Bioinspired composites with controlled alignment and distribution of anisotropic reinforcing particles

A dissertation submitted to
ETH ZURICH

for the degree of
Doctor of Sciences

presented by
Rafael Augusto Nicolosi Libanori
M.Sc. Materials Engineering, Federal University of São Carlos

Born on 26.01.1983
citizen of Brazil

accepted on the recommendation of

Prof. Dr. André R. Studart, examiner
Prof. Dr. Helmut Cölfen, co-examiner
Prof. Dr. Ralph Spolenak, co-examiner

2013
To my beloved wife
Gabriela Libanori

“It is the possibility of having dreams come true that makes life interesting”

Paulo Coelho
Acknowledgments

I would like to thank Prof. André R. Studart for giving me the opportunity to develop my PhD thesis in his group. He was much more than a PhD supervisor: his guidance and enthusiasm were crucial throughout my PhD thesis. Also, his personal advices during my first year here in Zürich were decisive to facilitate my adaptation in a country with very different cultural values. I also highly appreciate his encouragement and support to present my work at several important conferences in our research field.

I am very thankful to Dr. Randall M. Erb for his scientific support during my PhD studies, mainly in the projects where magnetic fields were involved. In addition to his scientific advise, I also enjoyed the friendship that we developed here in Zürich.

Special thanks to Prof. Ralph Spolenak and Prof. Helmut Cölfen for accepting the invitation to be co-examiners of this thesis.

This thesis certainly profited from the valuable and fruitful help of all the undergraduate and master students. Many thanks to Davi M. Montenegro, Frédéric H. L. Münch, Claudio Zihlmann, Frieder Reusch, Simon Bachmann, Hortense Le Ferrand, Alexander Johnson, Benjamin Hartmeier, Alain Reiser, Matthias Spörndli, Nuria Rothfuchs and Michelle Zanini.

Many thanks to Mrs. Gisela Angst, who assists our group in the administrative matters. She kindly helped me a lot during all my staying in Switzerland. I have enjoyed every single casual chat we had during the last four years.

I also would like to address my sincere thanks to Peter Kocher, Dr. Kirill Feldman and Beatrice Wegmann for their very special technical support and fruitful scientific discussion.

I could not forget to thank Jonathan Sander, Philipp Chen, Eve Loiseau, Tobias Niebel, Davide Carneli, Marianne Sommer, Dimitri Kokkinis, Etienne Jeoffroy and Ofer Tevet for the scientific discussions during our weekly group meetings and also for the funny moments, such as the annual cake competition and group trip.

Special thanks to Prof. Ludwig J. Gauckler, Prof. Markus Niederberger, Prof. Paul Smith and Prof. Theo Tervoort for sharing their equipment. I am also grateful for the innumerous friendships acquired throughout these years in the department, including Niklaus Klänzlin, Dorothan Koziej, Martin Süess, Florian Heiltag, Alessandro Lauria, Matthias Schamel, etc.
I highly appreciated all the support from the Department Administration office, in special Cristina Pederiva, Claudia Sigel, Lucie Rechsteiner, Andrea Schrott and Annemarie Kallen. Technical support from the workshop and from the IT office is also gratefully acknowledged in name of Martin Elsener, Christian Roth, Markus Müller and Marc Petitmermet.

I am very indebted for the supply of free material samples from Antaria (Australia), BASF (Germany), Huntsman (Switzerland) and ProChem (Switzerland).

Last but not least, I would like to express my gratitude with my parents and relatives. They have always supported my choices and encouraged me to make my dreams come true. Especially, I would like to thank my wife, Gabriela Libanori. She abandoned everything in Brazil to join me here in Switzerland for this adventure. I would probably need more pages than what I currently have in my whole PhD thesis to address every single action that she has taken to support me during the last four years.
Summary

Composite materials have replaced metallic materials in many structural components due to their high specific strength, cost-effectiveness and potential added functionalities. Despite their increasing importance in load-bearing applications, composites still present several limitations, particularly low resistance against wear, delamination and impact. In contrast, biological composites perform extremely well in abrasive environments and under impact loads even though they are comprised of relatively weak building blocks. As the availability of chemical elements in living organisms is rather limited, these materials had to evolve intricate microstructures through natural selection processes in order to compensate for the use of weak components. Replicating the microstructural design of biological systems enables the fabrication of bioinspired composites that exhibit unusual combination of mechanical properties. In this context, the primary goal of this thesis is the development of processing routes to manufacture synthetic materials that replicate design principles found in many natural materials. We mainly focus on the development of bioinspired composites with local mechanical properties tailored through the precise control over the orientation and distribution of reinforcing platelets within a polymeric matrix. Such general design principle is a hallmark of many biological composites, including mollusk shells, bone, teeth and plants.

