Supporting Information:

Bio-inspired platelet-reinforced polymers with enhanced stiffness and damping behaviour

Wilhelm Woigk[1], Kunal Masania [1,2,*], Fabian Stork[1], Alex Heusi[1], Erik Poloni[1] and André R. Studart [1,*]

[1] Complex Materials, Department of Materials, ETH Zürich, 8093 Zürich, Switzerland

[2] Current address: Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, Netherlands

* corresponding authors: k.masania@tudelft.nl, andre.studart@mat.ethz.ch

Content:

SI 1: Effect of frequency on the dynamic mechanical properties of the composites

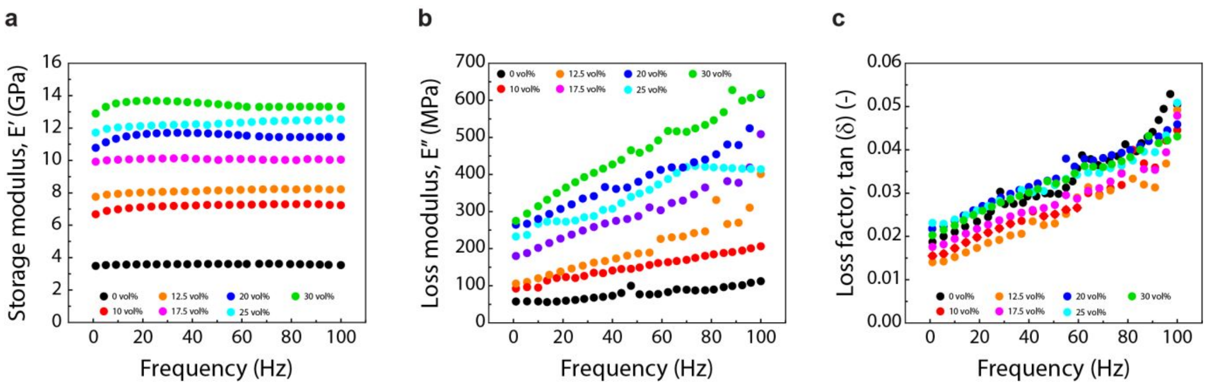


Figure S1: Dynamic mechanical properties of epoxies reinforced with different platelet concentrations as a function of the oscillatory frequency at constant deformation amplitude of 40 µm. (a) Storage modulus (E'), (b) loss modulus (E'') and (c) loss factor ($\tan(\delta)$) of composites prepared with thermoset epoxy (EP) matrix. The nearly constant E' modulus for a fixed platelet concentration reveals the linear-elastic response of the composites to the applied deformation.

SI 2: Viscoelastic properties of composites containing platelets aligned longitudinally in-plane or out-of-plane

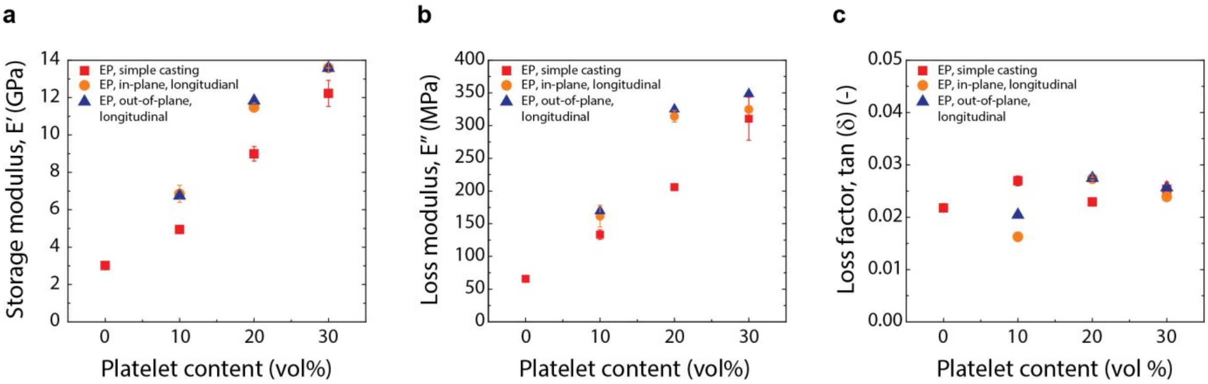
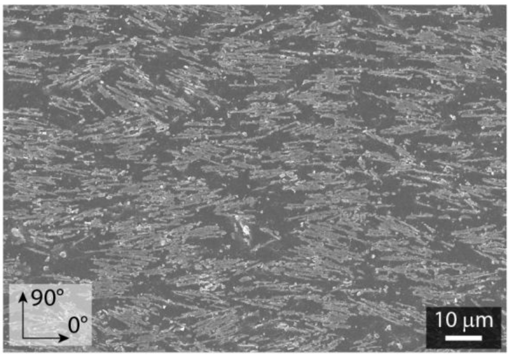


