

A transparent hybrid of nanocrystalline cellulose and amorphous calcium carbonate nanoparticles†

Denis Gebauer,^{ab} Vitaliy Oliynyk,^a Michaela Salajkova,^{cd} Jordi Sort,^e Qi Zhou,^{df} Lennart Bergström^a and German Salazar-Alvarez^{ad}

Nanocellulose hybrids are promising candidates for biodegradable multifunctional materials. Hybrids of nanocrystalline cellulose (NCC) and amorphous calcium carbonate (ACC) nanoparticles were obtained through a facile chemical approach over a wide range of compositions. Controlling the interactions between NCC and ACC results in hard, transparent structures with tunable composition, homogeneity and anisotropy.

The extraordinary performance of biological composites like bone, nacre, and the exoskeleton of brittle stars¹⁻³ is an important inspiration for the development of novel multifunctional materials.⁴⁻⁶ Nanocomposites,^{7,8} *i.e.* where the different constituent phases are of nanoscale dimensions, have the potential to combine useful optical characteristics,⁹ with an enhanced toughness¹⁰ and insensitivity to flaws.¹¹ Bionanocomposites are especially appealing as the use of biomaterials as constituents of composites can combine impressive properties with environmentally benign and energy efficient production routes.¹²

Cellulose is the most abundant biopolymer on Earth, found, for example, in the cell walls of green plants, cotton, some algae, and is also secreted by some bacteria. Wood pulp is mainly used for the production of paper, paperboard, and textiles but the fibrous structure of cellulose is also utilized for reinforced composites.^{13,14} Nanocrystalline cellulose (NCC) is the basic building unit of cellulose and is generally produced by acid hydrolysis of such fibres.¹⁵ NCC has large transverse and axial Young's moduli, superior to regular cellulose microfibrils¹⁶ and even Kevlar,¹⁷ which make it attractive as additive in polymer composites.¹⁵ Calcium carbonate, on the other hand, is

the most abundant biomineral (mussel shells, exoskeleton of corals and algae, the carapace of crayfish and lobsters), and μm sized crystals are an important industrial resource that is utilized as pigment or filler in paper, paint or plastics. Calcium carbonate has three anhydrous crystalline polymorphs, calcite, aragonite and vaterite; and three hydrated polymorphs, of which nanoparticles of amorphous calcium carbonate (ACC) can be found in both plants and organisms and can also be prepared synthetically.¹⁸⁻²¹

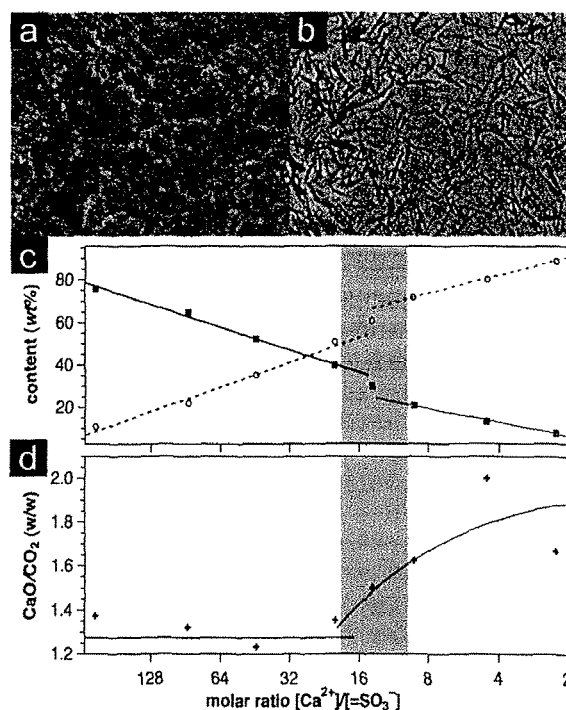


Fig. 1 Micrographs of ACC nanoparticles (SEM, a), and cellulose nanocrystals (TEM, b), scale bars 200 nm. Thermogravimetric analyses of the hybrids evidence exponential dependency of (c) the hybrid composition on the molar ratio of $[\text{Ca}^{2+}]/[=\text{SO}_3^-]$ when NCC (dotted lines, open circles) and ACC (solid lines, bold squares) are the matrices of the composites (left or right regions, respectively). (d) At low $[\text{Ca}^{2+}]/[=\text{SO}_3^-]$ ratios (high contents of NCC, green curve), the weight ratio CaO/CO_2 indicates deviations from stoichiometric calcium carbonate that should have a weight ratio of 1.27 (red straight line).

