Supporting Information

Calcium Carbonate with Nanogranular Microstructure yields Enhanced Toughness

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Hydrothermal Stability of ACC Nanoparticles

The main bands in the calcium carbonate infrared spectrum used for identification of calcium carbonate were the carbonate out-of-plane bending v_2 (875 cm⁻¹ in calcite and 866 cm⁻¹ in ACC) and the in-planebending peak, v_4 (712 cm⁻¹ in calcite, 744 cm⁻¹ in vaterite and not present in ACC). The ratio of these two peaks provides an additional measure of the disorder or lack of symmetry in the carbonate's environment, as well as the extent of crystallization.¹ The ratio is small in pure calcite (~1.4) due to its well-organized crystal structure, while it is markedly larger in ACC (larger than ~3 in some biogenic ACC structures²).



Figure S1: IR spectra for A) 2mM PAA-ACC and b) 0.2mM PAA-ACC nanoparticles tested at 25°C, 400°C and 600°C. The v_2 band shifts from 866 cm⁻¹ to 875 cm⁻¹ between 400°C and 600°C and the v_4 at 712 cm⁻¹ band appears at 600°C, indicating the crystallization of ACC into calcite.

2mM-PAA-ACC nanoparticles (**Figure** S1A, blue curve) show a distinct peak at 866 cm⁻¹ and a broadened peak below 800 cm⁻¹, indicating that calcium carbonate is in a fully amorphous state.¹ This infrared spectrum was observed to remain indefinitely stable at temperatures below 600°C.

The IR spectrum of 0.2mM-PAA-ACC (Figure S1B, **Figure** S2A, green curve) exposed to laboratory air exhibits a broad peak at 870 cm⁻¹ and no v_4 band, which indicates the predominant presence of ACC.

While these peaks became a single peak at 875cm⁻¹ after 24 hours of exposure to ambient air, indicating partial crystallization of ACC, they remained unchanged for a period of three days in an inert nitrogen atmosphere (**Figure S2C**). These results indicate that the polymer in 2mM-PAA-ACC stabilizes ACC and prevents any subsequent crystallization, while the smaller polymer content in 0.2mM-PAA-ACC is less efficient in stabilizing ACC upon prolonged exposure to humid air (40-50 %RH).

EtOH-ACC nanoparticles (SI, **Figure** S2A, red curve) exhibit a spectrum characteristic of ACC, with a well-defined peak at 866 cm⁻¹, and broadened peaks in the 700-750 cm⁻¹ regions. After ~4 h of exposure to ambient humidity, the broad peaks start to sharpen (**Figure** S2B), which is indicative of the increasing presence of both calcite and vaterite. After 24 hours of exposure to ambient air, only the calcite peak was detected, while the v_2/v_4 ratio decreased until it was only marginally larger than the characteristic v_2/v_4 ratio of calcite. Nevertheless, the crystallization of ACC was hindered by storing the synthesized material in an inert nitrogen atmosphere (**Figure** S2D).



Figure S2: A) ATR-IR spectra of 2mM PAA-ACC (blue), 0.2mM PAA-ACC (green), and EtOH-ACC (red) nanoparticles and calcite, as reference (violet). B) Time-series of ATR-IR spectra of EtOH-ACC nanoparticles exposed to ambient air. Inset shows the ratio of the v_2/v_4 bands over the course of 24 hours and the value for calcite, as reference. C) ATR-IR spectra of 0.2mM PAA-ACC nanoparticles under an

inert N_2 atmosphere during a 3-day period showing no changes of the spectrum with time. D) ATR-IR of EtOH-ACC nanoparticles stored in an inert N_2 atmosphere, showing that no crystallization occurred during a period of 4 days.



Figure S3: ATR-IR spectra for EtOH-ACC nanoparticles at 100, 200 and 450°C. A transition is observed from 200 to 450°C, where peaks associated with ammonia are not present anymore.

Thermogravimetry of ACC nanoparticles

The thermal decomposition of 2mM-PAA-ACC and 0.2mM-PAA-ACC nanoparticles (**Figure** S4) occurred in three different stages that were attributed to evaporation of residual water, thermal decomposition of PAA, and thermal decomposition of calcium carbonate, respectively. The calcium carbonate percentage was determined by assuming the residual weight is calcium oxide. This yields 41.7 ± 1.3 wt.% PAA in 2mM-PAA-ACC nanoparticles, while lowering the solution concentration of PAA to 0.2 mM results in 6.2 ± 0.5 wt.% PAA in 0.2mM-PAA-ACC. The molar ratio of CaCO₃ to the monomer is 1:1 in 2mM-PAA-ACC and 11:1 in 0.2mM-PAA-ACC.