Figure S2: Dynamic mechanical properties under oscillatory deformation of composites with increasing platelet concentrations. Data are shown for specimens containing platelets aligned longitudinally in-plane or out-of-plane in comparison to samples prepared by simple casting. (a) Storage modulus (E'), (b) loss modulus (E'') and (c) loss factor ($\tan(\delta)$) of composites prepared with thermoset epoxy (EP) matrix.

SI 3: Platelet orientation in PMMA-based composite

a



b

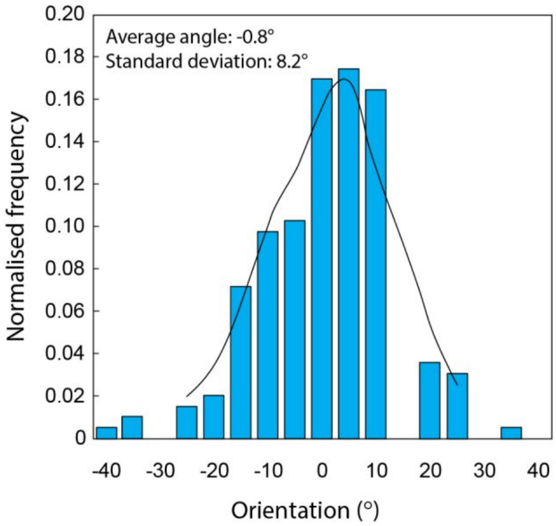


Figure S3: Platelet orientation achieved in the absence of an external magnetic field in a PMMA sample reinforced with 30 vol% Al_2O_3. (a) Scanning electron microscopy image depicting the majority of alumina platelets aligned in the horizontal direction parallel to the substrate. (b) Distribution of the platelet orientation quantified via image analysis.

SI 4: Tension-shear chain model

The mechanical properties of biomimetic regularly staggered composites can be quantified using a tension-shear chain model (Figure S4) [1,2]. This model predicts the elastic modulus of a staggered composite from the sum of uniaxial strains resulting from the tensile and shear stresses developed in the stiff phase and the soft matrix, respectively, upon tensile loading of the composite. For a representative unit cell of the staggered microstructure (Figure S4), the total strain ε_{tot} is given by:

$$\varepsilon_{tot} = \varepsilon_p + \varepsilon_m = \frac{\Delta L_p}{L} + \frac{\Delta L_m}{L} \qquad \text{(Eq. S1)}$$

where ε_p and ε_m are the strains in the platelet and soft matrix, respectively; L is the length of the platelet; and ΔL_p and ΔL_m are the longitudinal extensions due to the tensile and shear stresses on the platelets and soft matrix, respectively. The extension of the soft matrix (ΔL_m) is expressed as

$$\Delta L_m = 2\,\gamma_m\,h_m \qquad \text{(Eq. S2)}$$

where γ_m is the shear strain in the soft matrix and h_m the thickness of the matrix layer between two platelets (Figure S4).

