ARTIFICIALLY ROUGHENED MICROPLATELETS FOR HIGH-PERFORMANCE BIOINSPIRED COMPOSITES

Davide Carnelli*, Rafael Libanori, Tobias P. Niebel and André R. Studart

Complex Materials, Department of Materials, ETH Zürich, 8093 Zürich, Switzerland
*Email: davide.carnelli@mat.ethz.ch, Web Page: http://www.complex.mat.ethz.ch

Keywords: mechanical reinforcement, roughened platelets, mechanical interlocking, bioinspired composites

Abstract
Enhancing the stress transfer between matrix and reinforcing elements is a general problem in structural composites. In this work, such problem has been tackled by developing an approach to design the reinforcing elements that is inspired by the surface topography of the aragonite platelets in nacre. These platelets show surface asperities that lead to mechanical interlocking and frictional resistance when they slide across each other in the fracture process. The proposed solution consists in the modification of the surface of micrometer-sized platelets by roughening them with nanometer-sized spheres, which would act as asperities on the surface of the larger particles and promote energy dissipation during an applied mechanical deformation. Composites reinforced with roughened microplatelets exhibit improved mechanical properties and energy dissipation for both organic ductile epoxy and inorganic brittle cement matrices. Surprisingly, the mechanisms leading to such a toughening effect depend on the nature of the continuous matrix used. These findings lead to a better understanding of the role of reinforcement-matrix interlocking on the micron-scale mechanics of bioinspired composites and provide useful guidelines for the design and fabrication of tougher and lighter structural materials.

1. Introduction

The mechanical behavior of composite materials is strongly dependent on the interactions occurring at the interface between the matrix and the reinforcing elements.[1] Although chemical surface modification of the reinforcing elements has been widely utilized in state-of-the-art composites to promote strong bonding with the continuous matrix and maximize the stress transfer at the interface, the presence of mechanical interlocking mechanisms at the interfaces offer additional means to tailor the mechanics of the composite.[2]

Structural biological composites are prime examples where physical interlocking is utilized to enhance the mechanical behavior of the material.[3] In the nacreous layer of mollusk shells, for example, the presence of nanoasperities combined with the high volume fraction of the reinforcing elements allows an effective mechanical interlocking between adjacent stiff platelets.[4] These nanoasperities are randomly distributed across the surface of the aragonite platelets and exhibit a typical height of a few tens of nanometers and a diameter between 30 to 100 nm.[5] When the material is loaded along the plane in which the aragonite platelets are aligned, effective sliding requires progressively higher stresses to overcome the mechanical interlocking promoted by the surface asperities, leading to a remarkable strain hardening effect and improved resistance against material failure. As a result of the interactions between nanoasperities, compressive stresses are generated orthogonally to the loading direction, producing dilation bands that spread the deformation over large volumes.[3]

Excerpt from ISBN 978-3-00-053387-7

Attempts have been made to fabricate high performance bioinspired composites by replicating the design principles observed in the microstructure of structural biological materials. To combine strength, stiffness and toughness, interfaces are usually designed to enable multiple extrinsic toughening mechanisms, such as enhanced matrix deformation, fiber pull-out, frictional sliding, crack deflection, and interfacial debonding.[6] Inspired by nacre, interfacial interlocking has also been explored in the design of platelet-reinforced composites. In most cases, the formulation of such materials is adjusted to induce in-situ formation of morphological features on the surface of the platelets during the fabrication of composites with high volume fraction of reinforcing elements.[7, 8] While composites fabricated without mechanical interlocking nanostructures present the brittle behavior typically observed in ceramic-based materials, pronounced strain hardening and stable crack propagation are observed for materials exhibiting interfacial nanoasperities and mineral bridges.

In both the natural and man-made composites mentioned above, the high volume fraction of the reinforcing elements allows platelet-platelet interlocking through the interaction of platelet nanoasperities. Although such platelet-platelet interactions are not expected to happen at low reinforcement fractions, there are experimental and theoretical evidences that simple interlocking between platelets and the polymer matrix can already lead to enhanced mechanical properties.[9, 10] Despite these efforts, there is still limited understanding of the impact of morphological superficial features of reinforcing platelets on the mechanical properties, energy dissipation and failure mechanisms of microstructured bioinspired composites.

