

Transparent and Flexible Nacre-Like Hybrid Films of Aminoclays and Carboxylated Cellulose Nanofibrils

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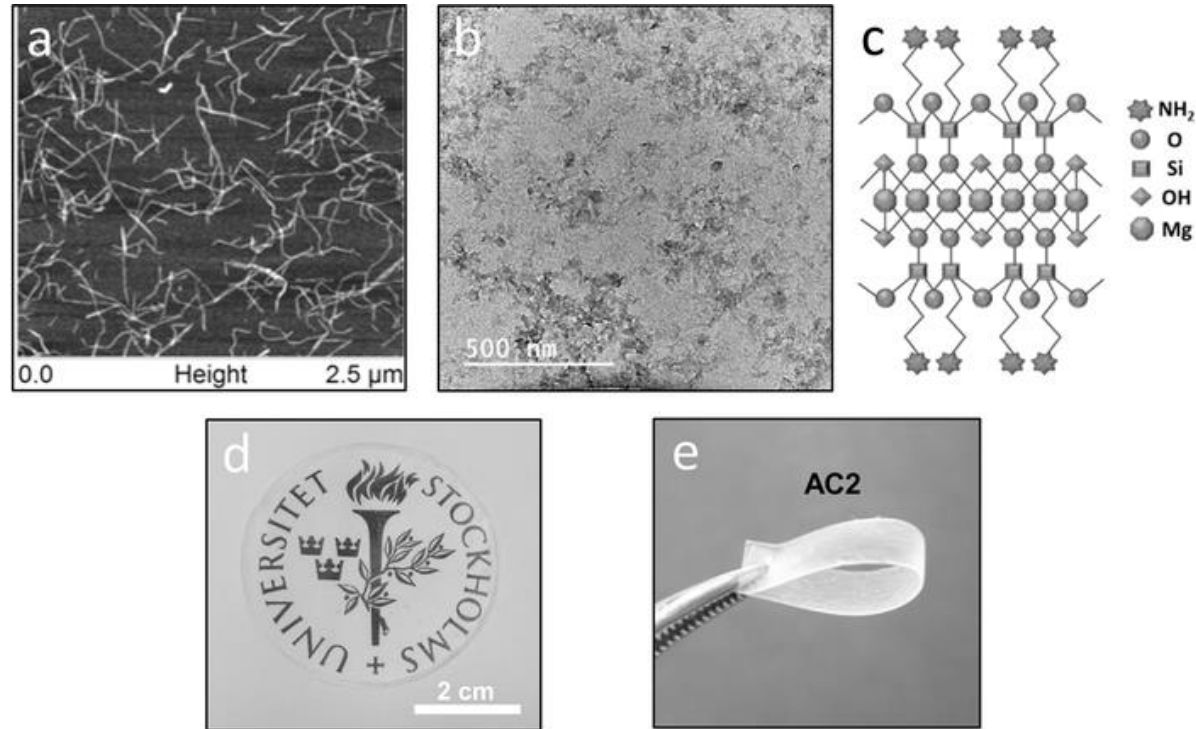
- ✓ Nacre also known as mother of pearl, is an organic-inorganic composite material produced by some molluscs as an inner shell layer; it also makes up the outer coating of pearls. It is strong, resilient, and iridescent.
- ✓ The secret of success is their hierarchically ordered structure at multiscale levels.
- ✓ It consists of about 95 weight % (wt%) of brittle aragonitic CaCO_3 and 5 wt % of organic materials.
- ✓ Nacre and other biological composites with extraordinary performance and functionalities, such as bone, enamel, and dentin, serve as an important inspiration for the design and fabrication of strong and multifunctional composite materials.
- ✓ Combining a high mechanical strength with a high degree of flexibility and optical transparency is of interest in, e.g., optoelectronics and barrier coatings.