A synthetic framework to manufacture polyurethane-based composites exhibiting a wide range of elastic modulus and mechanical strength is first developed to enable the fabrication of heterogeneous composites with locally tunable elastic modulus. Such wide range of properties is achieved by reinforcing a soft polyurethane matrix with hard molecular domains, nanoplatelets and microplatelets at progressively higher hierarchical levels. Control over the reinforcement spatial distribution and full entanglement of the polymer phase across the heterogeneous composite are obtained by solvent-welding individual layers with different concentrations of reinforcing elements. The deposition of patches of the multilayered composites on an elastomeric substrate at different preselected locations enables the creation of composites with tunable elastic modulus profiles in the in-plane and out-of-plane directions. To demonstrate the potential of these materials in combining unusual properties, such as stretchability with local surface stiffness, we fabricated single-patched elastomeric substrates with elastic modulus tuned to gradually increase from the bottom to the top of the patch. Remarkably, the strains experienced at the top of
the patch are reduced by two orders of magnitude as compared to the global strain applied in the substrate. The strain minimization mechanism exhibited by the graded composites is very effective in protecting brittle electronic components that are attached onto the patch surface, while keeping the underlying substrate highly stretchable.

Controlling the orientation of micron-sized reinforcing platelets to produce tailored 3D composite architectures is crucial to maximize the mechanical response of synthetic composites. In this thesis, we developed a robust and versatile processing technique to remotely program the orientation and arrangement of micron-sized alumina platelets in polymeric matrices using ultralow magnetic fields. Magnetization of alumina platelets is performed by adsorbing minimal amounts of superparamagnetic iron oxide nanoparticles on their surface. Alignment of the reinforcing platelets in the direction of externally applied load enhances significantly the mechanical properties of polymer-based composites. Steric effects and the rheological behavior of fluids containing platelet concentrations above a percolation threshold reduce our ability to obtain a high degree of platelet alignment. Such problem is tackled by supplying an additional energy in the form of mechanical vibration while the platelets are manipulated with the magnetic fields. This enables the creation of bulk platelet-reinforced composites exhibiting remarkable mechanical properties and alignment degree that approaches that of highly textured thin films made by the laborious layer-by-layer approach.

The knowledge gained on the control of the orientation and surface chemistry of alumina platelets for reinforcing purposes was also exploited to create multifunctional 2D particles with combined magnetic response and tunable optical properties. This was accomplished by developing a simple method to add further functionalities to magnetically-responsive alumina platelets. To illustrate the method, a fluorescent moiety is covalently attached onto the surface of silica-coated magnetic platelets through conventional silane chemistry. These multifunctional platelets enable spatial and temporal control over the emission of light from the particle surface, making them potential candidates for the assembly of smart optical devices.

In summary, this thesis shows the benefits of using a bioinspired approach to design high performance platelet-reinforced composites. The processing methods described here are relatively simple and can be easily adapted to current technologies for the large-scale production of composite materials.
Zusammenfassung


Basierend auf unserer Fähigkeit, die Orientierung und Oberflächenchemie von Aluminiumoxidplättchen zu kontrollieren, wurde eine einfache Methode entwickelt um diese weiter zu funktionalisieren, was die Herstellung von multifunktionalen Plättchen mit kombinierten magnetischen und optischen Eigenschaften erlaubt. Zur Illustration der Methode wurde durch Silan-Chemie eine fluoreszierende Schicht kovalent auf die Oberfläche von mit Siliziumoxid beschichteten magnetischen Plättchen angefügt. Diese multifunktionalen Plättchen erlauben räumliche und zeitliche Kontrolle über die Emission von Licht von der
Partikeloberfläche, was diese zu einem vielversprechenden Kandidaten für die Herstellungen von intelligenten, optischen Komponenten macht.