In this study, we developed composites reinforced with platelets modified using tunable asperities in order to thoroughly investigate the effect of platelet-matrix interlocking alone on the mechanical behavior of model systems containing either an organic, ductile epoxy-based resin or an inorganic, brittle cement paste as continuous matrix. First, we present a robust and versatile method to fabricate platelet-like reinforcing elements with tailored size and density of surface nanoasperities. Composites with artificially roughened platelets were then synthetized through vibration-assisted magnetic assembly using polymer resins or cement pastes as continuous phases. These two systems were finally structurally and mechanically characterized to shed light on the intrinsic microstructural mechanisms at the origin of the enhanced mechanical performance of interlocking interfaces.

2. Materials and Methods

2.1. Materials

Alumina platelets (RonAflair White Sapphire©, Merck KGaA, Germany, ~ 400 nm thick and ~ 8 µm diameter), silica nanospheres with average diameters of 100- and 250-nm (Angstrom Sphere monodispersed silica powder, Fiber Optic Center Inc., USA), cationic and anionic ferrofluids (EMG 605© and EMG 705©, respectively, Ferrotec Corporation, USA), a two-component epoxy system (Sikadur 300©, Sika AG, Switzerland) and portland white cement (CEM I 52,5 N, Holcim Ltd, Switzerland) were used as-received throughout this work. Polyvinylpirrolidone (PVP360, Mw = 360 kg/mol, Aldrich, Switzerland), ethanol absolute (EtOH, Aldrich, Switzerland), tetraethylorthosilicate (TEOS, 98%, Merck, Switzerland) and ammonium hydroxide (25wt%, Merck, Germany) were used to coat the platelets with a uniform silica layer. Distilled water was used to prepare the solutions and dispersions/suspensions.

2.2. Surface Modification Procedure

The roughening process implemented here relies on the electrostatic adsorption of oppositely charged particles. Alumina platelets modified with silica nanospheres are produced by mixing a suspension of negatively charged alumina platelets (C = 20 g/L) with a dispersion of positively charged silica nanoparticles (C = 0.7 g/L) in water at a pH between 6 and 7. In a typical procedure, 0.350 g of silica nanospheres are dispersed in 30 ml of water using a probe sonicator (VibraCell -130, Blanc-Labo SA,

Excerpt from ISBN 978-3-00-053387-7

France; 3s/5s pulse on/off, amplitude of 80% and time = 10 min). Subsequently, the silica nanoparticle dispersion is added to a suspension containing 10 g alumina platelets in 470 ml of water. The mixture is stirred for 48 hours to ensure that the electrostatic adsorption process is completed. After mixing, the platelets are filtered, rinsed with water (~1500 mL) and ethanol (~200 mL), and dried for 2 hours at 60°C. Next, the platelets are transferred to an alumina crucible and calcinated at 1050°C and 1200°C for the 100- and 250-nm silica nanospheres, respectively (heating rate = 1.7°C/min to reach 400°C and maximum power until final temperature, dwelling time = 4 hours). Alumina platelets modified with both 100- and 250-nm sintered silica nanospheres at 19% surface coverage were prepared using this procedure. The amount of silica needed for each surface coverage is obtained by estimating the respective weight fraction of silica nanospheres needed to cover the surface of one platelet assuming a 2D closed packing of spheres and densities of 1.80 g/cm^3 and 3.98 g/cm^3 for the silica and alumina, respectively. After sintering, 10 g of modified platelets are suspended in 500 ml water, sonicated for 30 min in an ultrasonic bath and sieved using a 20 µm pore size sieve. Finally, they are collected by filtration and dried at 120°C for 2 hours.

