DAMPING BEHAVIOUR OF BIO-INSPIRED NATURAL FIBRE COMPOSITES

Wilhelm Woigk[1], Kunal Masania[1], Silvan Gantenbein[1], Erik Poloni[1] and André R. Studart[1]

[1]Complex Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5 8093 Zurich, Switzerland
Email: wilhelm.woigk@mat.ethz.ch, Web Page: http://www.complex.mat.ethz.ch

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Abstract
Structural materials such as metals and fibre-reinforced plastics are stiff engineering materials used in many industrial fields. However, their high stiffness leads usually to the inability to dissipate energy via vibration damping. Contrarily, compliant materials such as rubbers and soft polymers exhibit an excellent damping behaviour, but lack in stiffness. Natural composites, such as wood, bone and seashells possess both high stiffness and high damping and thus combine properties that are generally mutually exclusive. In this study, the design principles of two biological composites, i.e. nacre and wood, were studied to design composites out of engineering materials which display a damping behaviour like the natural systems and are producible on a larger scale. The dynamic properties of nacre-inspired epoxy and flax fibre-reinforced composites were investigated and compared to structural engineering materials and to the biological materials served for the inspiration.

1. Introduction

Lightweight engineering materials such as fibre-reinforced composites are widely used in aerospace, automotive and sports equipment applications. They offer excellent specific properties but suffer generally from the inability to dissipate energy by vibration damping [1, 2]. Materials with high damping are desired for structural applications to suppress unwanted vibrations, in particular in mechanically dynamic systems. Therefore, the goal is to design energy absorbing structural components made from materials with a high viscoelastic behaviour. Viscoelasticity is characterised by a combination of elastic (solid) and viscous (fluid) material behaviour. At the same time, those energy absorbing materials should provide a high specific stiffness to be considered as lightweight, structural materials. However, most engineering materials, including composites, show poor damping performance since high stiffness and high energy dissipation are properties that are in general mutually exclusive [2].
Conversely, biological composites exhibit both high stiffness and damping due to hierarchical structuring of their reinforcements embedded in highly viscoelastic matrices [1–3]. For example, the staggered formation of mineral bricks embedded in a protein matrix at the most elementary level in bone and seashells provide both high stiffness and high viscoelastic loss. In particular, nacre in seashells is composed of staggered aragonite (calcium carbonate, $CaCO_3$) bricks in a soft protein matrix [4–7].

Despite the small amount of organic matrix (5 vol % [8]) between the brittle $CaCO_3$ bricks, the high elastic deformability of the matrix leads to the outstanding damping performance.
Similar outstanding damping behaviour and specific stiffness can be found in wood and bast fibres. Fibres such as flax, hemp and ramie became very popular in the last decade because of their low environmental footprint and good specific mechanical properties and are hence increasingly used as reinforcements in polymers [9–12]. Natural fibres are not only derived from low cost renewable resources, are biodegradable and CO_2 neutral but also offer high intrinsic damping properties, which is of high interest in the advanced sport equipment industry [13]. Similar to sea shells, the high damping of natural fibres lies in their microstructure. The fibre itself is a hierarchically arranged composite material comprised of highly crystalline and discontinuous cellulose microfibrils embedded in an amorphous matrix of lignin and hemicellulose. This is assumed to be the key factor why natural fibre composites exhibited an order of magnitude higher damping compared to metals and three times higher damping than glass and carbon fibre composites [13, 14].
In this research, we study the design principles of two natural systems, i.e. nacre and wood, and adapt their principles to engineering materials to obtain novel bio-inspired composites with simultaneous high stiffness and damping.

2. Materials and method

2.1. Materials

A diglycidyl ether of bisphenol A epoxy resin (Araldite LY 3585, Huntsman Advanced Materials, Switzerland) was used. The resin was mixed with an amine hardener (Aradur 3475, Huntsman Advanced Materials, Switzerland) in a stoichiometric ratio of 100:21 by weight of epoxy to hardener.
Aluminium oxide (Alumina, Al_2O_3) platelets (RonaFlair) were purchased from Merck, Germany. The platelets were surface functionalised with superparamagnetic iron oxide nanoparticles in order to make the platelets responsive to external magnetic fields [16, 17]. By rotating external magnets, the orientation of the platelets can be defined during the resin curing and thus can the anisotropy of the composite be tailored [15].
Flax fibres were obtained from Bcomp Ltd., Switzerland. A unidirectional (UD) fabric type 5009 with an areal weight of 300 g/m^2 was used.

