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Nacre-mimetics with synthetic nanoclays up to ultrahigh aspect ratios

Paramita Das[1], Jani-Markus Malho[2], Khosrow Rahimi[1], Felix H. Schacher[3], Baochun Wang[1], Dan Eugen Demco[1] & Andreas Walther[1]

[1]DWI–Leibniz-Institute for Interactive Materials, Germany.
[2] VTT Technical Research Centre of Finland, Finland.
[3] Friedrich-Schiller-University Jena, Germany.

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Introduction:

1. Hierarchically ordered arrangement of well tailored soft and hard building blocks combine high toughness with excellent mechanical strength and stiffness alongwith light weight character like NACRE.
2. Lightweight character of mechanically strong and tough biomaterials, finding corresponding biomimetic materials that allow large-scale and facile preparation for future load-bearing applications is of preeminent importance.
3. There is a major scientific and technological challenge as precise nanostructuration at such biomimetic compositions with high fractions of reinforcements is hard to combine with large-scale processing methods.
4. Various efforts have been taken but most of the approaches are limited to a very small scale, and remain technologically infeasible owing to energy-intensive and laborious multistep procedures.

In this paper:

- Using synthetic nanoclays with widely different aspect ratios up to 10,000 for self assembled artificial nacre based polyvinylalcohol (PVA)- coated nanoclay and demonstrating their mechanical and functional properties.

- Establishment of the relationships among structure formation, nanostructuration, déformation mechanisms and mechanical properties as a function of aspect ratio.