Magnetization of the modified platelets is also accomplished by employing an electrostatic adsorption process.[11] In a typical procedure, 200 mL of a diluted aqueous dispersion of ferrofluid (C = 1.9 µL/mL) is slowly added to 300 mL of a suspension containing 10 g of modified alumina platelets. The resulting mixture is stirred for 48 hours or until the supernatant is clear. Magnetized platelets are filtered, rinsed with water and ethanol, and dried for 2 hours at 60°C and for 24 hours at 150°C and 50 mbar.

2.3. Preparation of Composites

Polymer-based composites containing a nominal volume fraction of 15% roughened platelets were prepared by the vibration-assisted magnetic alignment technique using the epoxy resin to hardener ratio suggested by the manufacturer (100:34.5 in weight).[12] Platelets and epoxy resin are mechanically stirred for 45 min at 2000 rpm. To improve the dispersion, the total amount of platelets is divided into 3 equal portions, which are separately incorporated into the epoxy resin by mechanical mixing for 15 min. After that, the hardener is added and the mixture degassed by applying vacuum (10 mbar), with alternating cycles of vibration in a vortex mixer and ultrasonication using an ultrasonic bath at 50-55°C. After all bubbles are successfully removed, the mixture is cast in a 3.5 x 4.5 x 1.0 cm^3 Teflon mold. Biaxial alignment of platelets is obtained by fixing the mold on a vibrating table (amplitude of 3 mm and frequency of 50 Hz for 10 minutes) while a 5 x 5 x 2 cm^3 permanent magnet (magnetic field strength of approximately 1040 G) is rotated above the sample at a frequency of 4 Hz. Next, the sample is moved to an oven equipped with a solenoid system capable of providing a rotating magnetic field during the thermal curing of the samples. The first curing step is performed for 4 hours at 60°C, followed by removing the solenoids from the oven and performing a final curing step for 2 hours at 125°C. Composites with tailored microstructure are obtained by removing the material from the Teflon molds after cooling down to room temperature.

Commercially available portland white cement was used as matrix for the cement-based composites.[13] As reinforcing phase, two sets of platelets were used: (i) flat alumina platelets, and (ii) roughened platelets with 250 nm silica nanospheres and 19% coverage. A water-to-cement (w/c) ratio of 0.6 was used in the pure cement system. Instead, when a 10 vol% of the reinforcing platelets was added, a w/c ratio of 0.66 was employed to keep constant the volume fraction of water in the mixtures. To prepare the samples, platelets were first dispersed in distilled water and stirred on a magnetic plate for 5-10 min at a speed of 400-500 rpm. Then, white cement was added to the suspension under mixing. The resulting mixture was then cast into a silicone rubber mold. For systems containing magnetically responsive platelets, a rotating magnetic field was generated by rotating a 5 x 5 x 2 cm^3 permanent magnet at a frequency of 200-300 rpm for 10 min while mechanical vibration (100 Hz oscillation frequency, ≈ 2 mm oscillation amplitude) was performed. The samples were then stored for 1 day in a humidity chamber at 25°C and 95% relative humidity before being demolded and soaked in an aqueous solution saturated with calcium hydroxide for 6 further days.

Excerpt from ISBN 978-3-00-053387-7

2.4. Characterization Methods

Bars with nominal dimensions of 3 x 5 x 45 mm^3 and 6 x 4.5 x 70 mm^3 for polymeric and cementitious composites, respectively, were prepared for three-point bending tests. A tensile tester (Instron 4411, Instron, USA) equipped with a 500 N load cell was used to perform the three-point bending tests. A 30 mm support span and a displacement rate of 1 mm/min were utilized for the polymeric composites whereas a 60 mm support span and a 2 mm/min displacement rate was adopted for the cementitious composites. At least three samples were tested to calculate the reported average and standard deviation values for the mechanical properties studied in this work.

Roughened alumina platelets and fracture surfaces of freshly cleaved samples were observed by Scanning Electron Microscopy (SEM, LEO 1530, Zeiss GmbH, Germany) after sputtering with 5-10 nm layer of platinum.