Taking the platelet volume fraction φ in the unit cell to be

$$\varphi = \frac{h_p}{h_p + h_m} \qquad \text{(Eq. S3)}$$

one obtains

$$h_m = \frac{(1-\varphi)}{\varphi} h_p \qquad \text{(Eq. S4)}$$

Inserting Eq. S4 into Eqs. S1 and S2 leads to the following relation:

$$\varepsilon_{tot} = \frac{\Delta L_p + 2\,\gamma_m\,h_p(1-\varphi)/\varphi}{L} \qquad \text{(Eq. S5)}$$

Assuming linear-elastic conditions, the total strain ε_{tot} can be used to estimate the elastic modulus of the composite (E) using Hooke's law:

$$\frac{1}{E} = \frac{\varepsilon}{\sigma} \qquad \text{(Eq. S6)}$$

To simplify the analysis we assume the tensile stress σ to be dominated by the hard platelet phase. This allows us to express the effective tensile stress on the composite as $\sigma = \varphi\bar{\sigma}_p$, where $\bar{\sigma}_p$ is the average tensile stress in the platelet. Assuming the tensile stress σ to increase linearly from the end towards the center of the platelet, we can approximate the average stress $\overline{\sigma}_p$ to be half of the maximum stress in the middle of the rigid platelet (Figure S4).

In addition to the tensile stress within the platelets, the other two important parameters that need to be considered are the uniaxial extension in the platelets (ΔL_p) and the shear strain in the soft matrix (γ_m), which are given by the following relations:

$$\Delta L_p = \frac{\overline{\sigma}_p\, L}{E_p} \qquad\qquad \gamma_m = \frac{\tau_m}{G_m} \qquad \text{(Eq. S7)}$$

where E_p is the elastic modulus of the platelet, τ_m is the shear strain on the matrix and G_m is the shear modulus of the soft matrix. The shear modulus is given by $G_m = E_m/2(1+\nu_m)$ with ν_m and E_m being the Poisson's ratio and the elastic modulus of the soft matrix, respectively.

Considering a single platelet in equilibrium with the surrounding matrix, the normal force acting on the platelets (F_p) and the shear force acting on the matrix (F_m) can be balanced ($F_p = F_m$) to result in the following expressions for the stresses, σ_p and τ_m:

$$\sigma_p = \frac{F_p}{h_p\, t} \qquad\qquad \tau_m = \frac{F_m}{L\, t} \qquad \text{(Eq. S8)}$$

$$\sigma_p\, h_p\, t = \tau_m\, L\, t \qquad \text{(Eq. S10)}$$

$$\sigma_p = \tau_m \frac{L}{h_p} = \tau_m\, \rho \qquad \text{(Eq. S11)}$$

where $\rho = L/h_p$ is the aspect ratio of the platelet.

Assuming that the matrix yields at an uniform shear stress along the length of the platelet, the stress on the platelet (σ_p) should increase linearly from the edge towards the centre (Figure S4d). Taking the average normal stress, $\overline{\sigma}_p$, as an approximation for the stress on the platelet, Eq. S11 turns into

$$\overline{\sigma}_p = \frac{1}{2}\tau_m\, \rho \qquad \text{(Eq. S12)}$$

Inserting the total strain ε_{tot} (Eq. S5) with its components (Eq. S7) and the average tensile stress (Eq. S12) into Hooke's law (Eq. S6) one obtains the following relation for the elastic modulus of a staggered composite (E_c):

$$\frac{1}{E_c} = \frac{1}{\sigma_c L}\left[\frac{\overline{\sigma}_p L}{E_p} + 2\frac{\tau_m}{G_m}\, h_p\,(1-\varphi)/\varphi\right] \qquad \text{(Eq. S13)}$$

Assuming that the overall stress on the composite (σ_c) is carried mostly by the platelets ($\sigma_c \approx \varphi\bar{\sigma}_p$) and rearranging Eq. S13 to better illustrate the two contributions to the stiffness of the staggered composite, we arrive at the following relation:

$$\frac{1}{E_c} = \frac{1}{\varphi\, E_p} + \frac{4\,(1-\varphi)}{G_m\, \varphi^2\, \rho^2} \qquad \text{(Eq. S14)}$$