- ✓ Nacre-like and transparent hybrid films of positively charged AC and negatively charged carboxylated CNF have been produced.
- ✓ Aminoclay (AC), which is 3-aminopropyl functionalized magnesium phyllosilicate $[(\text{CH}_2\text{CH}_2\text{NH}_2)_8\text{Si}_8\text{Mg}_6\text{O}_{16}(\text{OH})_4]$ is a highly exfoliated and colloiddally stable plate-like nanoclay.
- ✓ The AC nanoparticles are positively charged and thus differ from most natural clays.
- ✓ CNF is a renewable nanomaterial characterized by a low density , optical transparency, high stiffness , and high tensile strength that has been used to produce nacre-like and nanoclay-based composites with a high stiffness and strength.
- ✓ These structures are produced by vacuum filtration of aqueous-based colloidal dispersions of AC and CNF particles with nanoclay contents ranging from 30 to 80 wt%.
- ✓ They are ionically bonded and display a visible light transparency above 70% and a strength and strain to failure that are significantly better than biogenic nacre.

Table 1. Composition, thickness, and density of the AC-CNF hybrid films.

Sample	Theoretical AC ratio [wt%]	TGA calculated AC ratio ^{a)} [wt%]	Film thickness [μm]	Film density [g cm^{-3}]	Relative density ^{b)}
CNF	0	0	19.1 ± 1.7	0.93 ± 0.08	0.58 ± 0.05
AC0.5	33.3	32.9 ± 1.1	21.5 ± 1.3	1.23 ± 0.07	0.68 ± 0.04
AC1	50	48.4 ± 0.7	23.1 ± 1.4	1.53 ± 0.09	0.78 ± 0.05
AC1.5	60	61.3 ± 0.8	28.1 ± 1.5	1.58 ± 0.08	0.78 ± 0.04
AC2	66.7	71 ± 0.4	32.6 ± 3.1	1.64 ± 0.15	0.78 ± 0.07
AC4	80	78.2 ± 1.2	49.2 ± 1.2	1.79 ± 0.04	0.79 ± 0.02

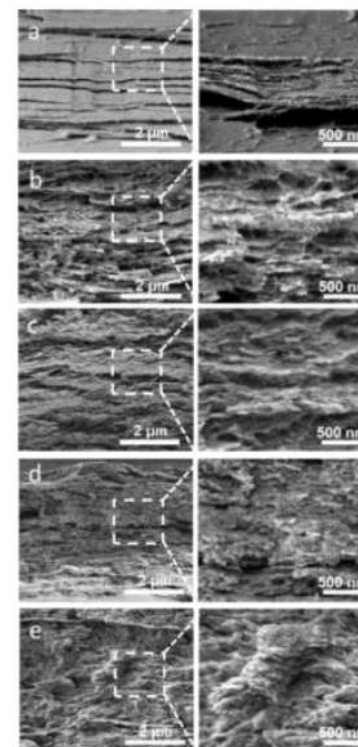
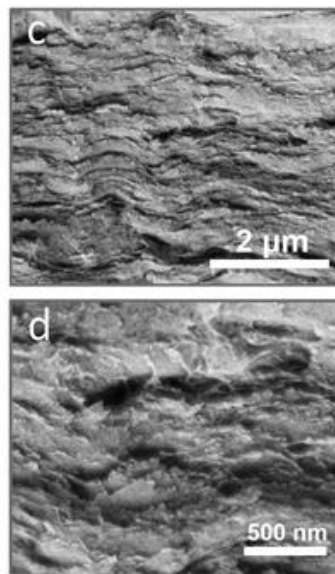
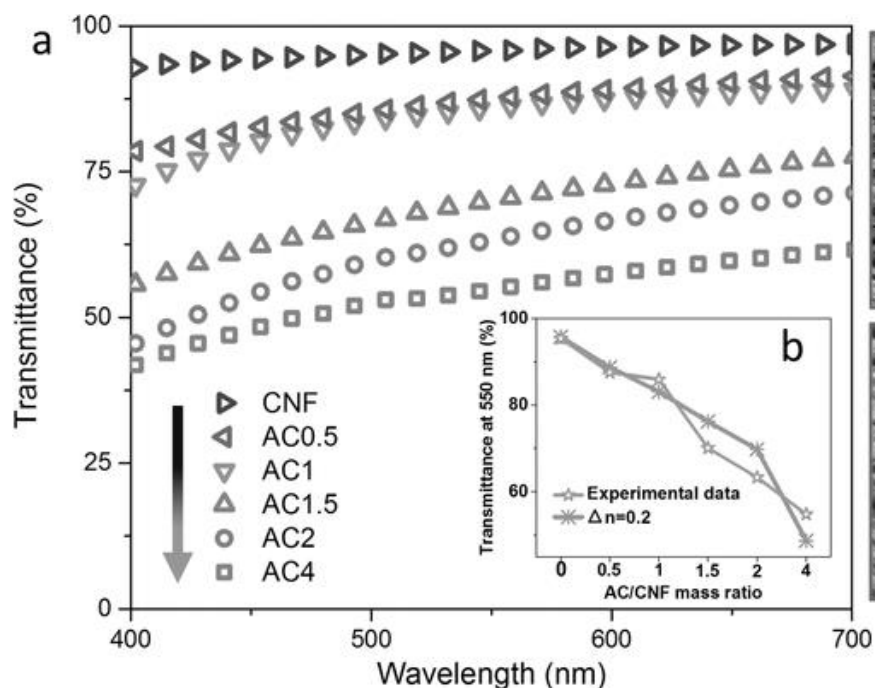
^{a)}Determined by TGA profiles in the plateau from 700 to 800 °C; ^{b)}Ratio of experimental density (ρ_{exp}) and theoretical density (ρ_{theo}) of AC-CNF films, $\rho_{\text{theo}} = 1/(\omega_{\text{AC}}/\rho_{\text{AC}} + \omega_{\text{AC}}/\rho_{\text{CNF}})$, where $\rho_{\text{CNF}} = 1.59 \text{ g cm}^{-3}$, $\rho_{\text{AC}} \approx 2.5 \text{ g cm}^{-3}$.