3. Results

Figure 1 illustrates the steps involved in the fabrication of roughened alumina platelets. Because of the opposite surface charges developed in water, silica nanospheres can be easily adsorbed on the surface of bare alumina platelets (figure 1, left column). Strong bonding of the nanoasperities on the alumina surface is achieved through partial melting of the silica nanospheres during thermal treatment (figure 1, central column). We hypothesize that the strong bonding results from the formation of a high-temperature liquid intermediate phase at the interface between alumina and silica. After attaching the silica nanospheres on the alumina surface, magnetization is achieved by adsorbing superparamagnetic iron oxide nanoparticles (SPIONs) on the roughened platelets (figure 1, right column). The easy access to commercial silica nanospheres with different particle sizes allows the fabrication of roughened platelets with different sizes and densities of nanoasperities. Although multiple processes are employed in the fabrication of the roughened platelets, relatively high yields ranging from 75% to 80% are obtained, indicating that this approach might be easily adapted to the typical large-scale process of ceramic powders.

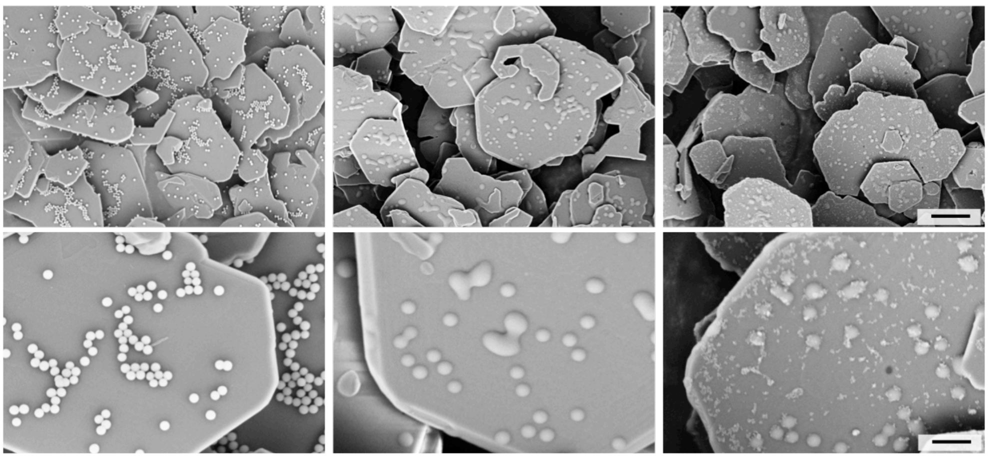

Figure 1. SEM images depicting the platelet morphology at each one of the main steps involved in the surface roughening and magnetization processes: alumina platelets with 100 nm silica nanospheres adsorbed on its surface (left); roughened alumina platelets after carrying out the sintering step (midlle); roughened platelets containing superparamagnetic iron oxide nanoparticles (SPIONs) adsorbed on their surfaces to provide magnetic response (right). The scale bars are 5 μm and 1 μm in the top and bottom rows, respectively.

Excerpt from ISBN 978-3-00-053387-7

Figure 2 shows representative flexural stress-strain curves and a summary of the mechanical properties obtained from the polymer-based composites. As illustrated in figure 2A, the pure epoxy can be deformed up to flexural strain as high as 18% without failure. Adding bare, randomly distruibuted alumina platelets into the epoxy resin results in a material exhibiting a quasi-linear elastic behavior with strain at rupture of only 1.8±0.1%. The random alignment of the platelets within the composite increases the flexural modulus by 2.3-fold as compared to the neat epoxy. Bi-axial alignment of flat platelets along the plane in which the tensile and compressive stresses are developed during the flexural test further increases the flexural modulus, maximum strength, and strain at rupture by 27%, 53% and 87%, respectively, as compared to those obtained with bare, randomly distributed platelets. Although the strain at rupture of the composite is significantly higher than that reinforced with flat, randomly distributed platelets, this composite still leads to relatively low strain at rupture (> 4%). Microstructured composites reinforced with platelets roughened with 100 nm silica nanospheres at 19% surface coverage exhibit strain at rupture about 70% higher as compared to those reinforced with flat, aligned platelets. Unlike the mutually exclusive relationship between toughness and strength commonly observed in structural materials, the enhancement in strain at rupture in the composite system reinforced with roughened platelets does not come at the expense of the ultimate flexural strength and elastic modulus: the use of roughened platelets in such composites leads to a modulus of toughness (area under the stress-strain curves) of 6.1±1.3 $MJ.m^{-3}$, which is 7.8-fold and 2.1-fold higher than of those reinforced with randomly distributed and aligned platelets, respectively.