^aDepartment of Materials and Environmental Chemistry, Stockholm University, SE-10691 Stockholm, Sweden. E-mail: german@mmk.su.se; Web: <http://www.mnk.su.se>; Fax: +46 8 15 21 87

^bDepartment of Chemistry, University of Konstanz, D-78457 Konstanz, Germany

^cFibre and Polymer Technology, Royal Institute of Technology (KTH), SE-100 44 Stockholm, Sweden

^dWallenberg Wood Science Center, KTH, SE-100 44 Stockholm, Sweden

^eDivision of Glycosciences, School of Biotechnology, KTH, SE-106 91 Stockholm, Sweden

^fInstitució Catalana de Recerca i Estudis Avançats and Departament de Física, Universitat Autònoma de Barcelona, E-08193 Bellaterra, Spain

† Electronic supplementary information (ESI) available: Additional experimental procedures and results.

In this study we use monodispersed spherical ACC nanoparticles with a diameter of 11.3 ± 0.5 nm (Fig. 1a, S1 and S2†). The well-defined ACC particles could be obtained by performing the synthesis in ethanol,¹⁹ where the minute solubility of calcium carbonate results in very high supersaturation levels that lead to a short nucleation event.²² NCC, 5–10 nm in diameter and 100–300 nm long (Fig. 1b), was prepared by hydrolysis of microcrystalline cellulose in sulfuric acid, which results in ~ 0.34 mmol g^{-1} of surface sulfonate groups ($=SO_3^-$, see Fig. S3†).

As discussed later on, it is impossible to obtain homogeneous hybrids from the spherical nanoparticles of ACC and the NCC by simply mixing the precursors. In order to achieve an even distribution, the NCC was pre-complexed with an excess of calcium in aqueous solution, *i.e.*, $n(Ca^{2+})/n(=SO_3^-) > 1$, then transferred to ethanol where the ACC was precipitated. Thermogravimetric analyses (TGA) of the different hybrids (Fig. 1c and S4†) show a decreasing content of NCC with increasing $n(Ca^{2+})/n(=SO_3^-)$ ratio. Evaluation of the TGA data (Fig. 1c and d) indicates that the relative contents of ACC and NCC within the hybrids depend exponentially on the pre-complexation molar ratios $n(Ca^{2+})/n(=SO_3^-)$. This dependence changes around $10 < n(Ca^{2+})/n(=SO_3^-) < 20$ (Fig. 1c). The hybrid that is formed at $n(Ca^{2+})/n(=SO_3^-) \approx 14$ contains ~ 30 wt% ACC, ~ 60 wt% NCC and ~ 10 wt% structural water. The transition region in Fig. 1c is also reflected by the mass ratio of $m(CaO)/m(CO_2)$ determined from calcination of the calcium carbonate content (Fig. 1d). When NCC is the major constituent, the data indicate deviations from stoichiometric calcium carbonate, *i.e.* the ACC phase of the hybrids contains a higher amount of calcium ions than carbonate ions (green line). At high contents of NCC, the sulfonate groups apparently balance the charge of missing surface carbonate ions and complex up to 36 mol% of the total calcium (Fig. 1d). The substitution of carbonate ions is likely to occur in the outer layer of the ACC nanoparticles, and would correspond to a shell of 0.5–1 nm. This effect is observable owing to the nanoscale dimensions of the ACC nanoparticles, where the fraction of charged surface groups is significant compared to the bulk. We thus infer that at a ratio near $10 < n(Ca^{2+})/n(=SO_3^-) < 20$ during pre-complexation (grey areas in Fig. 1c and d), the interaction of chemical groups on the surfaces of both phases is optimal. This value likely depends on the configuration (*i.e.* geometrical constraints at the given particle sizes and distributions of chemical groups) of the different phases of this study. At higher contents of ACC, the overall composition of the calcium carbonate phase is near the stoichiometric, *i.e.*, a weight ratio $m(CaO)/m(CO_2) = 1.27$.