2.2. Manufacturing of nacre-inspired and hierarchical natural fibre composite

Nacre-inspired composites were produced by introducing surface functionalised Al_2O_3 platelets into the two-component epoxy matrix. Rigorous mixing and degassing of the platelet containing resin was preformed using an ARE-250 (Thinky, USA) planetary mixer. First the platelets and the resin were mixed and the hardener added in a second step. The mixed resin system was then cased into a silicone mould and cured on a hot plate at 40 °C for 4h and post-cured in an oven at 120 °C for 1h. Samples with Al_2O_3 volume contents of 10, 20 and 30 % were manufactured. For the cases of generating a defined anisotropy by aligning the platelets, the curing was accompanied by a rotating magnet in the vicinity of the mould.
Hierarchical composites were produced by stacking UD flax fibre woven fabrics into a mould, in accordance with [17]. The epoxy matrix materials, either with or without platelets, were prepared as described above for the nacre-inspired composites and were introduced in a layer-by-layer application to allow for a homogeneous distribution of the platelets within the composite. The mould was then

closed with a sealed pressure die and placed in a press at 20 bars equipped with top and bottom heating plates. The temperature was set to 80 °C to allow for a rigorous fibre impregnation before resin curing.

2.3. Dynamic mechanical analysis

Dynamic mechanical analysis was carried on a Q800 (TA Instruments, USA) machine using a three-point-bending setup with a 20 mm span. The casted samples were grinded to a nominal size of 2 x 2 mm (thickness x width), whereas the length was 30 mm. Two samples were tested per material configuration, whereas each sample was tested twice. The samples were tested a constant temperature of 25 °C. A pre-force of 0.05 N was applied before testing and frequency sweeps (1 – 100 Hz) at constant amplitude of 40 µm and amplitude sweeps (5 – 100 µm) at constant frequency of 10 Hz were performed. The stiffness, loss and damping values presented here were extracted at 10 Hz and 40 µm, hence a total number of eight measurements were used for calculating the arithmetic average.

3. Results and Discussion

3.1. Dynamic Mechanical Analysis

A measure of damping is the loss factor, $\tan(\delta)$, which is the ratio of the loss modulus, E'', and the storage modulus, E'. Storage and loss moduli are the real and imaginary part of the complex modulus, E^*, respectively. The loss modulus, which is the product $E' \times \tan(\delta)$, is a figure of merit, commonly used to characterise damping properties of materials. The complex modulus was directly measured with the DMA test and the values for the material's damping performance were derived from it. We measured the damping behaviour for 10, 20 and 30 vol % platelet reinforced epoxy and compared it to the unreinforced reference material.

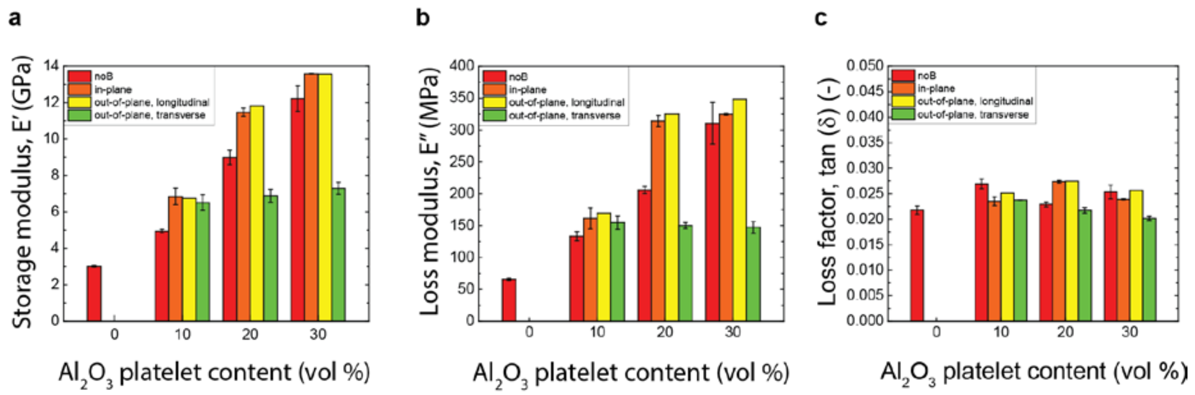

Figure 1. Dynamic Mechanical Analysis results for various platelet volume contents and different alignment strategies. a Storage modulus (real part of the complex modulus E^*). **b** Loss modulus, also referred to as damping figure of merit (imaginary part of the complex modulus E^*). **c** Loss factor (ratio of E'' and E').