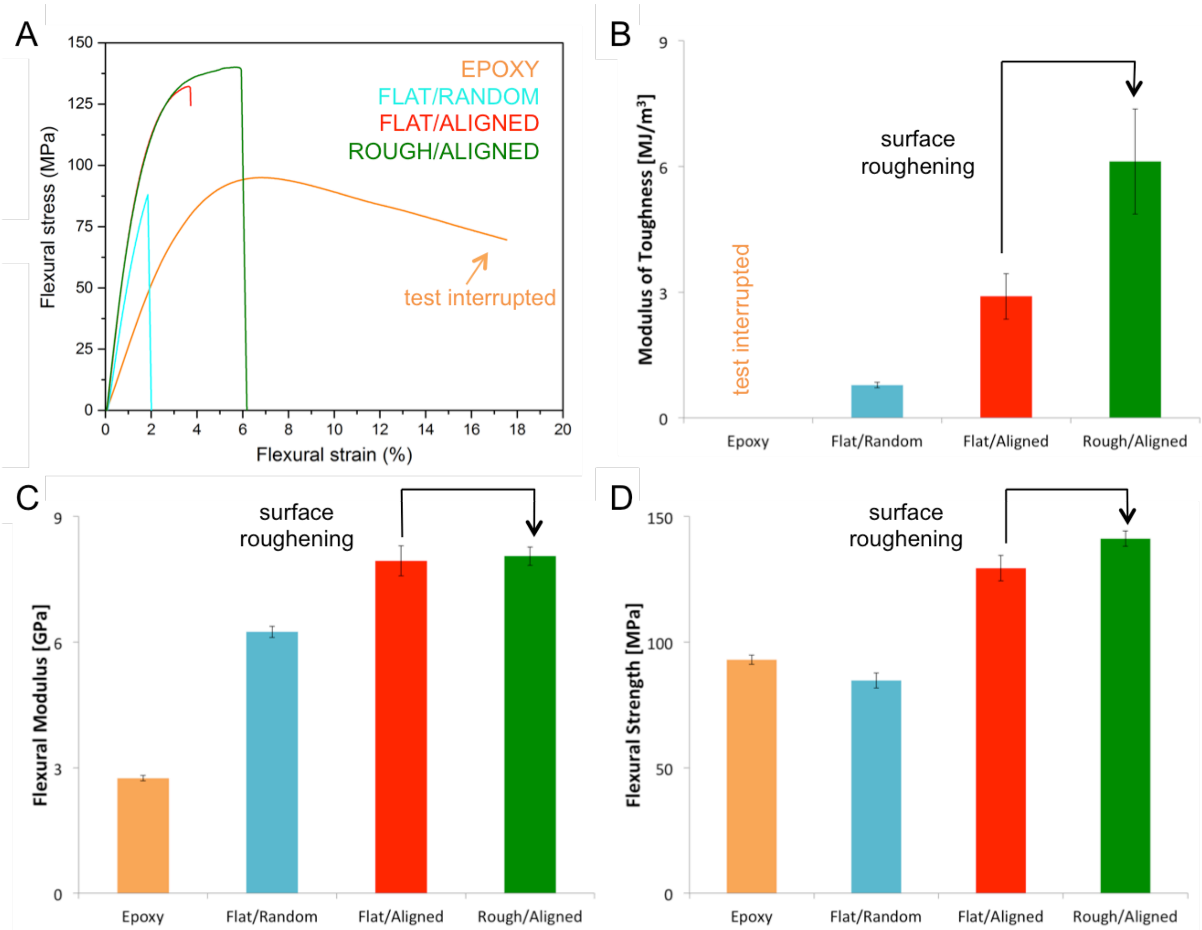

Figure 2. Mechanical behavior of polymer-based composites reinforced with roughened platelets with 100 nm silica nanospheres. Stress-strain curves of the composites (A) clearly show the enhancement of mechanical properties due to the magnetic alignment and surface roughening on modulus of toughness (B), flexural modulus (C), and flexural strength (D).