The nanoscale dimensions of the components, similar average refractive indexes \bar{n} (calcium carbonate $\bar{n} \approx 1.58$ – 1.59 ,^{23,24} cellulose $\bar{n} \approx 1.56$ – 1.60),^{25,26} and their low bulk absorption coefficient²⁶ suggest the possibility to produce transparent hybrids. The photographs in Fig. 2 demonstrate the optical transparency of NCC–ACC hybrids deposited on quartz substrates (see also optical transmittance in Fig. S7†). Using different solvents during the preparation of the films could further minimize light scattering by lowering the density of scattering centers. SEM and AFM micrographs in Fig. 2a–c show examples of the microstructure of hybrids deposited onto silicon wafers with different compositions (see also ESI, Fig. S5†). At an ACC content of ~ 30 wt% (Fig. 2a), the SEM and AFM images show that the NCC network is homogeneously mixed with the ACC nanoparticles. At low ACC content (~ 14 wt%, Fig. 2b), the ACC nanoparticles are present as clusters embedded in a matrix of NCC.

At high content of ACC (~ 53 wt%, Fig. 2c), the spherical nanoparticles dominate in the images whereas the NCC is barely visible. Apparently, both the NCC and ACC have a strong tendency to aggregate, thus resulting in inhomogeneous hybrids if the constituents are above or below the composition where most of the ACC remains bound to the surface of the NCC upon syntheses, due to electrostatic interactions.

We have made an attempt to estimate and compare the magnitude of the attractive van der Waals interactions between the separate species and the ACC with NCC. It is important to note that the Hamaker constant for the interaction of cellulose with cellulose across a polar solvent is 40% larger than the interaction between cellulose and crystalline calcium carbonate.²⁷ As the Hamaker constant decreases with a decrease in atomic density, the Hamaker constant for ACC should be lower than for calcite, suggesting that the

30 % 14 % 53 % ACC

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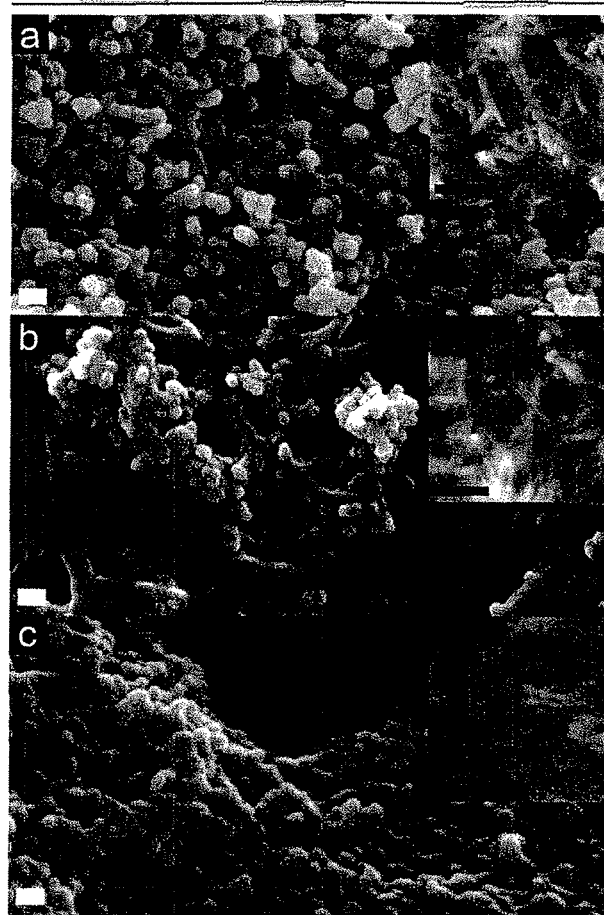


Fig. 2 (Top panel) Photograph of ~ 10 μm thick hybrids spin-coated on $\sim 1 \times 1$ cm^2 quartz substrates showing the transparency of the films. The values correspond to wt% ACC. (a–c) SEM and AFM (insets) micrographs of hybrids with different compositions. Note that the samples for SEM were coated with a ~ 10 nm thick layer of carbon. (a) Most homogeneous hybrid with ~ 30 wt% ACC, (b) NCC with ~ 14 wt% ACC, and (c) ~ 53 wt% ACC. Scale bars: 100 nm, insets 400 nm.