Figure 1 shows the storage modulus, E' (1a), the loss modulus, E'' (1b) and the loss factor, $\tan(\delta)$ (1c) for different alignment strategies as a function of the Al_2O_3 platelets volume concentration. The alignment strategies consisted in either not exposing the composites to magnetic fields (Figure 2, noB)

or in exposing them to fields rotating in different directions (Figure 1, in-plane and out-of-plane in longitudinal and transverse directions). In Figure 1a and b one can see that both E' and E'' increase with increasing platelet volume content. The increase, however, is dependent on the alignment strategy. The moduli of the in-plane and out-of-plane longitudinal specimens increase almost similarly. This is not surprising as both specimen configurations differentiate only by a 90° rotation in the longitudinal axis. Thus, the platelets are still oriented in the loading direction and the high aspect ratio positively affects the stress transfer in the composite. Contrarily, the out-of-plane transverse specimens have the platelets oriented in a detrimental direction. The effective surface of the platelets is only their thickness, which is much smaller than their diameter. Thus, storage and loss moduli are only increasing up to a certain extend and remain constant in spite of higher platelet contents. In the three other configurations, the increase in the platelet volume content decreases the space between two adjacent platelets, thus reduces the thickness of the soft material. This increases both, the stiffness as a results of the incorporation of a hard phase and the damping figure of merit due to an enhanced shear deformation mechanism. A total relative increase of 350 % and 430 % for the E' and E'' respectively, could be obtained for the 30 vol% platelet reinforced epoxy as compared to the pristine epoxy.
Since E' and E'' increase similarly, the ratio of these parameters, which is the loss factor, remains almost unaffected. In fact, an initial increase of the loss factor when introducing 10 vol % of platelets was observed. Upon further platelet introduction, the loss factor was nearly unaffected independent of the alignment strategy used.

3.2. Modelling the damping behaviour of nacre-inspired composites

We adapted the model proposed by Zhang et al. [3] to analytically describe the damping properties of our alumina/epoxy staggered composites. The model has been derived from a tension-shear-chain (TSC) model that may be used to calculate the stiffness of hierarchical staggered composites [5]. The TSC model is used under the assumption that the hard platelets carry the majority of the load in form of tensile stress, whilst the soft matrix transfers these stresses via uniformly distributed shear.

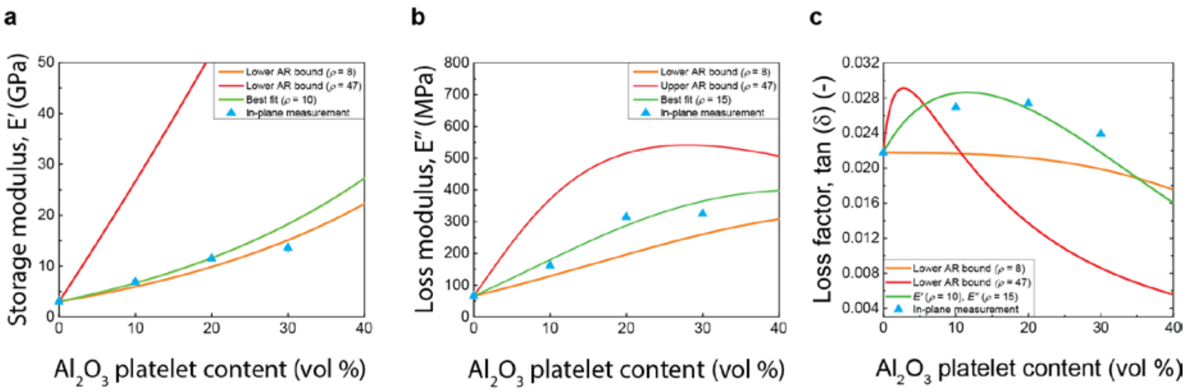

Figure 2. Tension-shear chain modelling of dynamic properties as a function of platelet volume concentration. a Storage modulus, $\boldsymbol{E'}$. The measurements are in a good agreement with the model when an AR of 10 is chosen. **b** Loss modulus, $\boldsymbol{E''}$. The measurements are in a good agreement with the model when an AR of 15 is chosen. **c** Loss factor, $\mathbf{tan}\ (\boldsymbol{\delta})$ as the ratio of $\boldsymbol{E''}$ and $\boldsymbol{E'}$.