Excerpt from ISBN 978-3-00-053387-7

To further investigate the role of the matrix on the overall energy dissipation mechanisms of materials reinforced with roughened platelets, we studied composites comprising a purely elastic and brittle cement matrix. Representative stress-strain curves obtained in flexural tests for 7 days old samples and the relevant mechanical properties as a function of open porosity are reported in figure 4A and figures 4B-D, respectively. In total, three different classes of cement-based composites were prepared for mechanical testing: pure white cement pastes, white cement pastes reinforced with randomly distributed flat platelets, and white cement pastes reinforced with randomly distributed roughened platelets. As the mechanical properties of the cement-based composites depend on their porosity [14], pure white cement specimens containing water-to-cement ratios of 0.50, 0.55, 0.60, 0.65 and 0.70 were prepared and the open porosity of the obtained samples was measured with the Archimedes method. The dashed line in figures 3B-D shows the linear trend obtained for modulus of toughness, flexural modulus and maximum flexural strength as a function of porosity for the pure white cement pastes prepared at different water-to-cement ratios. An average flexural modulus and flexural strength of 7.37±0.04 GPa and 8.79±0.62 MPa, respectively, were obtaibned for the cement-based composites with randomly distributed flat platelets; an increase by 27% and 35%, respectively, was achieved for composites with roughened platelets. In terms of modulus of toughness, the increase due to the roughened surface of the platelets is about 56% than randomly distributed flat platelets. The porosity of the systems reinforced with roughened platelets results about 4% higher than with bare platelets, as a rough surface is possibly more prone to stabilization of air bubbles and the higher viscosity of the slurry containing roughened platelets makes more difficult to remove the bubbles during the degassing step of the sample preparation procedure.