RESULT AND DISCUSSION

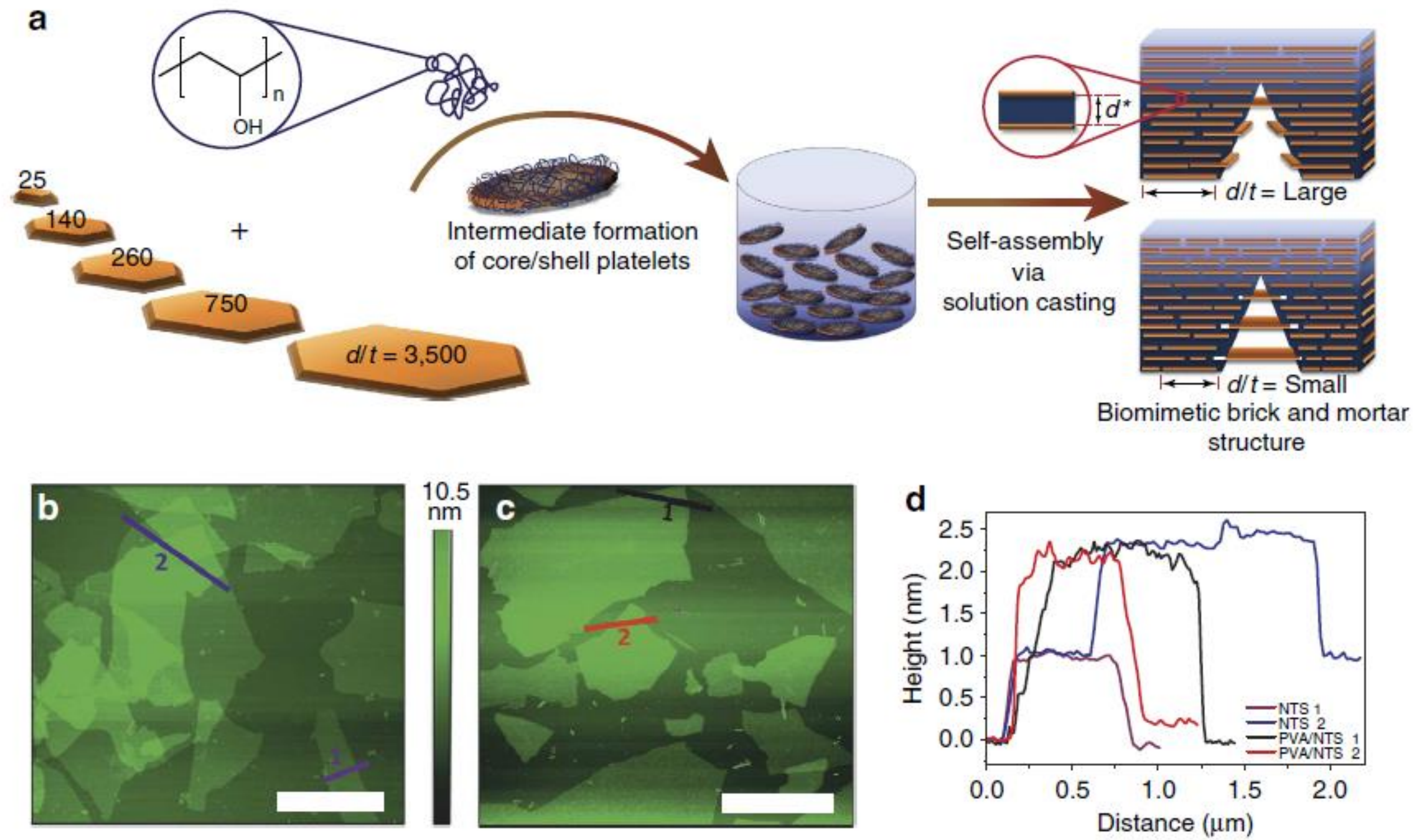


Figure 1: Preparation of artificial nacre and AFM characterization of NTS nanoclay before and after coating with PVA. **(a)** Artificial nacre via concentration-induced self-assembly of polymer-coated nanoclay platelets with intrinsic hard/soft architecture. **(b,c)** AFM height image of **(b)** pristine NTS (scale bar, 2 mm) and **(c)** PVA coated core/shell NTS nanoplatelets on freshly cleaved mica (scale bar, 2 mm), with **(d)** the corresponding section analysis

RESULT AND DISCUSSION

Table 1 | Overview of used synthetic nanoclays.

Name*	Abbreviation	Type	Dimension (nm)			Aspect ratio ($d_{avg}/t^{\dagger}$)
			Average (STD)	Min-Max	Literature	
Laponite	LAP	Na-Hectorite	25 ± 4‡	20-31‡	25[55,56]	25
Sumecton	SUM	Na-Saponite	140 ± 100§	35-600§	50[56]	140
Montmorillonite	MTM	Natural Na-Bentonite	260 ± 200§	30-1,000§	280[56]	260
Sodium fluorohectorite	NHT	Fluorohectorite	750 ± 500§	121-3,000§	3,000[50]	750
Sodium tetrasilicic mica	NTS	Synthetic mica	3,500 ± 2,500§	650-14,000§	≤5,000[56]	3,500

*Common names or trade name.
†An average thickness *t* of 1nm is considered for all nanoclays as obtained from AFM (see Supplementary Fig. 5).
‡Determined by DLS (Supplementary Fig. 2).
§Determined based on statistical image analysis of SEM micrographs counting more than 300 particles, and averaging over major and minor axis.