Water, ethanol, and ammonia were detected in EtOH-ACC nanoparticles by FTIR just after synthesis, with ammonia comprising ~15.8 \pm 2.9 wt.% of the total dry mass. Ethanol evaporated during storage in a dry N₂-atmosphere, but ammonia was still detectable by FTIR below a temperature of 450°C. The onset temperature of calcium carbonate decomposition (~620 \pm 21 °C) is only slightly altered with respect to pure calcite (648 °C).



Figure S4: Representative thermograms showing the mass loss (in weight %) vs. temperature for 2mM PAA-ACC, 0.2mM PAA-ACC, EtOH-ACC, calcite and PAA-Ca²⁺. In 2mM-PAA-ACC, 0.2mM-PAA-ACC, and PAA-Ca²⁺, the decomposition of PAA starts at a higher temperature compared to pure PAA solutions (~252°C, not shown). To demonstrate that this increase in thermal stability (Figure S5b) is caused by crosslinking of the polymer with calcium and calcium carbonate, the diagram shows that PAA - Ca²⁺ complexes start to decompose at 408°C.



Figure S5: A) Composition (in weight percentage) of dry calcite, 2m-PAA-ACC, 0.2 mM-PAA-ACC and EtOH-ACC obtained from TGA. B) Onset temperatures for the decomposition of calcium carbonate, PAA, and ammonia (in EtOH-ACC).

Kinetics of mineralization Ultraviolet-visible spectrophotometry

PAA solutions (0.2 and 2mM) were complexed with Ca²⁺ (100 mM) for 5 hours by stirring gently at 300 rpm. After 5 hours of complexation, ammonium carbonate (100 mM) was introduced into the polymer solutions to begin the mineralization process of PAA-ACC. To study the mineralization of EtOH-ACC, a 2mM ethanolic calcium chloride solution was placed in a sealed container with ammonium carbonate. At selected periods of time spanning a period of 5 hours, a 1-ml aliquot of each solution was transferred to a clean cuvette for UV-Vis measurements. A UV spectrophotometer (Shimadzu, UV-2450) was used to obtain total absorbance measurements of the mineralizing nanoparticles in solution. Nanopure water and ethanol were used as the background measurements. Three separate measurements were collected at each point for each sample.



Figure S6: Measured absorbance during mineralization of 2mM-PAA-ACC (blue circles), 0.2mM-PAA-ACC (green triangles) and EtOH-ACC nanoparticles (red diamonds).

The initial measurement for 0.2mM-PAA-ACC and 2mM-PAA-ACC gives the turbidity of the solution containing PAA-Ca²⁺ globules. Upon the addition of carbonate ions to the PAA-ACC solutions, the turbidity was observed to increase indicating the onset of mineralization of the PAA-Ca²⁺ globules. The rise in absorbance for the 2mM PAA-ACC samples is markedly faster during the first 60 minutes and it plateaus after 120 minutes of reaction. Negligible fluctuations in the absorbance occur thereafter, indicating that the particles have fully mineralized and are stable in solution. 0.2mM PAA-ACC also shows a fast and steady increase in absorbance. The total absorbance is an order of magnitude smaller than that observed in the 2mM PAA-ACC solutions, indicating a smaller content of mineralized nanoparticles in the solution. EtOH-ACC shows no detectable increase in absorbance during the first 15 minutes of exposure to ammonium carbonate. The turbidity in the solution then reaches a maximum after 120-180 minutes. At

longer reaction times, a decrease in the absorbance was observed due to the sedimentation of the largest nanoparticles.



Figure S7: AFM topography (left column) and phase images (right column) of A) 2mM-PAA-ACC, B) 0.2mM-PAA-ACC, and C) EtOH-ACC nanoparticles, all imaged at room humidity. D) Size (diameter) distribution of PAA-ACC particles and of EtOH-ACC particles. E) Size distribution of nanograins within particles. The mean value of particle and nanograin size (D_{av}) is given for each distribution assuming a Gaussian unimodal distribution. RMS roughness of 2mM PAA-ACC, 0.2mM PAA-ACC and EtOH-ACC is 0.14±0.08nm, 0.16±0.05nm and 0.12±0.04nm, respectively.

Nanoindentation on single ACC nanoparticles



Figure S8: Contour density plots of (approach) indentation curves on A) 2mM PAA-ACC, B) 0.2mM PAA-ACC, C) EtOH-ACC nanoparticles and D) calcite measured in a dry N_2 atmosphere. At least 10 indentation maps (each map with 64 indentation curves taken on an area of 200 by 200 nm on single particles) were analyzed per material. The black lines illustrate nanogranular rearrangements during indentation. Indentation experiments were conducted with a wear-resistant diamond coated sharp tip at an approach speed of 100 nm/s.