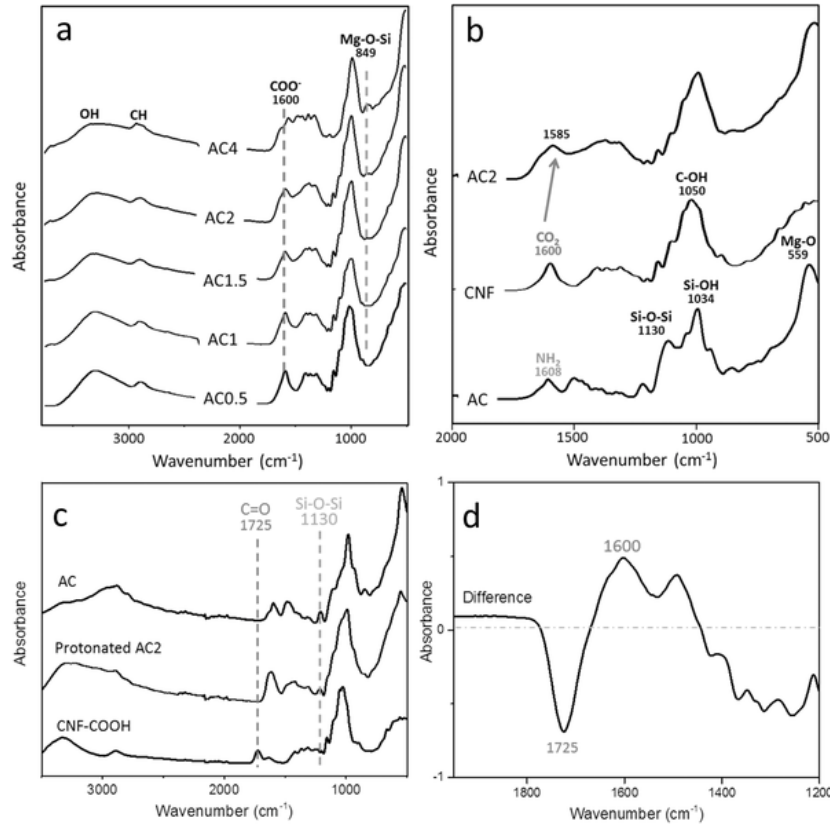
Structure and properties of cellulose nanofibrils (CNF), aminoclay (AC), and the AC-CNF hybrid films. a) AFM image of CNF. b) Transmission electron microscopy (TEM) image of AC. c) Atomic structure of AC. d) Digital photo of the AC1 film placed on top of an image of the Stockholm University logo. e) Illustration of the flexibility of an AC-CNF hybrid film with a mass ratio of 2.