“There are two different types of people in the world: those who want to know and those who want to believe”

Friedrich Nietzsche
Chapter 1

INTRODUCTION

1.1 Aim and organization of the thesis

The primary goal of this thesis is to develop fabrication routes that lead to composite materials whose microstructures replicate the design principles found in biological materials. We are particularly interested in implementing local tailored properties in platelet-reinforced composites through programming the orientation and distribution of platelets in all three dimensions in their microstructure. Our efforts were dedicated to processing techniques that could potentially be adapted to current technologies used in the production of polymer-based composite materials. To maximize the mechanical properties of our bioinspired composites, we focus on approaches that direct the assembly of reinforcing platelets in suspensions and polymeric resins at high volume fractions.

This thesis is divided in 11 chapters. In this first chapter, we introduce the topic through a short analysis of the practical benefits and the potential limitations of using composites in load-bearing applications. Subsequently, we present the main strategies used by nature to tackle these limitations and we highlight the advantages of using the bioinspired approach to design synthetic composites with superior mechanical performance.

Chapters 2 and 3 report a strategy to fabricate heterogeneous composites with extreme mechanical gradients by controlling the spatial distribution of reinforcing platelets in an elastomeric matrix. In chapter 2, we develop a hierarchical reinforcement approach to obtain polyurethane-based composites covering a wide range of mechanical properties. The ability to fabricate a new family of composite materials whose elastic moduli can be finely tuned by adjusting the concentration of nano- and micro-platelets in a single polymeric matrix enabled us to create the stretchable heterogeneous composites described in Chapter 3. These composites
combine stretchability with local surface hardness and are efficiently used to protect hard electronic components against delamination in proof-of-concept experiments of relevance for flexible electronics.

Chapters 4 and 5 explore the use of ultralow magnetic fields to control the microstructures of platelet-reinforced composites. While chapter 4 describes a simple approach to produce magnetically responsive alumina platelets and their directed-assembly into complex composite architectures reinforced in three dimensions, chapter 5 presents a strategy to enhance the degree of platelet alignment in epoxy-based composites with higher concentration of magnetized platelets. In both chapters the mechanical response of the resulting composites are explained in light of their microstructures.

In chapter 6 we describe a method to prepare multifunctional platelets exhibiting fluorescent and magnetic properties. This combination of properties enables temporal and spatial control of the light emission from the particle surface by applying ultralow magnetic fields. Finally, chapters 7 and 8 contain the conclusions and the outlook of this thesis and chapters 9-11 are appendices with supplementary information pertinent to main chapters of this thesis.

1.2 Composites as structural materials

The rapid development of high-performance composites has allowed material scientists and engineers to replace many metallic materials in structural applications. A recent example is the newest aircraft manufactured by Boeing, the Dreamliner 787 model. For the first time in the history of commercial aviation, composites are listed as the primary material used in the construction of an aircraft, which accounts for up to 50% of its total weight. (1) A schematic map showing the distribution of the different materials used in the Boeing 787 aircraft is shown in Figure 1.1a. Replacing denser metallic parts by materials with a higher specific strength in the airframe of an aircraft reduces significantly its fuel consumption. In fact, implementation of composite technologies in commercial aviation represents a turning point in terms of energy saving. According to Boeing, the Dreamliner 787 can save up to 20% fuel as compared to previous generations of jets (Figure 1.1b). (2) In addition, airframes built with composite materials require a remarkably lower amount of fasteners and drilled holes, accounting for 30% savings in maintenance costs (Figure 1.1c). (3)
Introduction

Figure 1.1. a) Schematic drawing showing the distribution of composites and metallic materials in the fuselage of the aircraft Boeing Dreamliner 787. Adapted from ref. (4) b) Relative fuel consumption of different generations of aircrafts produced by Boeing since late 1950s. (2) c) Comparison of the maintenance costs between Boeing 787 and 767 models (3). d) Typical laminar microstructure of long-fiber composites used to build the fuselage of aircrafts. Adapted from ref. (5) Layers exhibiting fibers aligned at different directions are used to enable in-plane reinforcement of the polymeric matrix.