RESULT AND DISCUSSION

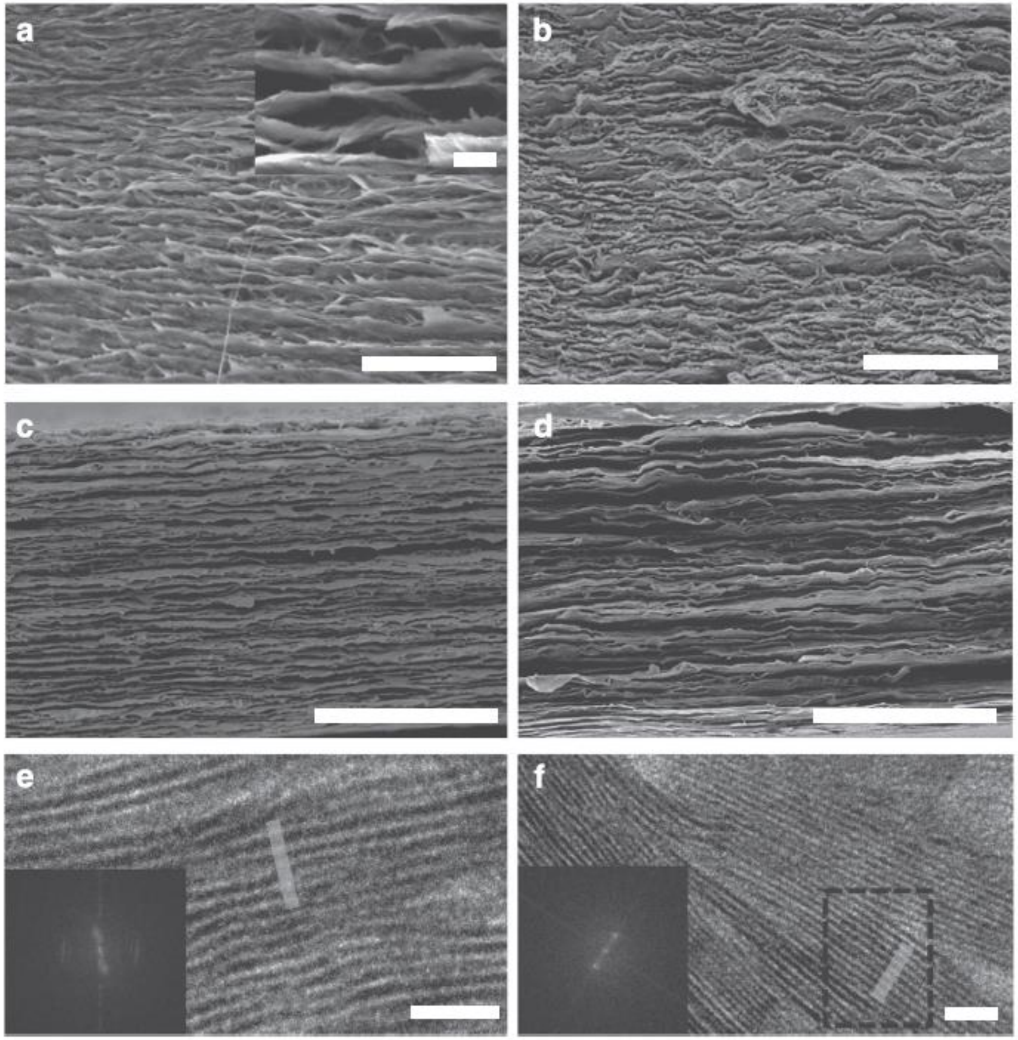