$$T = \exp \left[-4 \frac{\pi^4}{\lambda^4} \left(\frac{n_{AC}^2 - n_{matrix}^2}{n_{AC}^2 + 2n_{matrix}^2} \right) \cdot d^3 \cdot \phi \cdot z \right] - S_0$$

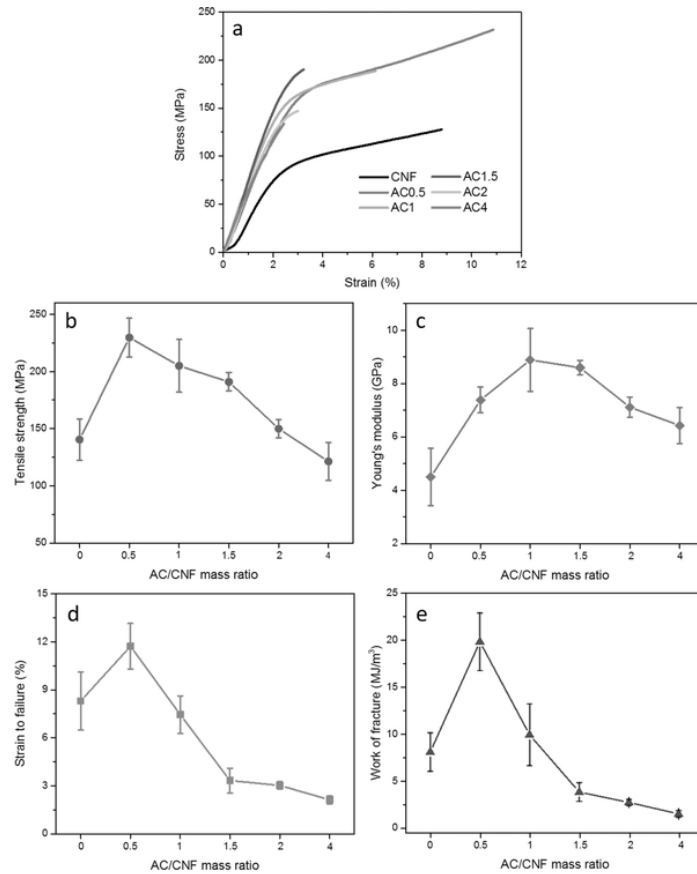
where T is the transmittance, λ is the wavelength, n_{matrix} is the refractive index of the CNF matrix, n_{AC} is the refractive index of the AC, d is the AC particle diameter, ϕ is the volume content of AC, and z is the thickness of hybrid film. The S_0 term corresponds to the intrinsic scattering of the CNF matrix.



Optical transparency of AC-CNF films with varying AC/CNF mass ratios and cross-sectional SEM images of AC1 film. a) Transmittance of films within the visible wavelength region. b) Transmittance of AC-CNF films at 550 nm c) Low-resolution image of AC1 film. d) High-resolution image of AC1 film. The average film thickness of the hybrid films varies from 19 to 49 μm with increasing AC/CNF ratios.