High-performance composite materials used in the fuselage of the 787 Dreamliner are mainly comprised of long glass or carbon fibers embedded in an epoxy matrix. (6) These fibers are typically tens of micrometers in diameter and reinforce the material along the long axis of the fibers. (7) To enable in-plane reinforcement, layers with unidirectional fibers can be laminated at varied angles (Figure 1.1d) or weaved into 2D arrays. Because of the lack of aligned reinforcing elements in the out-of-plane direction, these materials present several limitations such as high susceptibility to delamination, (8) damage by impact, (8, 9) low resistance against wear (10) and mechanical failure due to long-term fatigue. (11)
1.3 Structure and mechanical behavior of biological composites

In contrast to synthetic composites, the reinforcing building blocks of natural materials are assembled into a 3D structure so that both in-plane and out-of-plane reinforcements are achieved. A classical example is the 3D reinforcement design found in seashells (Figure 1.2a). While an outer layer exhibiting prismatic calcium carbonate particles aligned out-of-plane provides surface hardness and resistance against impact and wear, in-plane mechanical strength and toughness arise from aragonite platelets aligned parallel to the surface. (12, 13) A similar bilayer structural design is also observed in the human tooth (Figure 1.2b). The inner layer (dentin) consists of mineralized collagen fibrils in a meshed network oriented perpendicular to the load direction during mastication. (14) This structure provides mechanical resistance against in-plane deformations and arrest cracks that are eventually formed at the tooth surface. To provide surface hardness and resistance against mastication wear, the human tooth is covered by a durable material that contains 1D mineral crystals (enamel) oriented out-of-plane. (15) This combination of layers with reinforcing particles aligned at different orientations enhances the mechanical properties of these materials along all loading directions.

The remarkable improvement of mechanical properties that can be achieved through microstructural design is illustrated in Figure 1.2c. In this Ashby diagram, the resistance against crack initiation, $K_{IC}$, is plotted as a function of the elastic modulus for various natural materials and their main mineral components. For instance, seashells (dark green region) exhibit fracture toughness that is at least one order of magnitude higher than pure CaCO$_3$ (dark red region). Similarly, the $K_{IC}$ of enamel, dentin and bone (light green regions) are also several times higher than its main mineral constituent, hydroxyapatite (light red region). These examples clearly demonstrate the enormous potential of adjusting the microstructures of materials to maximize their mechanic performance in specific applications.
Adjusting the position and local concentration of reinforcing particles is another important aspect of the microstructural design of biological materials. This strategy enables local reinforcement of structural weak points and thus delocalizes strains that would otherwise lead to a premature failure of the material. In mammalian bones, this local reinforcement is accomplished by positioning anisotropic reinforcing particles around weak points in the osteon structures. (20) In addition, there are several other examples of composites exhibiting locally controlled concentrations of reinforcing building blocks in nature. This strategy is very often used as a means to reduce mechanical stresses at the interface between materials.
Chapter 1

of dissimilar mechanical properties. For instance, the attachment of compliant tendons to stiff bones is performed by a functionally graded tissue called tendon-to-bone insertion whose mechanical properties are adjusted by changing the alignment degree of collagen fibrils and the relative local concentration of mineral phase across its length (Figure 1.2d). (19) The gradual change in mechanical properties in combination with the use of the same organic matrix across the material, i.e. collagen, ensures efficient stress transfer with no macroscopic defects that could favor interfacial failure. Similar mechanically graded materials also play an important role in the protection mechanisms of some deep-sea fishes and gastropods. (21, 22) This gradient in mechanical properties ensures an efficient energy dissipation mechanism and increases the penetration resistance of dermal armors. Replicating this design principle in artificial composites may lead to materials exhibiting unusual combination of mechanical properties.

1.4 Bioinspired approach

The possibility of combining the wealth of chemical compositions available in synthetic materials with the microstructural design principles exhibited by biological systems enables the fabrication of bioinspired composites exhibiting unusual combination of mechanical properties. In one example, micrometric alumina platelets with a favorable aspect ratio are assembled with chitosan to form a layered composite with outstanding mechanical behavior. (23) Since alumina is considerably stiffer and stronger than calcium carbonate found in seashells, the resulting synthetic composites present tensile strength as high as 300 MPa, which is at least twice as high as that of Nacre. Furthermore, the relatively low volume fraction of reinforcing elements (20 vol%) as compared to Nacre (95 vol%) results in composites exhibiting plastic deformation of up to 20% and work of fracture that is at least two orders of magnitude higher than those of layered composites reinforced with nanoplatelets. (24, 25)