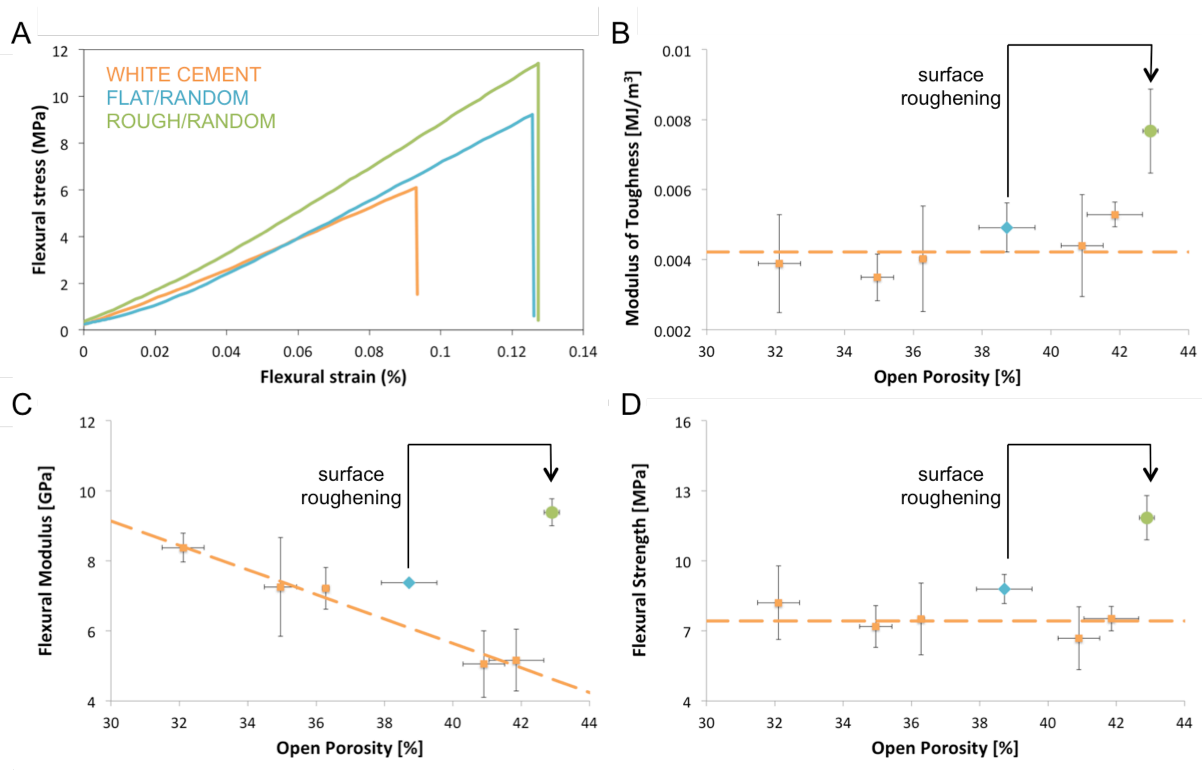

Figure 3. Effect of alumina platelets roughened with 250 nm silica nanospheres in cement-based composites. Representative stress-strain curves in three point bending test (A). Modulus of toughness (B), flexural modulus (C), and flexural strength (D), and as a function of the open porosity for pure white cement, randomly distributed flat platelets, and randomly distributed roughened platelets.

Excerpt from ISBN 978-3-00-053387-7

4. Discussion

The underlying mechanisms leading to the improvement of the mechanical performance of the microstructured composite materials seem to be very different between the polymer- and the cement-based materials. Indeed, depending on the mechanical behavior of the matrix alone, roughened platelets are able to contribute with different mechanisms to enhance the energy dissipation of the resulting composite. In the case of epoxy-based composites the enhanced modulus of toughness likely originates from the increased plastic deformation of the matrix, whereas for cement-based composites this is achieved through an increase in both flexural modulus and strength. Figure 4 gives evidence of this interpretation by directly comparing the percentual increases in modulus of toughness, flexural strength, flexural modulus, and ultimate strain for the two different roughened systems as compared to compositions containing flat platelets.

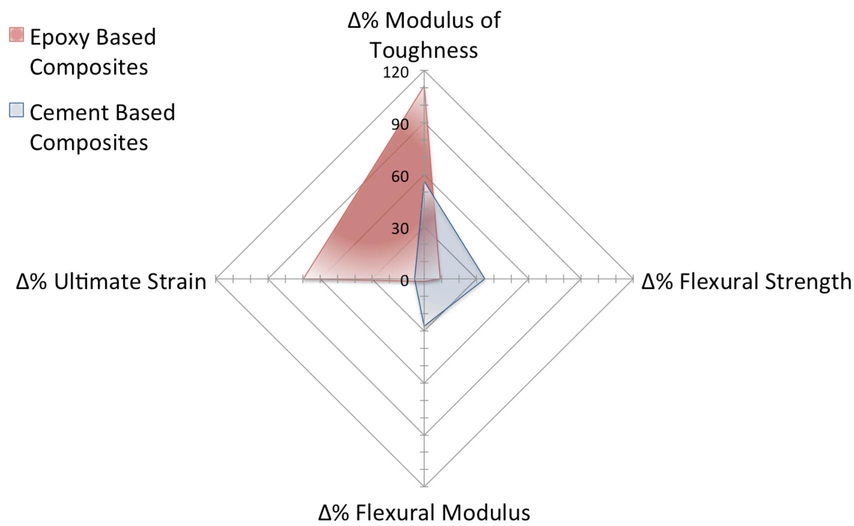

Figure 4. Radar chart showing the relative increase in modulus of toughness, flexural strength, flexural modulus, and ultimate strain achieved upon addition of surface roughness to reinforcing platelets in epoxy- and cement-based systems.