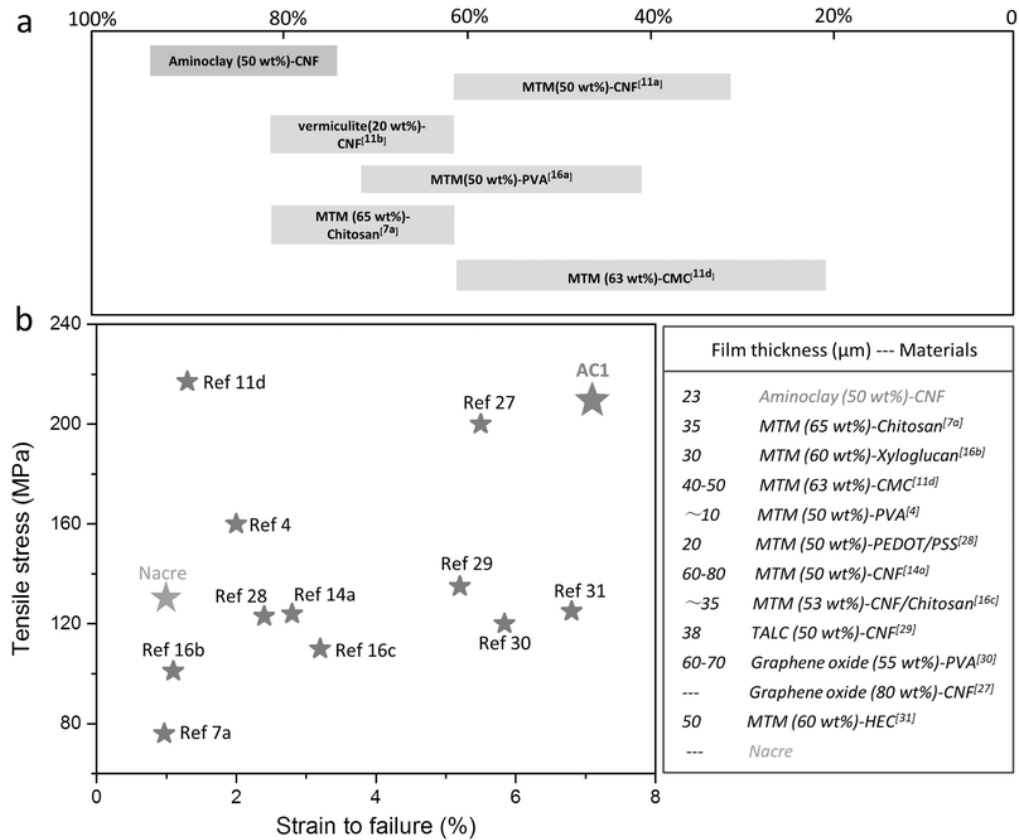


FTIR spectra of AC-CNF hybrid films. a) Characteristic bands of both CNF and AC nanoparticles from 3800 to 500 cm^{-1} . b) Amplified spectra of AC, CNF, and AC2 films between 2000 and 500 cm^{-1} . c) FTIR spectra of AC, protonated CNF (CNF-COOH), and the corresponding protonated AC2 films. d) The subtracted spectra of protonated AC2 film with the spectra of protonated CNF using the CH band of CNF at 2890 cm^{-1} as an internal reference.



Mechanical properties of AC-CNF hybrid films as a function of the AC/CNF mass ratio ranging from 0 to 4. a) Stress–strain curves. b) Tensile strength at rupture. c) Young's modulus. d) Strain to failure. e) Works of fracture. All measurements were performed at 50% relative humidity and 25 °C, at a strain rate of 1 mm min⁻¹.

Comparison of optical transparency and mechanical properties:



Comparison of optical transparency and mechanical properties of aminoclay (50 wt%)-CNF hybrid film with previously reported CNF/polymer-nanoclay films. a) Transmittance of visible light (400–700 nm). b) Tensile strength, strain to failure, and film thickness of the AC1 hybrid film (AC/CNF mass ratio of 1) compared with previously reported hybrid films of CNF and/or polymers and inorganic plate-like particles (MTM, talc, and graphene oxide). PEDOT:PSS, TALC, PVA and HEC refer to poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate), [30] talcum, polyvinyl alcohol and hydroxyethyl cellulose, respectively.

- ✓ Synthetic clay nanoparticles with a positive surface charge and carboxylated CNF with a negative surface charge have been used to fabricate nacre-like hybrid films.
- ✓ Infrared spectroscopy and SEM EDAX show that the AC particles form ionic bonds with the CNF with a homogeneous distribution of the AC particles within the fibrous CNF matrix.
- ✓ The hybrids films display a very high transparency that was related to the homogeneous distribution of the AC nanoparticles.
- ✓ The ionically bonded AC-CNF hybrid films displayed a combination of high tensile strength and large strain to failure that significantly surpass the biogenic nacre and polymer-clay films.
- ✓ The outstanding mechanical and optical properties of the flexible AC-CNF hybrid films were related to the relatively low aspect ratio of the AC nanoparticles and the ionic bonding between the cationic clays and the anionic CNF.

Thank you