Another family of synthetic brick and mortar composites with volume fraction of inorganic reinforcement reaching up to 80 vol% has been recently produced by the freeze casting approach. (26) In this method, a suspension of alumina nanoparticles is frozen under controlled conditions to form a layered structure of segregated nanoparticles and ice, which is subsequently removed by sublimation. Sintering of the porous structure results in a ceramic scaffold that can be further pressed and impregnated with low-viscosity polymers. Fracture toughness investigations indicate
the confluence of several intrinsic and extrinsic toughening mechanisms acting at multiple length scales, which remarkably enhance the resistance of the material against crack propagation. These bioinspired composites exhibited fracture toughness as high as 30 MPa.m$^{1/2}$, which is considerably higher than typical values observed in biological materials, such as nacre and cortical bone with 9 MPa.m$^{1/2}$ and 25 MPa.m$^{1/2}$, respectively. Such remarkable resistance against crack propagation exhibited by this bioinspired composite is very unusual for a material with fracture strength above 200 MPa and it surpasses by far the toughness of the material’s building blocks alone. Applying such bioinspired approach to the fabrication of artificial composite systems enables the development of materials with unprecedented mechanical performance.

1.5 References


HIERARCHICAL REINFORCEMENT OF POLYURETHANE-BASED COMPOSITES WITH INORGANIC MICRO- AND NANO-PLATELETS

Rafael Libanori, Frédéric H. L. Münch, Davi M. Montenegro, André R. Studart

This chapter was published in:
Composites Science and Technology, 72 (2012), 435-445

Supplementary material to this chapter is attached as Appendix 1.

2.1 Abstract

Hierarchically reinforced structures are widespread in nature but less common among man-made materials. In this paper, we show that polyurethane-based thermoplastic polymers can be hierarchically reinforced with laponite nanoplatelets and alumina microplatelets to reach strength and elastic modulus that are, respectively, 7- and 29-fold higher than that of the pure polymer matrix (91.7 MPa and 6.97 GPa, respectively). We find that the selective reinforcement of the polyurethane hard domains with laponite nanoplatelets is key to keep the polymer matrix sufficiently ductile for the incorporation of high concentrations of alumina microplatelets. Effective reinforcement of the polymer with microplatelets of different surface chemistries was only possible after annealing the composite at 130°C to promote strong bonding at the oxide/polymer interface. Large-area composite films and bulk parts exhibiting good alignment of alumina microplatelets were obtained through conventional tape-casting. The concept of hierarchical reinforcement demonstrated here can be explored to obtain composite materials covering a wide range of mechanical properties using only a few reinforcing building blocks within the same polymer matrix.
2.2 Introduction

Polyurethanes find widespread use in biomedical, structural and automotive applications. (1, 2) The mechanical behavior of this copolymer can be tuned from soft and rubbery to hard and stiff by simply changing the ratio of hard to soft segments in the macromolecule's backbone. (1) The addition of reinforcing filler particles into polyurethanes greatly increases their versatility by extending the range of mechanical properties that can be achieved and possibly incorporating further functionalities. (3-6)

Materials exhibiting mechanical behavior that can be tuned over a wide range by changing the fraction of one or more of their constituents are important in many technological and natural systems. Polymeric substrates potentially used in flexible electronics for example should have locally tuned mechanical response in order to reduce the mechanical mismatch between the flexible substrate and the hard metallic circuitry. (7, 8) Keeping one of the constituents as continuous phase while varying the concentration of other building blocks to control the mechanical properties is an interesting approach because it potentially eliminates interfaces that work as stress concentrators. (7)

Because of their rather limited choices with regards to chemical compositions, living organisms are able to build biological materials with very different mechanical properties by just controlling the distribution and arrangement of a few types of building blocks within the same continuous matrix. This is the case for example of the long threads used by mussels to anchor themselves on rocks, where high strength, elasticity and surface wear resistance are combined by locally changing the cross-linking density of the organic matrix throughout the material. (9) Likewise, materials like seashells, fish scales, bone and teeth have their degree of mineralization and the orientation of inorganic building blocks locally adjusted to vary the material's stiffness by nearly an order of magnitude. (10-16) Remarkably, the concentration of inorganic phase dispersed within a polymeric matrix can be as high as 95 vol% in such mineralized biological materials. Although the underlying design principles are still being investigated, (17) the organization of building blocks of different sizes into hierarchical structures is a reoccurring approach used by living organisms to tailor the properties of natural materials.