Figure 2 shows the analytical dynamic properties of the staggered alumina/epoxy composites as a function of alumina platelet volume content. Storage and loss moduli are shown in Figure 2a and b, whereas the loss factor is depicted in c. Those diagrams also illustrate the measured storage and loss moduli along with the loss factor, as discussed in section 3.1.
The models contain parameters such as the elastic moduli of the hard platelets, E_p, and the soft matrix, E_m, which were experimentally determined. Other parameters such as the storage and loss shear moduli of the matrix, G'_m and G''_m, were calculated from the elastic modulus assuming isotropic material behaviour. The remaining parameter, i.e. the platelet aspect ratio (AR), ρ, was used as a function shape parameter and was determined to provide the best fit of the analytical model to the experimental data. AR of 10 and 15 were determined for storage and loss modulus, respectively. Those two values are within the standard deviation of the platelet's AR. The average AR of the platelets used is 27 with a scatter between 8 and 42. Since the determined AR values are very close to each other and the lower region of the measured error, it is assumed that the aspect ratios as fitting parameter are very similar.
It is apparent that the storage modulus has a monotonically increasing behaviour with increasing platelet volume content, which follows the Voigt bound (rule of mixtures). Contrary, the loss modulus reveals a maximum at a certain volume fraction. Consequently, a maximum is also expected for the loss factor as it being calculated by the quotient of loss and storage modulus. The existence of maxima, in particular in the loss modulus allows one to predict an optimal damping behaviour and to design a material that observe a damping figure of merit. For example, the aspect ratio can be tuned in order to achieve the maximum damping figure of merit for a given platelet volume content [3].

3.3. Damping behaviour of hierarchical flax fibre reinforced composites

It is reported that only a few materials exhibit a damping figure of merit at low frequencies (< 10 Hz) above 0.6 GPa. In particular engineering materials such as metals, glasses, ceramics and even continuous fibre-reinforced composites have quite low loss moduli. Soft metals, porous ceramics and biological composites such as cortical bone, nacre, wood and bamboo are materials with comparable high loss moduli. In addition, polymers have good viscoelastic properties and are due to their low density favourable damping materials [1, 2, 18]. It is further reported that structural hierarchies within materials corroboratively affect the strength, fracture toughness and defect tolerance [19–21]. The influence of hierarchal intricate structures is not well reported in the literature. Consequently, we added high loss flax fibres [12] into the polymer matrix to enhance the stiffness with the goal to not compromise the inherent good damping properties of polymers. Natural fibres have a very low material density, just marginally higher than the density of the polymer used in this study. Thus, the addition of lightweight natural fibres allows us to increase the stiffness of the composite without adding significant weight.
We prepared UD flax fibre reinforced composite (FFRP) plates with matrices that had 2.5, 5 and 7.5 vol% of alumina platelets of the initial matrix volume. Specimens with longitudinal and transverse fibre directions were tested in flexural DMA.

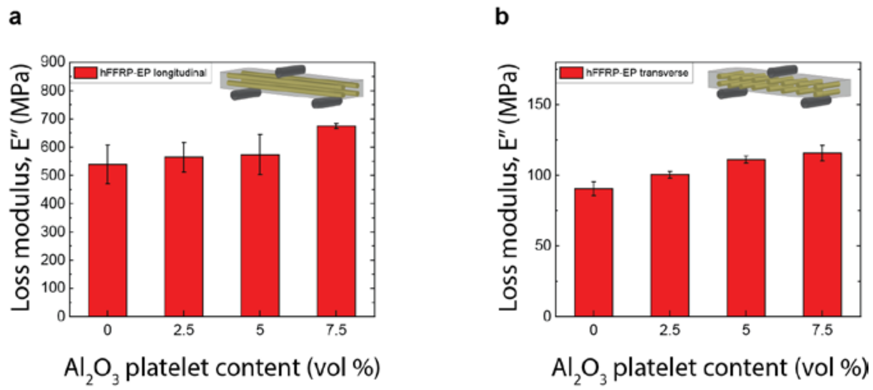

Figure 3. Damping figure of merit for hierarchical flax fibre reinforced epoxy composites. a longitudinal and **b** transverse direction.