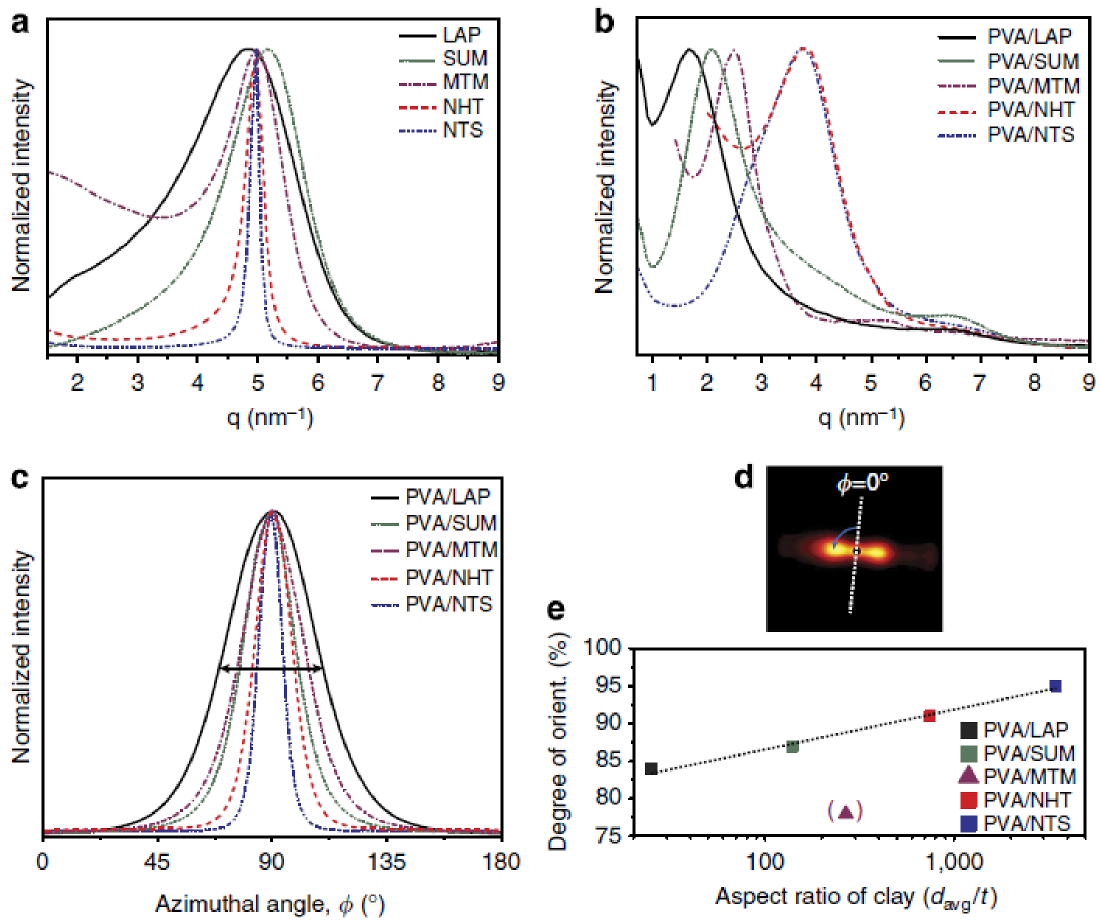


