Orientation of clay particles in biomimetic films

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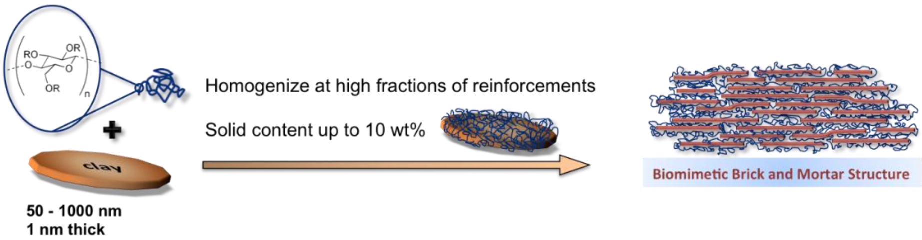

Figure 1: Sketch of the film formation process [1].

We analyzed biomimetic films inspired by the structure of natural nacre. The well aligned hard/soft structure is characterized by high mechanical stiffness and strength. The investigated films consist of the natural clay sodium montmorillonite (MTM), and as soft energy-dissipative component sodium carboxymethyl cellulose (CMC) is used. The films were prepared by a high-shear homogenization progress of the CMC/MTM dispersions that allows for large-scale applications. In this process, core-shell platelets form. During water removal, the particles self-assemble into a layered structure (s. Fig. 1). Films with different ratios of CMC to MTM were prepared. The film thickness is 30-200µm [1].

As the periodicity of the CMC/MTM structure is about 1 to 3 nm, WAXS measurements are well suited to determine the lattice spacing and the orientation of the clay particles. Measurements were performed at the MiNAXS beamline P03. The energy was set to 13 keV corresponding to a wavelength of 0.954 Å. Data were taken by a Pilatus 300k detector. For quantitative evaluation of the orientation of the MTM particles, the samples were measured at two different incidence angles $\varphi = 15°$ and 90° with respect to the film surface.

Scattering patterns are shown in Fig. 2. For $\varphi=90°$, isotropic scattering patterns were observed for all samples. The asymmetric scattering pattern received for $\varphi=15°$ state that the clay platelets are oriented predominantly parallel to the surface of the film. Furthermore for films with high MTM content, Bragg peaks can be observed which proves the formation of a regular structure. In order to determine the lattice spacing, scattering curves were calculated by integrating ±20° around the maximum of the Bragg peak. Fig. 3 shows that the Bragg peak shifts to smaller q-values with rising CMC content. The corresponding distance between the clay platelets varies linearly with the CMC content (s. inset, Fig. 3) [1]. Additionally, a decrease of intensity and a broadening of the peak can be observed. Higher CMC fractions results in a wider distribution of stacking distances and a loss of long range order. For the highest CMC fractions, no Bragg maximum or shoulder appears in the scattering curve.

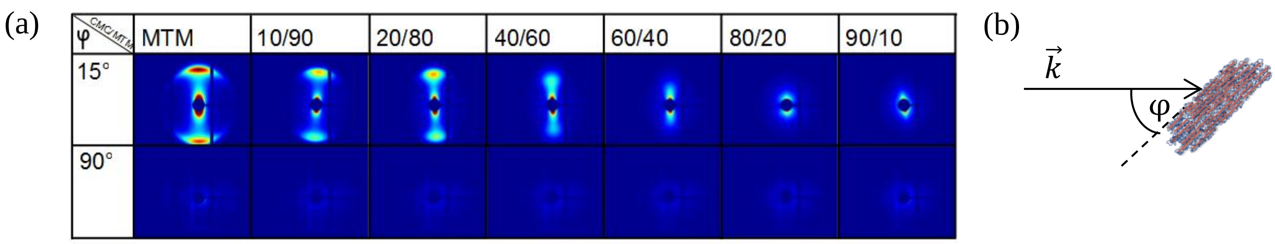

Figure 2: (a) Scattering patterns of films with different ratio of CMC to MTM recorded at incidence angles of $\varphi = 15°$ and 90° with respect to the film surface (b) [1].

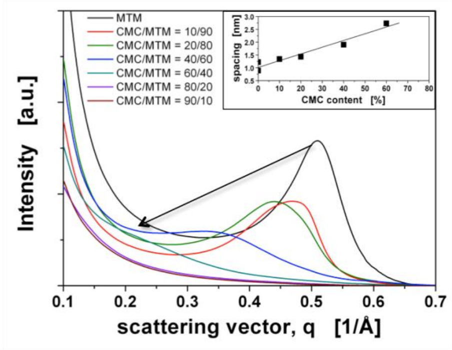

Figure 3: Scattering curves of CMC/MTM films. Inset: layer spacing depending on the CMC content [1].

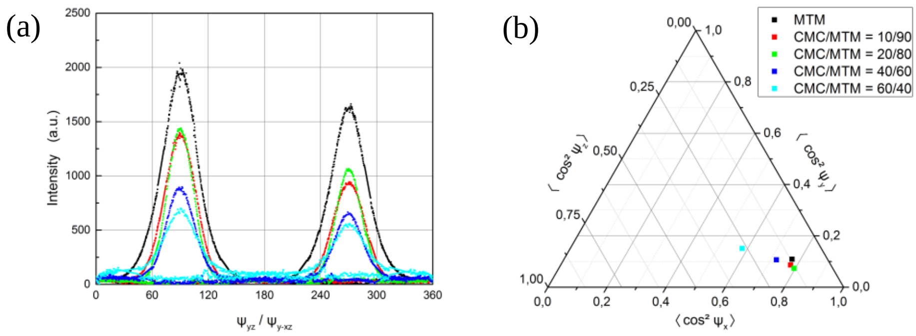

Figure 4: (a) Azimuthal integration for the Bragg peak and (b) Wilchinsky-diagram representing the calculated orientation parameter.

In previous work, our group has determined orientation parameters for clay particles in a polyethylene matrix [2,3]. For films, a similar evaluation is possible. Further details on the calculation can be found in [4]. Results are summarized in a Wilchinsky diagram [5]. Up to a CMC content of 20%, orientation parameters of $\langle \cos^2 \Psi_x \rangle = 0.75 - 0.8$ show that clay particles are predominantly oriented parallel to the surface of the film. For CMC/MTM = 60/40, the clay is less oriented $\langle \cos^2 \Psi_x \rangle = 0.58$. For higher concentrations no characteristic length can be observed, thus no orientation parameter is determined. However, scattering patterns show a slightly preferred orientation parallel to the surface.

In conclusion, our measurements quantify how the layer spacing can be tuned by variation of the CMC content. However, an increase of the CMC amount also results in a loss of long-range order and orientation.

References

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