Indentation maps in ambient air

The samples were exposed to ambient air for 4 h during the indentation measurements. Each single extension curve on at least 6 indentation 2D maps per material were fit to the DMT model³ to estimate the Young's modulus of the nanoparticles. The variability observed in the 2D indentation maps is also reflected into a distribution of elastic moduli for each system, as shown in **Figure** S9A. A trimodal distribution with peak means at 1.59 ± 1.3 , 5.03 ± 2.17 and 9.37 ± 2.31 GPa describes well the results for 2mM-PAA-ACC nanoparticles, while for 0.2mM-PAA-ACC nanoparticles the peaks shift to larger values 2.88 ± 1.97 , 8.53 ± 2.61 and 12.9 ± 4.07 GPa. EtOH-ACC nanoparticles exhibited a narrower distribution of elastic moduli in ambient air compared to N₂-atmosphere, with three peaks at 2.32 ± 2.70 , 8.12 ± 4.63 and 18.80 ± 6.14 GPa.

Once the maximum load of the measurement was achieved, the tip was immediately retracted, exhibiting considerable adhesion under all conditions. The hysteresis between the indentation curves upon loading and unloading is reflected in the difference between the elastic moduli obtained by fitting the DMT model to the approach and retraction curves (**Figure** S9B). In contrast to the results in a dry N₂-atmosphere, Figure S9B shows a larger discrepancy between retraction and extension E-moduli for 2mM-PAA-ACC and 0.2mM-PAA-ACC.

The integration of the area between the approach and retract indentation curves gives the elastically and inelastically dissipated energy (W) throughout the indentation test.^{4, 5} As shown in **Figure** S9C-D, larger energy is dissipated by 0.2mM-PAA-ACC and 2mM-PAA-ACC nanoparticles, while EtOH-ACC nanoparticles dissipates the smallest amount of energy. This trend can be correlated to the adhesion energy, which is highest for the two PAA-ACC materials.

A log-log plot of the elastic modulus versus the dissipated energy yields also here a nearly linear correlation (Figure S9C); a power law with an exponent of -0.33 and -0.21 describes this relationship for 2mM-PAA-ACC and 0.2mM-PAA-ACC nanoparticles, respectively, while for EtOH-ACC nanoparticles, the exponent (~-0.22) is not very different from the value in dry N₂. We note that the dependence of the dissipated energy on the elastic modulus is much weaker for PAA-ACC in ambient air than in the N₂atmosphere. It is thus possible that PAA-hydration enhances the viscoelastic response of PAA-ACC, and hence, the dissipated energy due to the viscous component of the deformation. The presence of water could lead to the formation of a capillary meniscus that increases the attractive force independently on the elastic modulus, and hence, adhesion. However, the decrease in adhesion for EtOH-ACC does not support this phenomenon.



Figure S9: A) Probability density function (PDF) of fitted Young's elastic moduli of ACC nanoparticles. Fits of multimodal Gaussian distributions to the PDF yield following peak means, widths and frequencies: 2mM-PAA-ACC: 1.59 ± 1.3 GPa (61%), 5.03 ± 2.17 GPa (29%) and 9.37 ± 2.31 GPa (10%); 0.2mM-PAA-ACC: 2.88 ± 1.97 GPa, (61%), 8.53 ± 2.61 (29%) and 12.9 ± 4.07 GPa (10%); EtOH-ACC: 2.32 ± 2.70 (56%), 8.12 ± 4.63 GPa (31%), and 18.80 ± 6.14 GPa (13%). Calcite (not shown) has an elastic modulus of 128 GPa. B) Young moduli calculated from approach vs. retraction curves in indentation tests. Solid black line indicates a fully elastic behavior. C) Log-log diagram of dissipated energy vs. Young's modulus obtained from approach curves. D) Dissipated energy as a function of the adhesion energy for the measurements performed in ambient air. The color legend is: blue for 2mM-PAA-ACC, green for 0.2mM-PAA-ACC and red for EtOH-ACC nanoparticles.



Figure S10: PDF of adhesion energy obtained by integration of the negative portion of the retraction curve measured in A) a dry N_2 -atmosphere and in B) ambient air.



Figure S11: PDF of dissipated energy given by the area enclosed by the approach and retraction curves gives during the indentation tests in A) a dry N₂-atmosphere and in B) ambient air.



Figure S12: Comparison of the Young's modulus of the different systems in dry nitrogen atmosphere and at room humidity (40-50 %RH). The values were obtained from the fit of the DMT model to approach and retraction curves in indentation 2D-maps.

References

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