Figure 2: Electron microscopy characterization of the cross sections. SEM images of **(a)** PVA/LAP (scale bar, 2 mm; inset at higher magnification and scale bar, 250 nm), **(b)** PVA/SUM (scale bar, 2 mm), **(c)** PVA/NHT (scale bar, 5 mm), **(d)** PVA/NTS (scale bar, 5 mm) showing a layered ordered arrangement of the nanoclays, embedded in a nanoconfined PVA matrix. SEM images clearly show the increase of platelet size from **a to d**. TEM images of ultrathin cross sections of **(e)** PVA/SUM and **(f)** PVA/NTS (scale bar, 10 nm) showing alternating hard and soft layers. The dark and grey lines correspond to nanoclay and polymer, respectively. Fourier transform analysis of the sample (e) or marked area of the sample (f) are shown as insets.



Degree of orientation,

$$\Pi = \frac{(180 - \mathrm{FWHM})}{180} \times 100 \quad (1)$$

Figure 3: XRD characterization of the nanostructure of the layered nacre-mimetics. 1D XRD of **(a)** pure nanoclays and **(b)** nacre-mimetic materials. **(c)** Azimuthal intensity distribution profiles of the primary diffraction peak extracted from 2D XRD. Intensities are normalized to the peak maximum, **(d)** 2D XRD image of PVA/LAP at 10–15 beam inclination with respect to the plane of the film, **(e)** The degree of orientation calculated from the full-width at half maximum according to equation **(1)** for all nacre-mimetics. The value for nacre-mimetics based on natural MTM is shown in brackets, as it is clearly outside of the trend for the materials based on synthetic nanoclays, and neglected for the linear fit.

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Table 2 | Structural characterization of various nacre-mimetics.