The tension-shear-chain model (Eq. S14) is a simple sum of the stiffness contribution of the hard platelet and the soft matrix with the assumption that the stiffness of the staggered composite comes purely from the elastic modulus of the platelet and the shear stiffness of the soft matrix. However, previous work has shown that the resin-rich region between the ends of two adjacent platelets can significantly add to the composite's stiffness [3]. To account for this region, in which tensile stresses develop in the matrix, the tension-region parameter α was introduced, which is added as a factor to Eq. S14:

$$\frac{1}{E_c} = \frac{1}{\varphi\, E_p} + \frac{4\,(1-\varphi)}{\alpha\, G_m\, \varphi^2\, \rho^2} \qquad \text{(Eq. S15)}$$

The value of α depends on several geometrical parameters and properties of the composite, as follows:

$$\alpha = 1 + \frac{8\, h_m}{(1-\nu_m)\rho\, \varphi\, l_m} \qquad \text{(Eq. S16)}$$

With the assumption that $h_m = l_m$ [3], the parameter α can be expressed in the simplified form:

$$\alpha = 1 + \frac{8}{(1-\nu_m)\rho\, \varphi} \qquad \text{(Eq. S17)}$$

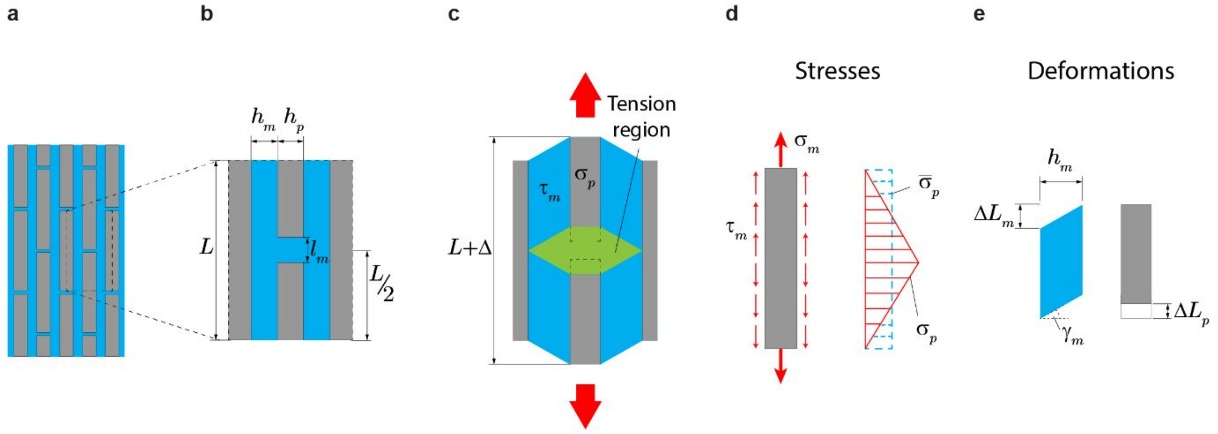


Figure S4: Schematic representation of the tension-shear chain model used to predict the mechanical properties of the investigated composites. (a) Staggered architecture of the composite. (b) Unit cell highlighting the length (L) and the thickness (h_p) of the stiff platelets, as well as the thickness (h_m) and height (l_m) of the soft matrix. (c) Stresses and deformations developed within the composite upon tensile mechanical loading (deformation Δ). (d) Stresses acting in and around a stiff platelet. $\overline{\sigma}_p$ represents the average tensile stress in the stiff platelets, whereas τ_m corresponds to the shear stress in the soft matrix. (e) Platelet normal and matrix shear deformation upon tensile loading. Adapted with permission from [3]. Copyright 2014 The American Society of Mechanical Engineers.

The above description of the elastic modulus of the composite can be expanded to predict also the complex elastic and shear moduli, $E^* = E' + iE''$ and $G^* = G' + iG''$, respectively. The storage modulus (E') can be directly calculated from Eq. S15 by replacing E_c by E', E_p by E'_p, and G_m by G'_m [3]. In turn, the loss modulus E'' can be calculated as follows:

$$E'' = \frac{4\, E'^2_p\, \rho^2\, (1-\varphi)\, \alpha\, G''_m}{\left[\alpha\, G'_m\, \rho^2 + 4\, E'_p\, (\varphi^{-1} - 1)\right]^2} \qquad \text{(Eq. S18)}$$

where G''_m is the shear loss modulus of the soft matrix.