In contrast to hard biological materials, artificial polymers reinforced with inorganic particles become remarkably brittle above a critical volume fraction of the inorganic phase, which is characterized by a substantial decrease in the work of fracture. (18-20) Since the critical particle concentration leading to such reduction in
the work of fracture is typically lower than 30-50 vol%, the range of mechanical properties that can be covered using a given polymer matrix reinforced with inorganic particles is rather limited in artificial composites.

New reinforcing strategies are thus required to circumvent the loss in work of fracture and further increase the strength and stiffness attainable with artificial composites. In this study, we combine inorganic reinforcing particles at two different length scales to produce large-area highly structured polyurethane-based composites with a wide spectrum of properties using the same polymer matrix. We present a thorough experimental and theoretical investigation on the processing and mechanical properties of the proposed hierarchical composites. The selective reinforcement of the hard domains of polyurethane with nanoplatelets (21) is shown to be key to allow for the addition of high concentrations of microplatelets before the work of fracture is significantly reduced. Blending the polyurethane matrix with polyvinylpyrrolidone further increases the strength and stiffness of the hierarchically reinforced composites to levels that cannot be achieved with reinforcements at one single length scale.

2.3 Experimental procedure

2.3.1 Materials

The commercial thermoplastic polyurethane Elastollan C64D (BASF, Germany) was used as polymeric matrix in the platelet-reinforced composites. The hard segments of such polyurethane contain 1,6-hexanediol, 1,4-butanediol and 4,4'-diisocyanatodiphenylmethane, whereas the soft segments consist of an adipic acid-based polyester. (22) Alumina platelets with diameter of 7.5 µm and thickness of 200nm (Figure 2.1e, Alusion®, aspect ratio: 37.5, Antaria Limited, Australia) and Laponite RD platelets with diameter of 25 nm and thickness of 1nm (aspect ratio: 25, ProChem, Switzerland) were used as reinforcing building blocks.

N,N-dimethylformamide (DMF, Honeywell Inc., Germany), tetrahydrofuran (THF, Aldrich, Switzerland), acetic acid glacial (HAc, Carlo Erba Reagent Inc., Italy), polyvinylpyrrolidone (PVP, M_w = 40000 g/mol, Aldrich, Switzerland), 3-aminopropyltriethoxysilane (APTES, 98%, Aldrich, Switzerland), 6-nitrodopamine sulphate (ND, SuSoS, Switzerland) were of technical grade, unless otherwise stated.
2.3.2 Surface modification of microplatelets

Alumina platelets were surface modified using three different coupling agents: APTES, ND and PVP. It is assumed that APTES forms a multilayered structure due to the self-condensation of silanol groups, whereas ND adsorbs only as a monolayer onto the alumina surface. PVP is expected to adsorb through weak hydrogen-bonding interactions on the platelet surface.

The surface modification with APTES was performed in DMF using acetic acid as catalyst. In a typical reaction, 5 g of alumina platelets were added to a solution of acetic acid (2 mL) in DMF (400 mL). The mixture was stirred for approximately 20 minutes at room temperature. The resulting powder was washed five times with THF and dried in vacuum (10 mbar) at room temperature for 24 hours. The silanized platelets were characterized by FT-IR (DRIFT mode) and TGA and then kept under dry conditions until use.

The attachment of ND onto the alumina surface was also carried out in a DMF solution. In this case, 4 g of alumina platelets were added to 20 mL of a solution of ND in DMF (8 mM). The resulting mixture was stirred at room temperature for 24 hours. Next, the modified alumina platelets were washed 5 times with THF to remove any physically adsorbed ND from the alumina surface. The powder was dried in vacuum (10 mbar) at room temperature for 24 hours and then characterized by FT-IR (DRIFT mode) and TGA.

The physical adsorption of PVP onto alumina surfaces was performed by first adding the required amount of PVP to DMF and stirring the solution at room temperature until complete dissolution of the polymer. Alumina platelets were then added into the PVP/DMF solution and the resulting mixture was stirred for 24 hours. Finally, the obtained mixture was directly used to prepare platelet/polymer suspensions for tape casting as described in the next sections.

2.3.3 Preparation of platelet/polymer suspensions

Suspensions containing nano- and microplatelets were prepared by adding the inorganic components to DMF and then dissolving the PU pellets at room temperature.