Name	Aspect ratio (d_{avg}/t)	Polymer content (wt%)		d^*-spacing (nm)*	Degree of orientation (%)
		EA	TGA		
PVA/LAP	25	57.5	52.7	3.70	84
PVA/SUM	140	49.5	47.3	3.03	87
PVA/MTM	260	37.8	ND	2.54	78
PVA/NHT	750	26.3	36.3	1.66	91
PVA/NTS	3,500	23.5	23.6	1.68	95

ND, not determined.
*Determined by XRD.

RESULT AND DISCUSSION

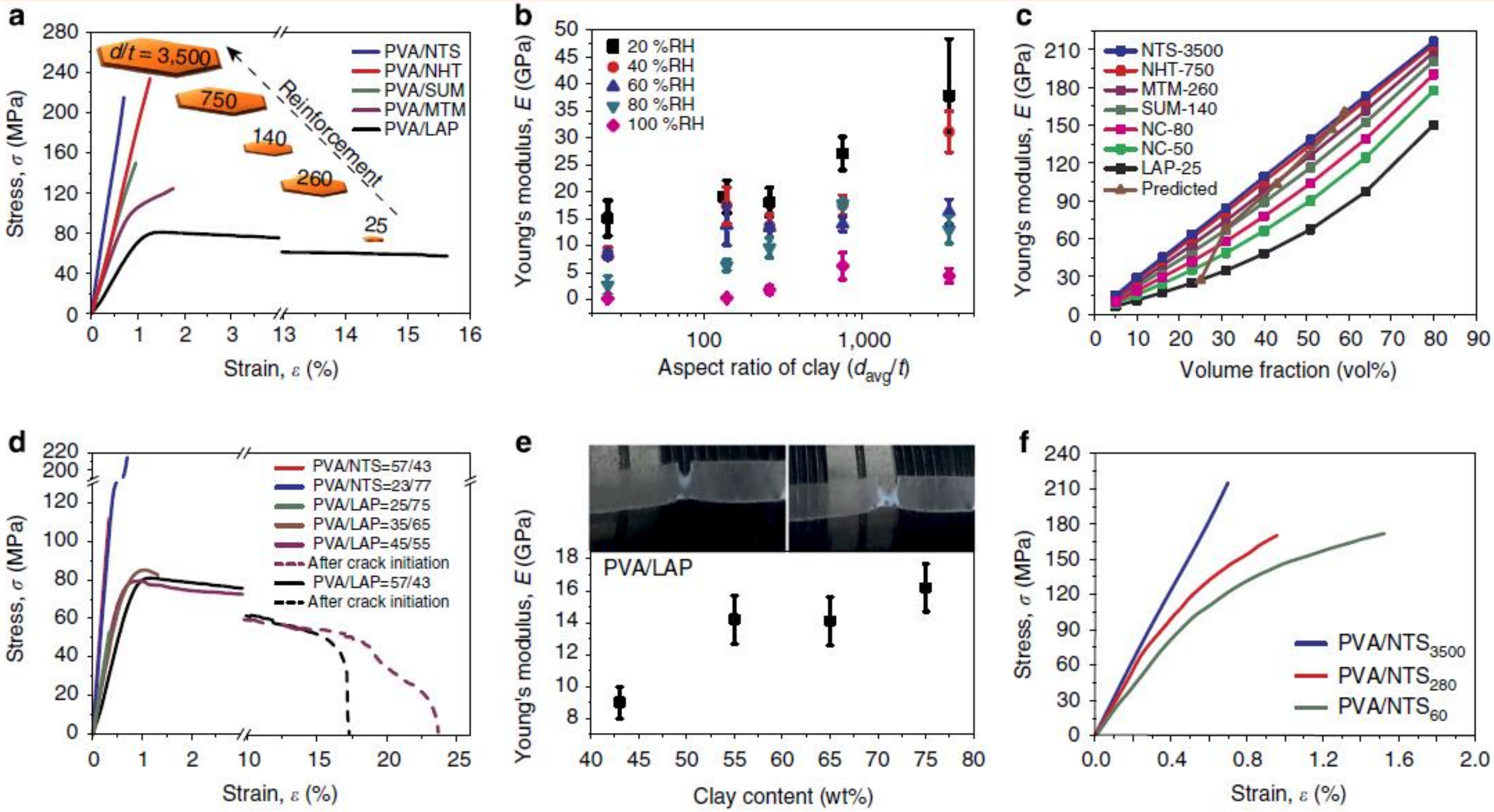

Figure 4: Tensile mechanical properties of nacre-mimetics**.** **(a)** Influence of the aspect ratio of nanoclays on tensile mechanical properties measured at 40 %RH for nacre-mimetics prepared from isolated core/shell particles. **(b)** Dependence of Young's modulus of nacre-mimetics on the aspect ratio of nanoclay at different %RH. **(c)** Variations of Young's modulus with volume fraction of reinforcement are shown for different aspect ratios following the Halpin Tsai model, considering E_m = 2.3 GPa at 40 %RH , E_r = 270 GPa and t = 1 nm (NC = nanoclay). The predicted values for our nacre-mimetics are added, considering the actual polymer content and the aspect ratio of the individual nanoclay. **(d)** Influence of polymer content on tensile mechanical properties for PVA/NTS and PVA/LAP (40 %RH, polymer content indicated in w/w within the panel). Dotted lines indicate stable crack propagation. **(e)** Dependence of Young's modulus of PVA/LAP on polymer content. Photographs of PVA/LAP = 45/55 sample show the crack initiation and stable crack propagation. **(f)** Effect of platelet size of fluidized/fragmented NTS nanoclay on tensile mechanical properties of corresponding nacre-mimetics based on perfect core/shell particles