Hamaker constant for NCC and ACC could be as low as half of that for NCC–NCC. Furthermore, at short separation distances, s , the vdW interactions are proportional to s^{-32} and s^{-1} for long parallel cylinders and spheres, respectively.²⁸ Thus the low Hamaker constant for ACC–NCC together with geometrical constraints suggests that NCC–NCC aggregation is energetically favoured over heterogeneous assembly. Thus, when the electrostatic interactions between ACC–NCC are balanced the size of NCC ordered domains increases as the amount of ACC decreases (see Fig. S6†). However, the final morphology of the hybrid also depends on the evaporation rate of the solvent, as this influences the ordering of the NCC.²⁹

The structuring of the hybrids brings changes at the macroscopic scale, too: the hybrid with ~30 wt% ACC shows a most homogeneous coverage on silicon wafers, whereas the other hybrids form discontinuous coatings (ESI, Fig. S8†). Furthermore, nano-indentation measurements show tunable mechanical properties depending on the composition of the hybrids and the resulting microstructure (see Tables 1 and S2, and Fig. S9†). The reduced Young's moduli, E_r , obtained for the hybrids are similar to those reported for NCC films³⁰ and in softer regions of retro-synthesized nacre,³¹ in which high organic contents are suspected (chitin and insoluble proteins as main components besides calcium carbonate). The hybrid with the highest inorganic content (53 wt% ACC) shows the largest E_r . It should be noted that in spite of the relatively large transverse Young's modulus of single NCC,³² the bonding strength between cellulose nanocrystals and the matrix plays a crucial role in the properties of such composites, often resulting in an overall reduction of elastic constants with respect to pure NCC.³³ The hardness, H , of the hybrids is comparable to those observed in related biogenic composites such as dentin (~70 wt% hydroxyapatite, 20 wt% collagen fibers, and 10 wt% water; $H \approx 0.5$ GPa).³⁴ The lower H of the hybrid with 30 wt% ACC, compared to those hybrids with lower or higher ACC content, is likely due to the weaker nature of the ACC–NCC interactions as compared to the NCC–NCC and ACC–ACC interactions, which, in turn, render this hybrid with higher plasticity (see Table S2†). Note that the hybrids did not show morphological changes even after 6 months, similar to ACC films stabilized with poly(acrylic acid).³⁵

Our results show that optically transparent and relatively hard hybrids of nanocrystalline cellulose and amorphous calcium carbonate may be obtained over a wide range of compositions. The hybrid that contains ~30 wt% inorganic content shows the most even distribution of NCC and ACC nanoparticles. The ACC–NCC interactions are important in controlling the properties of these hybrids. The design of advanced functional hierarchical materials can thus be obtained through careful tuning of the chemical compositions and interactions at given geometric constraints. Transparent and

hard cellulose films can find potential use in packaging and labels. The composition and thermal behaviour of these hybrids suggest a potential use as flame retardants.

Experimental

Aqueous dispersions containing NCC were mixed with 10 mM calcium chloride (calcium chloride hexahydrate, Sigma-Aldrich no. 21108) solution, in different proportions (see Table S1†). The NCC–Ca²⁺ mixtures were stirred for 30–40 min at room temperature and then transferred into a large beaker containing 2 L ethanol (99.9%, VWR no. 20820.293). After stirring for 5 minutes, 10 mM sodium carbonate (Sigma-Aldrich no. S7795) solution was added to the ethanol dispersions (*cf.* Table S1†). Then, the beaker was sealed, and the mixtures were stirred for 30 min. After removing the magnetic stirrer bar, the solutions were left standing for additional 30 min and the supernatant was decanted. The precipitate was centrifuged and washed sequentially with ethanol and acetone (VWR no. 20066.296). Finally, the precipitate was resuspended in acetone with the help of an ultrasonic bath. The concentrations of the hybrids were determined gravimetrically and are given in Table S1†. For further experimental details see ESI Section S1†.

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Table 1 Summary of the mechanical properties of the hybrid ACC–NCC films obtained from nanoindentation experiments. Listed values of maximum penetration depth h , reduced Young's modulus E_r , and hardness $H \pm 1\sigma$ standard deviation from a statistical average of 50 indentations

ACC (wt%)	h/nm	E_r/GPa	H/GPa
14	153 ± 3	3.3 ± 0.1	0.39 ± 0.03
30	181 ± 7	3.0 ± 0.2	0.27 ± 0.03
53	155 ± 12	6.4 ± 0.3	0.41 ± 0.02

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