Figure 3 shows the development of the damping figure of merit (loss modulus, E'') as a function of the alumina platelets volume content for flax fibre reinforced epoxy composites. Loss moduli in longitudinal (Figure 3a) and transverse (Figure 3b) are shown. Due to the introduction of the flax fibres, the E'' increases from initially 65 MPa for pure epoxy up to 540 MPa for longitudinal and 91 MPa for transverse FFRP, respectively. The introduction of Al_2O_3 platelets increased the E'' in both directions only marginally, with a more pronounced relative increase of 11, 23 and 28 % in the transverse direction. The negligible enhancement of the loss moduli with increasing platelet content suggest that the fibres influence the damping behaviour stronger than the platelets. This leads to the conclusion that the internal friction inside the fibres governs the energy dissipation in the hierarchical FFRP.

Interestingly, the developed material reached the damping figure of merit design guideline of 0.6 GPa. This particular design guideline is shown as the bold dashed line in the Ashby charts in Figure 4a and b. Both charts illustrate the stiffness against the damping loss factor. Figure 4a depicts a broad comparison of engineering materials such as ceramics, metals and composites along with hard and soft polymers. Figure 4b provides a close-up view to better illustrate the property achievements one can obtain when introducing platelets and natural fibres. We are able to match the stiffness and vibration damping properties of wood with the 30 vol% in-plane aligned platelet-reinforced epoxy composites. Further, we can reach a loss modulus of 600 MPa when incorporating natural fibres. This measure distinguishes our material from most of commonly used engineering materials, which are not able to reach this boundary.

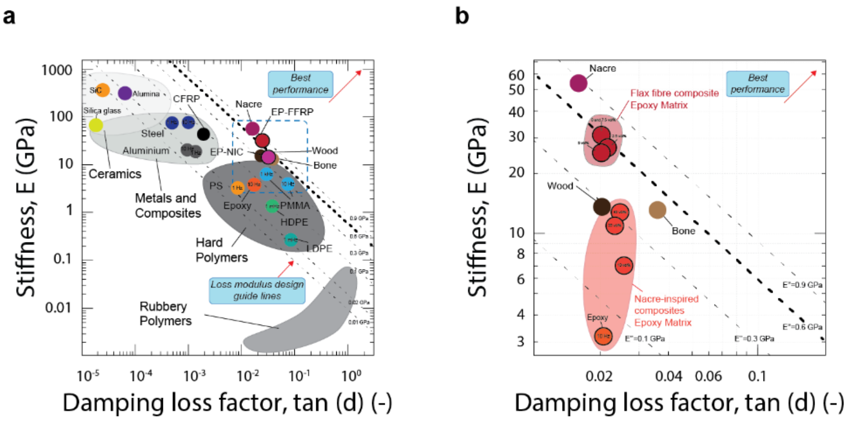

Figure 4. Ashby diagrams of damping properties showing the storage modulus, E'' against the damping loss factor, $tan\ (\delta)$. a Broad overview with the comparison of ceramics, metals and composites, hard polymers and rubbery polymers (adapted from [1, 18]). **b** Close-up view of the dashed region in a showing the nacre-inspired epoxy and hierarchical natural fibre composites.

4. Conclusions

In this project, we studied the design principles of two biological systems that display simultaneously high viscoelastic loss and stiffness. Seashells and wood are biological composites that comprise a hard reinforcing phase embedded in a soft matrix. The key aspect for the high viscoelastic loss in both composites is the ability of the soft matrix to transfer the stresses upon loading through large shear deformation, whereas the hard phase causes the high stiffness. We adapted the design principle of nacre and wood, and introduced ceramic Al_2O_3 micro-platelets and natural flax fibres into a soft epoxy matrix. The following conclusions can be drawn:

(1) Through external rotating magnetic fields, we are able to tailor the micro-structure and hence tune the anisotropy of the composite.
(2) The damping figure of merit can be increased by 4-times when introducing 30 vol% Al_2O_3 platelets and aligning them in the in-plane direction. The damping properties matches biological composites like natural wood and is in a similar range with cortical bone.
(3) A tension-shear-chain model can be employed to model the viscoelastic properties of staggered composites and it can be used as a tool to design highly damped materials.
(4) Natural fibres with a low density and an intrinsic viscoelastic loss exhibit damping properties that are not achievable with most engineering materials. At the same time these materials are lightweight and have a low environmental footprint.

Acknowledgments

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References

[1] R. S. Lakes, "High damping composite materials: Effect of structural hierarchy," *J. Compos. Mater.*, vol. 36, no. 3, pp. 287–297, 2002.

[2] P. Zhang, M. A. Heyne, and A. C. To, "Biomimetic staggered composites with highly enhanced energy dissipation: Modeling, 3D printing, and testing," *J. Mech. Phys. Solids*, vol. 83, pp. 285–300, 2015.