RESULT AND DISCUSSION

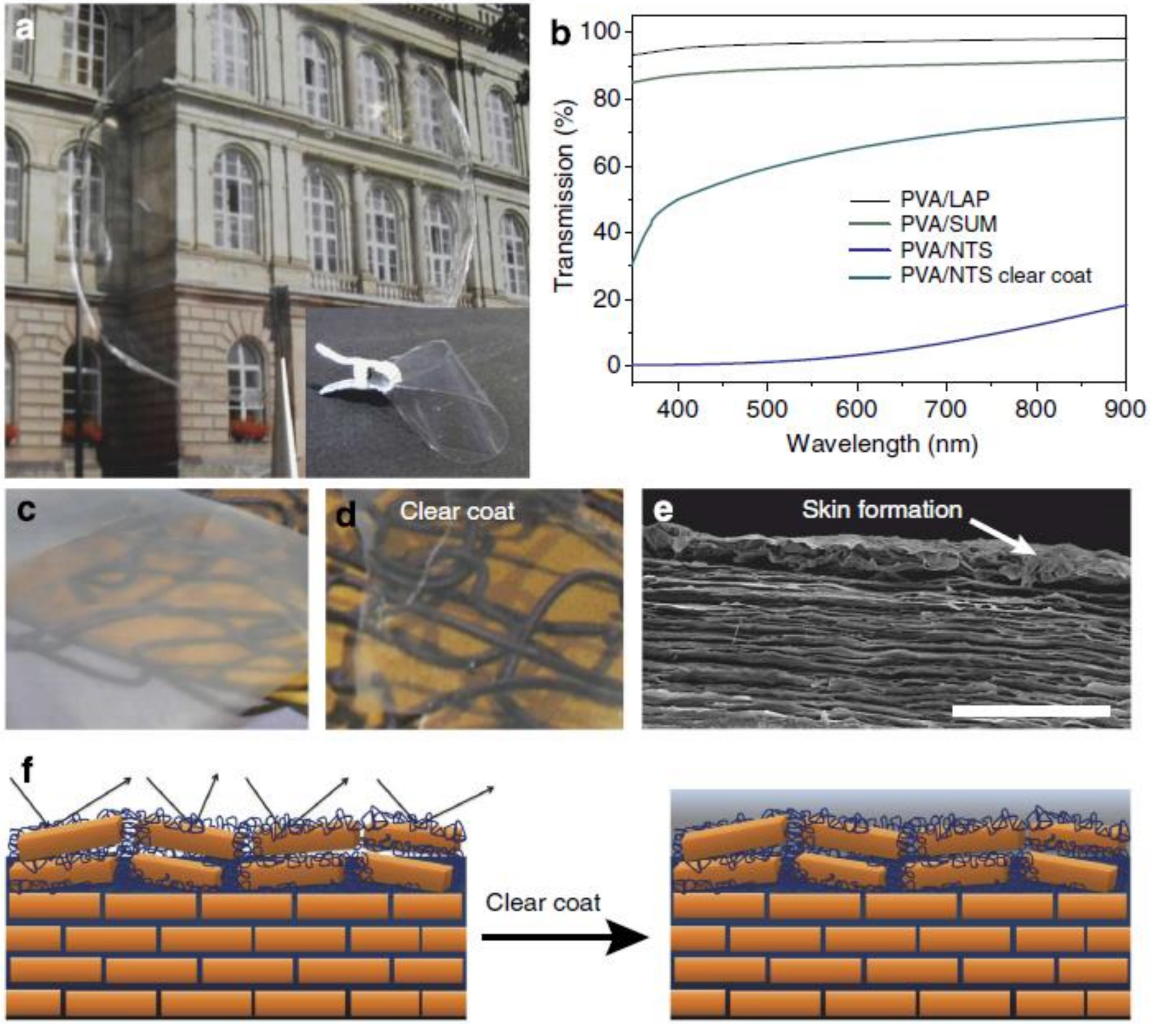

Figure 6: Optical properties of nacre-mimetics based on synthetic nanoclays with various aspect ratios**. (a)** Photographs of an almost fully transparent PVA/LAP film. **(b)** Transparency by UV-Visible spectroscopy (normalized to 25 mm thickness). (c,d) Nacre-mimetics with larger nanoclay (PVA/NTS) show translucency, but require a clear-coat matching the refractive index of the nacre-mimetics closely to become almost transparent. (e) SEM depicting the skin formed during preparation of a PVA/NTS nacre-mimetic (scale bar, 5 mm). (f) Schematic (not in scale) showing how a clear coat of matching refractive index diminishes surface scattering by providing a smooth top surface layer

RESULT AND DISCUSSION

Table 3 | Oxygen barrier properties of PVA/nanoclay nacre-mimetics.

Material	Aspect ratio	RH (%)	Oxygen permeability $cm^3 \cdot mm \cdot m^{-2} \cdot day^{-1} \cdot atm^{-1}$
PVA/LAP	25	80	0.136
PVA/SUM	140	80	0.056
PVA/MTM[36]	260	80	0.325
PVA/NTS	3,500	80	0.005 (0.004)*

*SD based on three specimens is given in brackets.

SUMMARY AND CONCLUSION

1. Establishment of the correlation among structure formation, nanostructuration, mechanical deformation modes and functional properties for self-assembled artificial nacre using synthetic clays with PVA.
2. Demonstrating large progress of mechanical and functional properties of self-assembled polymer/nanoclay nacre-mimetics by using synthetic nanoclays with 3 aspect ratios covering three orders in magnitude (25–3,500).
3. Highly ordered, large-scale nacre-mimetics obtained even for low aspect ratio nanoplatelets and showing pronounced inelastic deformation with very high toughness, while those formed by ultralarge nanoplatelets exhibit superb stiffness and strength.
4. Regarding functionalities, glass-like transparency, and excellent gas barrier

SIGNIFICANCE

- Similar studies on functionalized clays and other water dispersible materials like CNCs can also be used as reinforced materials.

- Other aspects for such type of materials can be also looked upon like superhydrophobicity.

THANK YOU