The TSC model explained above assumes a perfect arrangement of the staggered brick-and-mortar structure, which considers an overlap length of the platelet of L/2, and a uniform shear stress distribution at the platelet-matrix interface, which is the case in real biological materials [4]. Moreover, stresses and deformations in the transverse direction are neglected due to the large aspect ratio of the stiff platelets [5].

It is important to mention that the effective aspect ratio of the platelets used in the prediction of the storage and loss moduli of the composites was estimated taking into account the area of the interface between the platelet and the soft matrix. This approach considers the fact that the model assumes squared platelets of length L, whereas the actual particles are better approximated as discs of diameter D_d (Figure S5). Using the interfacial area as the relevant parameter for stress transfer at the platelet-matrix interface, we therefore assume our platelets to have a square-equivalent geometry with length $L_{eq.} = (\sqrt{\pi}/2)D_d$ in our theoretical predictions (Figure 3).

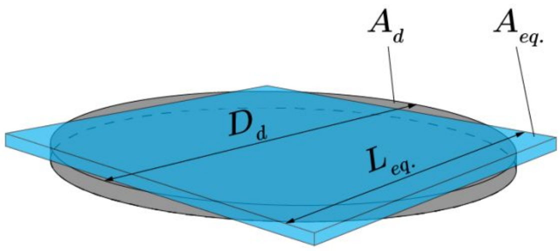


Figure S5: Schematic representation of a disc-shaped platelet of diameter D_d and the corresponding hypothetical squared platelet of side length L_{eq} and equivalent surface area ($A_d = A_{eq}$) used for the theoretical predictions (Figure 3).