Laponite nanoplatelets were exfoliated in DMF using the solvent-exchange procedure described by Liff and co-workers. (23) In a typical procedure, 2 g of laponite were added to approximately 200 mL of deionized water and the resulting
suspension was stirred until complete exfoliation of the nanoclay. Next, approximately 400 mL of DMF were added to the aqueous suspension and the resulting mixture was stirred for 2 hours. Water was then removed from the suspension through evaporation in a R-215 rotavapor (Buchi, Switzerland) at 76 mbar and 60°C. To ensure that a minimum amount of water remains in the final suspension, the bath temperature was raised slowly to 70°C as soon as a decrease in the vapor temperature was observed. The final concentration of laponite in DMF was determined by gravimetric analysis.

To prepare composites reinforced with nanoplatelets only, 107 mL of a 5.6 mg/mL suspension of laponite exfoliated in DMF was added to a 250mL Erlenmeyer flask and the total volume was completed with pure DMF to 160 mL. In the case of hierarchical composites, 2.149 g of alumina platelets were also added to the nanoplatelet suspension. Platelet/polymer suspensions used for tape casting were obtained by adding 2.4 g of PU pellets into the platelet suspensions and stirring overnight.

2.3.4 Tape casting

The viscosity of the platelet/polymer suspension was adjusted by slowly evaporating DMF in a rotavapor (10 mbar, 60°C) until a total volume of approximately 80 mL was obtained. The viscous suspension was then poured onto a polyethylene (PE) substrate (15 cm x 30 cm). Tape casting was performed by hand in one specific direction using a doctor blade with a slit height of 2 mm. The remaining DMF was removed in a drying oven (Memmert, UNE 200, Germany) at 60°C for 24 hours. Before performing the mechanical tests, the dried composites were annealed at 130°C for 3 hours and kept in a desiccator for, at least, 24 hours.

2.3.5 X-Ray diffraction

The alignment of alumina platelets in the polymer matrix was assessed by X-ray diffraction (XRD) using the rocking curve (ω scan) technique. In brief, a high-resolution scan is performed at high 2θ angles (85° < 2θ < 95°) and one diffraction peak is selected. The 2θ angle corresponding to the selected diffraction peak is fixed and the sample is slowly rocked by an angle ω while acquiring the data. In order to take into account tilt-defocusing and absorption effects, the data was corrected using
the software TexturePlus, which was kindly supplied by Mark Vaudin (NIST, Gaithersburg). The full width at half maximum (FWHM) of the resulting intensity versus $\omega$ curves was used as a measure of the platelet degree of misalignment. All XRD measurements were performed in a X'Pert PRO equipment (PANalytical, The Netherlands).

2.3.6 Surface analyses

Covalent attachment of coupling agents (APTES and ND) was confirmed by Diffuse Reflectance Infrared Fourier Transform (DRIFT, Perkin Elmer – Series 2000, USA) and Thermogravimetric Analysis (TGA/SDTA 851E, Mettler Toledo, Switzerland). DRIFT spectra (64 scans; resolution: 2 cm$^{-1}$) were obtained by mixing the platelets in KBr (2 wt%) and grinding the resulting powder in a mortar. TGA measurements were performed in air (50 mL/min) at a heating rate of 10°C/min.

2.3.7 Differential Scanning Calorimetry (DSC):

DSC was performed in as-cast and annealed composites (DSC822, Mettler Toledo, Switzerland) using a heating rate of 10°C/min and a flow rate of 200 mL/min under nitrogen atmosphere.

2.3.8 Microstructural characterization

Tape-cast samples were cut, dipped into liquid nitrogen and freeze fractured to reveal the cross-section. The cross section was then mounted in a sample holder, sputtered with a 5 nm-thick platinum layer and imaged using a scanning electron microscope (LEO 1530, Zeiss, Germany).

2.3.9 Mechanical testing

Mechanical properties of composite films were measured under tensile mode in a universal mechanical testing machine (Instron 4411, USA). Standard dog bone samples were punched from 100 $\mu$m-thick composites films with the tested region being 12 mm x 2 mm. Samples were pulled at a strain rate of 10 mm/min. Elastic
moduli were taken as the slope of the resulting stress-strain curves in the linear elastic regime. The yield strength of the material was taken as the intercept between the extrapolated slopes from the linear elastic regime and the plastic deformation region of the stress-strain curves. The work of fracture was calculated from the area under the stress versus strain curves. At least 3 samples were measured to obtain the reported average and standard deviation values. For standard deviations higher than 10%, 2 additional samples were tested and taken into account in the calculations.

