacuum dried, B) RH 40 %, C) RH 50 %, and D) RH 75 %. Average curves are presented with standard deviation for at least 5 samples.

Figure 5. Effect of humidity on the mechanical properties for MTM/PDADMAC (white) and MTM/PDADMAC/dGMP (red): A) tensile strength, B) maximum strain, C) tensile modulus and D) work to failure per volume (integral of the stress-strain curve), which is an indication of toughness of the material, with standard deviation. The dGMP treated films are stronger and stiffer than polymer-clay films without the treatment. At higher relative humidities (50 and 75 %) the dGMP treatment increases simultaneously strength, strain, stiffness and toughness compared with untreated film.

The humidity has a strong and characteristic effect on the compositions, see **Figure 4** and **Figure 5**. In MTM/PDADMAC the strength and stiffness (Young's modulus) decrease upon

increasing humidity due to the plasticizing effect of water molecules. However, the maximum strain is roughly unchanged. The strength of the dried samples is comparable to the previous results on uncrosslinked MTM/PDADMAC.³⁰ In the present research, however, the modulus was slightly higher because the PDADMAC content was only 23 ± 2 wt% instead of 30 wt% probably due to the extra washing in the present case. At different humidities MTM/PDADMAC/dGMP behaves substantially differently from MTM/PDADMAC. While the humidity reduces strength and modulus, we can observe clear and distinct increase of the maximum strains. The MTM/PDADMAC/dGMP shows 60 % larger strain-to-failure than the MTM/PDADMAC at 75 % RH. The most interesting properties we observe at 50 % RH, where modulus 13.5 GPa, strength 67 MPa, strain 1.24%, and work-to-failure 0.58 MJ/m^3 are all well above the unmodified MTM/PDADMAC. Even if the improvement is not drastically large, it is still conceptually remarkable as such a synergistic improvement is considered to be one landmark in the process to identify biomimetic concepts. The films prepared here have the strength in the same range with nacre and even higher strain at failure than nacre but they do not have as high stiffness.

It becomes obvious that, in the present case, water is needed to plasticize the soft layers to allow lubrication and sliding, and it can also mediate hydrogen bonds. Note, that the brittleness is suppressed in moist conditions is qualitatively similar than in the tensile behavior of nacre³⁵: in the hydrated state the organic phase is plasticized by water and it can deform and maintain the cohesion between the inorganic platelets over large deformations, which allows the relatively large strains observed in mechanical testing. In dry state the movement of organic layer is prohibited, which is seen as lower strain at failure.

Conclusions

We have demonstrated a facile route for preparation of nacre-mimetic nanoclay-polymer composites, in which the addition of hydrogen bonding groups to the aligned and self-assembled polymer-coated nanoclay-platelets leads to a synergistic improvement of strength, modulus, and strain. This is accomplished by electrostatically coating the anionic MTM sheets by cationic PDADMAC surface layers, which in turn bind anionic dGMP groups, capable of hydrogen bonding recognition interactions with other dGMP-moieties. In the wet state, we find synergistic improvements; The best performance is shown for 50 % RH where the tensile modulus is 13.5 GPa, strength 67 MPa, strain 1.24%, and work-to-failure 0.58 MJ/m³. This indicates that the hydrogen bonding molecules can act as a viscous dissipating and sacrificial bonding phase and validates to pursue improvement randomly distributed non-covalent bonding sites as means to obtain sacrificial bonds and synergistic mechanical properties in layered composites. The shown supramolecular approach gives a possibility to tune the mechanical properties on-demand by complexing polymer-clay films with different molecules.

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ASSOCIATED CONTENT

Supporting Information. Collected mechanical testing results, additional elemental analysis results and suggested dGMP position in the structure. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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