# BIOINSPIRED CLAY NANOCOMPOSITES OF VERY HIGH CLAY CONTENT

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## Abstract
*It is difficult to prepare clay nanocomposites of high volume fraction clay. Layer-by-layer methods have been successful, but are difficult to use in large-scale production. In the present study, papermaking techniques are used for fabrication of oriented clay platelet nanocomposites. Materials are characterized by TEM, SEM, XRD and mechanical and barrier properties are measured and fire retardance performance is demonstrated. High strength and stiffness is demonstrated and the potential for bionanocomposites is discussed, in particular with moisture durability in mind.*

The development of nanostructured clay composites by Toyota researchers was a groundbreaking achievement in the field of polymer composites with mechanical function. Since then, the field of clay nanocomposites has grown dramatically and inspired development of new classes of materials in this category._The difficulties encountered with dispersion and nanostructural control in man-made nanocomposites have motivated attempts to prepare bioinspired composites. The work by Tang et al.[1] on artificial nacre was thus a seminal study in that the layered and parallel orientation of inorganic platelets in nacre was mimicked and it was possible to reach high inorganic content (Vf ≈ 50%), a modulus of 11 GPa and a tensile strength of 100 MPa. MTM clay platelets were combined with a charged, water-soluble polymer in an elaborate layer-by-layer (LbL) deposition process. However, this process is time-consuming and most likely difficult to extend from laboratory practice to large scale industrial processing.

The work by Walther et al [2,3] therefore meant major progress, since nacre-mimicking oriented composites with excellent properties were produced using a simple and industrially scalable water-based processing approach akin to papermaking. This approach was subsequently extended to other composites based on a biopolymer matrix such as nanofibrillated cellulose [4,5]. This class of high volume fraction clay nanocomposites with nacre-like organization is of scientific as well as major technical interest. Favorable performance characteristics include high tensile strength, high modulus, the potential for ductility analogous to nacre, good gas barrier properties since the clay platelet organization is providing a tortuous path for gas molecules so that gas diffusion is more difficult, favorable fire retardance characteristics, probably related to gas barrier properties but also perhaps due to sintering mechanisms in the clay platelets, optical transparency is possible provided the clay platelets are well dispersed. The reason all these characteristics have not been generally observed with clay nanocomposites is the high degree of order in the materials. The platelets are oriented in-the-plane, with little out-of-plane orientation. One should also point out that it is possible to prepare very thin coatings or films, which still has substantial mechanical integrity. In Fig 1, the preparation philosophy is illustrated.

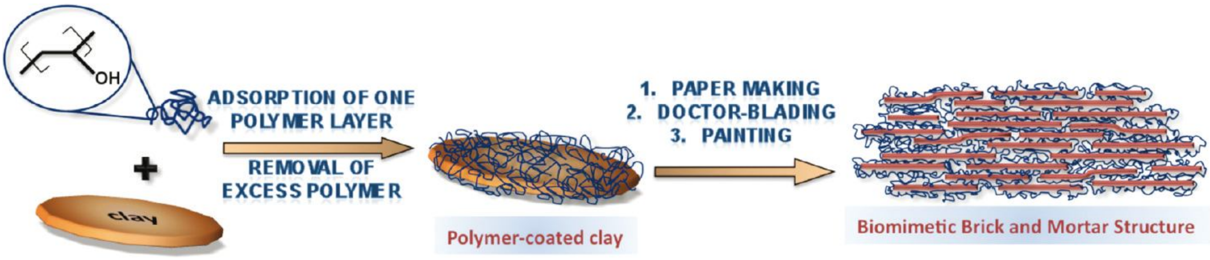


**Figure 1.** Description of preparation scheme introduced in ref [2], image from the same paper. Clay platelets are exfoliated and then coated by the polymer. The high clay volume fraction material is then formed by, for instance, vacuum filtration (paper-making).

An interesting extension of the work is to use biobased polymers. Xyloglucan has been used as an engineering polymer recently [6]. In the plant cell wall it has the function to link cellulose microfibrils. It can be dissolved in water, and is processable by papermaking approaches. We recently combined it with clay and found high reinforcement efficiency at a clay content of 20 wt%, see Table 1. One may also note some ductility of the material, despite a comparably high inorganic content.

| Sample | Tensile strength, MPa | Tensile strain at break, % | Elastic modulus, GPa |
|---|---|---|---|
| Samples conditioned at 50%RH and 23°C | | | |
| Xyloglucan | 92.9 ± 5.8 | 8.9 ± 2.0 | 4.1 ± 0.15 |
| XG/1% MTM | 89.1 ± 6.9 | 15.5 ± 2.9 | 5.1 ± 0.53 |
| XG/2.5% MTM | 96.2 ± 6.7 | 12.2 ± 1.7 | 5.9 ± 0.1 |
| XG/5% MTM | 103.9 ± 2.7 | 6.6 ± 1.9 | 6.2 ± 0.48 |
| XG/10% MTM | 114.3 ± 6.3 | 3.8 ± 1.2 | 8.6 ± 0.26 |
| XG/20% MTM | 123 ± 7.4 | 2.1 ± 0.31 | 11.6 ± 1.7 |

**Table 1.** Example of a caption (Times New Roman 10 pt, centered-text alignment. Leave 6 pt space before the caption and a blank single line after it).

The class of clay nanocomposites with oriented clay platelets is interesting. Coatings are a promising form for these materials, but one may also consider films and even cast composites. Multifunctional characteristics result from the clay. To fully utilize nanocomposites, it is apparent that the structure needs to be controlled at the nanoscale. In the present materials, it is possible to tailor the distribution of polymer matrix so that only a monolayer of polymer is coating each platelet. This is a major step forward compared with the approach to just mix nanoparticles with polymers and hope for good properties.

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