[3] P. Zhang and A. C. To, "Highly Enhanced Damping Figure of Merit in Biomimetic Hierarchical Staggered Composites," *J. Appl. Mech.*, vol. 81, no. 5, p. 051015, 2014.

[4] I. Jäger and P. Fratzl, "Mineralized Collagen Fibrils: A Mechanical Model with a Staggered Arrangement of Mineral Particles," *Biophys. J.*, vol. 79, no. 4, pp. 1737–1746, 2000.

[5] H. Gao, B. Ji, I. L. Jäger, E. Arzt, and P. Fratzl, "Materials become insensitive to flaws at nanoscale: Lessons from nature," *PNAS*, vol. 100, no. 10, pp. 5597–5600, 2003.

[6] B. Ji and H. Gao, "Mechanical properties of nanostructure of biological materials," *J. Mech. Phys. Solids*, vol. 52, pp. 1963–1990, 2004.

[7] F. Barthelat, Z. Yin, and M. J. Buehler, "Structure and mechanics of interfaces in biological materials," *Nat. Rev. Mater.*, p. 16007, 2016.

[8] H. D. Espinosa, J. E. Rim, F. Barthelat, and M. J. Buehler, "Merger of structure and material in nacre and bone - Perspectives on de novo biomimetic materials," *Prog. Mater. Sci.*, vol. 54, no. 8, pp. 1059–1100, 2009.

[9] P. Wambua, J. Ivens, and I. Verpoest, "Natural fibres: can they replace glass in fibre reinforced plastics?," *Compos. Sci. Technol.*, vol. 63, no. 9, pp. 1259–1264, Jul. 2003.

[10] B. Dahlke, H. Larbig, H. D. Scherzer, and R. Poltrock, "Natural Fiber Reinforced Foams Based on Renewable Resources for Automotive Interior Applications," *J. Cell. Plast.*, vol. 34, pp. 361–379, 1998.

[11] J. Holbery and D. Houston, "Natural-fibre-reinforced polymer composites in automotive applications," *J. Miner. Met. Mater. Soc.*, vol. 58, no. 11, pp. 80–86, 2006.

[12] M. Rueppel, J. Rion, C. Dransfeld, C. Fischer, and K. Masania, "Damping of carbon fibre and flax fibre angle-ply composite laminates," *Compos. Sci. Technol.*, vol. 146, pp. 1–9, 2017.

[13] F. Duc, P. E. Bourban, and J. A. E. Månson, "The role of twist and crimp on the vibration behaviour of flax fibre composites," *Compos. Sci. Technol.*, vol. 102, pp. 94–99, 2014.

[14] F. Duc, P. E. Bourban, C. J. G. Plummer, and J. -a. E. Månson, "Damping of thermoset and thermoplastic flax fibre composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 64, pp. 115–123, Sep. 2014.

[15] R. M. Erb, R. Libanori, N. Rothfuchs, and A. R. Studart, "Composites Reinforced in Three Dimensions by Using Low Magnetic Fields," *Science (80-.).*, vol. 335, no. 2006, pp. 199–204, 2012.

[16] R. Libanori, R. M. Erb, and A. Studart, "Mechanics of Platelet-Reinforced Composites Assembled Using Mechanical and Magnetic Stimuli," *Appl. Mater. Interfaces*, vol. 5, 2013.

[17] W. Woigk *et al.*, "Mechanical properties of tough plasma treated flax fibre thermoplastic composites," in *ECCM 2016 - Proceeding of the 17th European Conference on Composite Materials*, 2016, no. July.

[18] M. Brodt and R. S. Lakes, "Composite Materials Which Exhibit High Stiffness and High Viscoelastic Damping," *J. Compos. Mater.*, vol. 29, no. 14, pp. 1823–1833, 1994.

[19] P. Fratzl and R. Weinkamer, "Nature's hierarchical materials," *Prog. Mater. Sci.*, vol. 52, no. 8, pp. 1263–1334, 2007.

[20] D. Sen and M. J. Buehler, "Structural hierarchies define toughness and defect-tolerance despite simple and mechanically inferior brittle building blocks," *Sci. Rep.*, vol. 1, pp. 1–9, 2011.

[21] A. R. Studart, R. Libanori, and R. M. Erb, "CHAPTER 15 Replicating Biological Design Principles in Synthetic Composites," in *Materials Design Inspired by Nature: Function Through Inner Architecture*, The Royal Society of Chemistry, 2013, pp. 322–358.