SI 5: Size distribution of the alumina platelets

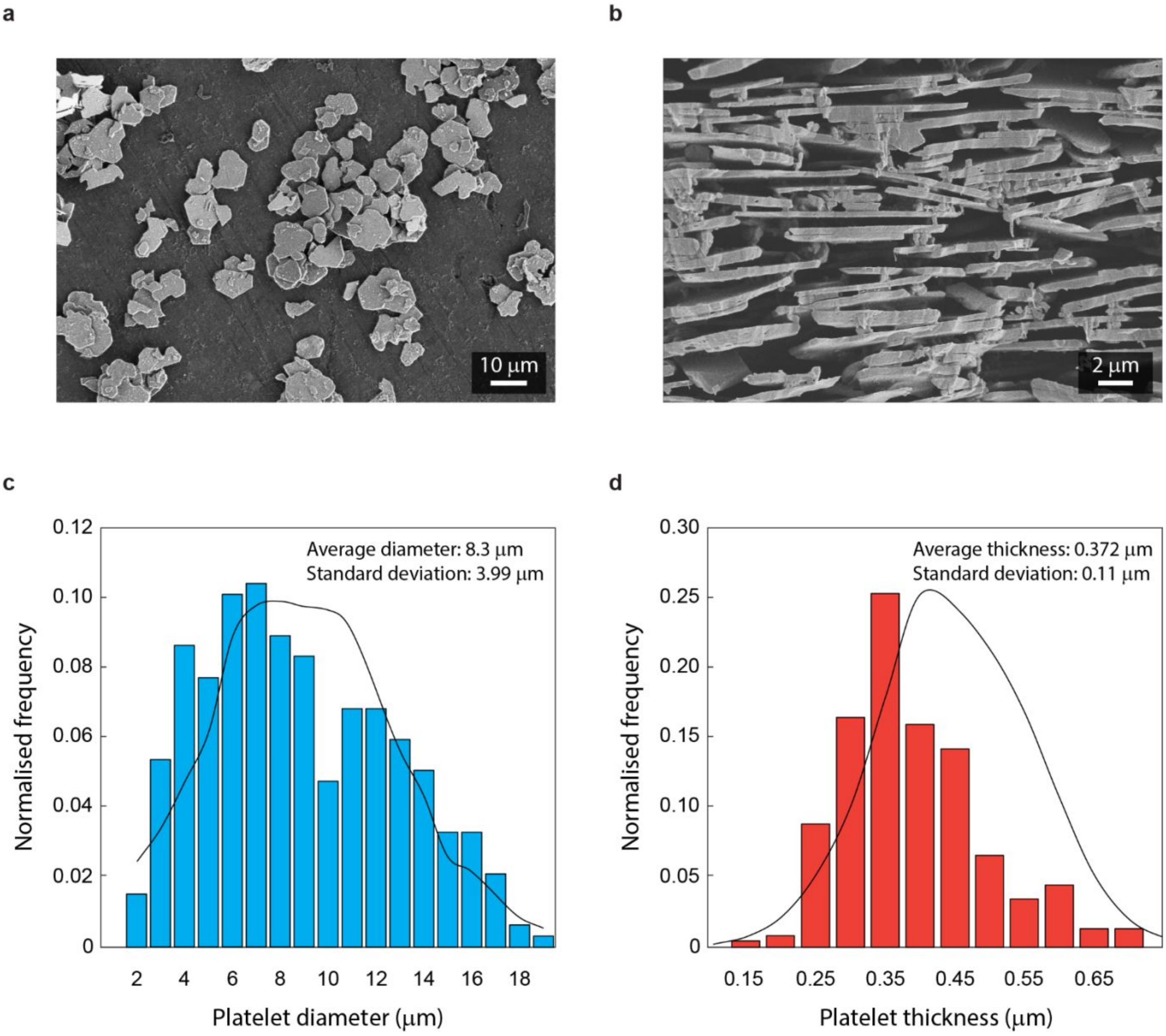


Figure S6: a,b SEM images used to measure (a) the diameter and (b) the thickness of the alumina platelets. **c,d** Size distributions of the alumina platelets in terms of (c) diameter and (d) thickness. 337 and 226 platelets were measured to determine the diameter and the thickness, respectively.

SI 6: Determination of the shear loss modulus of the nacre matrix

The design map displaying the loss modulus of nacre (Figure 5b) was created using the staggered composite model (Eq. 2). The elastic storage modulus of the hard platelets, E'_p, and the shear storage modulus of the matrix, G'_m, were assumed to be 70 GPa and 0.07 GPa, respectively. The E'_p value was taken from typical data for calcium carbonate, whereas the G'_m value was obtained using the relation G'_m = E'_p/1000, which has been widely reported in the literature [1,3]. The shear loss modulus, G''_m, was calculated from the experimentally measured elastic loss modulus of nacre, E''_{nacre} = 0.85 GPa, using the following equation:

$$G''_m = \frac{E''_{nacre}\left[\alpha\, G'_m\, \rho^2 + 4\, E'_p\, (\varphi^{-1} - 1)\right]^2}{4\, E'^2_p\, \rho^2\, (1-\varphi)\, \alpha} \qquad \text{(Eq. S19)}$$

Solving Eq. S19 for nacre using an aspect ratio (ρ) of 9 [3] and a volume fraction (φ) of 0.95 leads to a shear loss modulus G''_m = 0.003589 GPa.

References

[1] Ji B, Gao H. Mechanical properties of nanostructure of biological materials. J Mech Phys Solids 2004;52:1963–90. doi:10.1016/j.jmps.2004.03.006.

[2] Ji B, Gao H. Elastic properties of nanocomposite structure of bone. Compos Sci Technol 2006;66:1209–15. doi:10.1016/j.compscitech.2005.10.017.

[3] Zhang P, To AC. Highly Enhanced Damping Figure of Merit in Biomimetic Hierarchical Staggered Composites. J Appl Mech 2014;81:051015. doi:10.1115/1.4026239.

[4] Liu G, Ji B, Hwang KC, Khoo BC. Analytical solutions of the displacement and stress fields of the nanocomposite structure of biological materials. Compos Sci Technol 2011;71:1190–5. doi:10.1016/j.compscitech.2011.03.011.

[5] Qwamizadeh M, Lin M, Zhang Z, Zhou K, Zhang YW. Bounds for the dynamic modulus of unidirectional composites with bioinspired staggered distributions of platelets. Compos Struct 2017;167:152–65. doi:10.1016/j.compstruct.2017.01.077.