5. Conclusions

Nanoasperities on the surface of micrometer-sized platelets alumina platelets were found to strongly improve the mechanical properties of platelet-reinforced epoxy- and cement-based materials. To study and explore this effect, a procedure was developed to modify the surface of alumina platelets with artificial roughness of known size and surface coverage. The interfacial roughening procedure is simple and can be employed to fabricate reinforcing building blocks with a wide range of surface roughness parameters. The addition of alumina platelets with 19% surface coverage and 100/250 nm surface asperities increased the modulus of toughness of epoxy-based and cement-based composites by 110% and 56%, respectively. Surprisingly, the mechanisms leading to such a toughening effect depends on the nature of the continuous matrix used. In a brittle matrix like cement, increased toughness is achieved through an improved stress transfer enabled by the roughened platelets. Conversely, toughening in a ductile epoxy matrix occurs due to enhanced plastic deformation caused by the interfacial interlocking mechanism promoted by the nanoasperities on the surface of the platelets. These findings lead to a better understanding of the role of reinforcement-matrix interlocking on the micron-scale mechanics of bioinspired composites and provide useful guidelines for the design and fabrication of tougher and lighter structural materials.

Excerpt from ISBN 978-3-00-053387-7

Acknowledgments

The authors would like to thank the JONAS Research Network (Joint Research Network on Advanced Materials and Systems), BASF Construction Materials & Systems Research and the Swiss Competence Center for Energy Research (SCCER - Capacity Area A3: Minimization of energy demand) for financing the research.

References

[1] D. Hull and T.W. Clyne. *Toughness of composites - An introduction to composite materials.* Cambridge University Press, 1996.

[2] H. Qian, E.S. Greenhalgh, M.S.P. Shaffer, and A. Bismarck. Carbon nanotube-based hierarchical composites: a review. *Journal of Materials Chemistry*, 20:4751–4762, 2010.

[3] K.S. Katti, D.R. Katti, S.M. Pradhan, and A. Bhosle. Platelet interlocks are the key to toughness and strength in nacre. *Journal of Materials Research*, 20:1097–1100, 2005.

[4] J.W.C. Dunlop, R. Weinkamer, and P. Fratzl. Artful interfaces within biological materials. *Materials Today*, 14:70–78, 2011.

[5] A. Lin and M.A. Meyers. Growth and structure in abalone shell. *Materials Science and Engineering: A*, 390:27–41, 2005.

[6] R.O. Ritchie. The conflicts between strength and toughness. *Nature Materials*, 10:817–822, 2011.

[7] E. Munch, M.E. Launey, D.H. Alsem, E. Saiz, A.P. Tomsia, and R.O. Ritchie. Tough, bio-inspired hybrid materials. *Science*, 322:1516–1520, 2008.

[8] F. Bouville, E. Maire, S. Meille, B. Van de Moortele, A.J. Stevenson, and S. Deville. Strong, tough and stiff bioinspired ceramics from brittle constituents. Nature Materials, 13:508–514, 2014.

[9] Y. Zhang, H. Yao, C. Ortiz, J. Xu, and M. Dao. Bio-inspired interfacial strengthening strategy through geometrically interlocking designs. *Journal of the Mechanical Behavior of Biomedical Materials*, 15:70–77, 2012.

[10] Y. Li, C. Ortiz, and M.C. Boyce. Bioinspired, mechanical, deterministic fractal model for hierarchical suture joints. *Physical Review E*, 85:031901, 2012.

[11] R.M Erb, R. Libanori, N. Rothfuchs, and A.R. Studart. Composites reinforced in three dimensions by using low magnetic fields. *Science*, 335:199–204, 2012.

[12] R. Libanori, R.M. Erb, and A.R. Studart. Mechanics of platelet-reinforced composites assembled using mechanical and magnetic stimuli. *ACS Applied Materials & Interfaces*, 5 :10794–10805, 2013.

[13] D. Carnelli, R. Libanori, B. Feichtenschlager, L. Nicoleau, G. Albrecht, and A.R. Studart. Cement-based composites reinforced with localized and magnetically oriented Al_2O_3 microplatelets. *Cement and Concrete Research*, 78:245–251, 2015.

[14] H.F. Taylor. *Cement Chemistry.* Thomas Telford: 1997.

Excerpt from ISBN 978-3-00-053387-7