2.3.10 Bulk composite parts

Thicker composite parts were produced by stacking 20 equally-sized 100 µm-thick films obtained through tape casting. Solvent welding was performed in between individual films by applying a thin layer of DMF onto the two opposing surfaces of the films using a cotton swab. The films were then put in between two glass slides and firmly pressed by hand. The procedure was repeated until the 20 layers were stacked. The resulting material was put in the oven at 130°C for 3 hours to remove the excess of DMF and to ensure good adhesion between the laminates.

2.4 Results and discussion

2.4.1 Tape-casting of suspensions with nano- and microplatelets

Large-area polymer-based composite films were obtained by tape casting suspensions containing reinforcing particles dispersed in a solution of polyurethane in dimethylformamide (DMF), as schematically illustrated in Figure 2.1a. Suspensions with laponite nanoparticles were prepared using a solvent exchange method (23) in order to enable complete dispersion of the nanoplatelets and to favor their segregation into the hard segments of the polyurethane (Figure 2.1b).

The thickness of the composite films ranged from 80 to 150 µm. Tuning the rheological behavior of the suspension prior to casting is crucial to obtain homogeneous films with well-controlled thickness. We found that suspensions exhibiting an apparent yield stress of approximately 6 Pa and a pronounced shear-thinning behavior (Figure 2.1d) are fluid enough to ensure easy flow under the action of the shear stresses imposed by the blade during tape casting and at the same time
are able to retain their shape after casting and thus avoid excessive spreading over the substrate. The finite yield stress and high viscosity at low shear rates of the cast suspension is also important to avoid sedimentation of the alumina microplatelets during the drying process (Figure 2.1d). The presence of laponite nanoplatelets in the PU/DMF initial solution is key to achieve such rheological behavior. Taking into account an approximate blade velocity of 10 cm/s and a blade height of 2 mm typically used in our experiments, we estimate a shear rate of 50 s\(^{-1}\) during the tape casting process. At this shear rate, the suspension exhibits an apparent viscosity of 0.3 – 0.4 Pa.s, which allows for easy flow during casting and is also sufficiently high to prevent internal flow of particles and thus unwanted heterogeneities during the drying process.

Figure 2.1. a) Flowchart describing the solvent-exchange processing route 10 used to prepare the hierarchically reinforced composites. b) Schematic drawing of the highly structured composite consisting of polyurethane (PU) hierarchically reinforced with laponite nanoplatelets and alumina microplatelets. c) 1.5 mm-thick composite parts obtained by stacking and hot-pressing individual tape-cast films. d) Rheological behavior prior to tape casting of a typical suspension containing laponite platelets, polyurethane and DMF (laponite:PU volume ratio of 1:9 and PU:DMF weight ratio of approximately 1:35). The yield stress of the suspension, the operating point during tape casting, and the estimated threshold viscosity (\(\eta_{thr}\)) needed to avoid sedimentation of microplatelets in the suspension within 6 hours are also indicated in the graph. e) SEM micrograph of the alumina microplatelets used in this study (scale bar: 10 \(\mu\)m)
Because of its ease of operation and up-scalability, (25) tape casting enabled the preparation of large areas of composite films that could eventually be stacked together and hot-pressed to produce bulker composite parts, as illustrated in Figure 2.1c. This approach can potentially be used to fabricate composite components as large as those made using bulk processing techniques like extrusion or injection molding.

In addition to up-scalability, tape casting also induces favorable alignment of reinforcing particles due to the shear stresses applied under the blade in the casting direction (Figure 2.2a). The alignment of alumina microplatelets containing either polyvinylpyrrolidone (PVP) or aminopropyltriethoxysilane (APTES) as surface modifiers were confirmed by scanning electron microscopy of cross-sections of the as-cast films (Figure 2.2b,c). The degree of alignment of the microplatelets within the matrix was experimentally assessed through X-Ray diffraction using the rocking technique. (19, 20, 24) Examples of the angular distribution of microparticles in tape-cast composites as a function of the volume fraction of microplatelets are shown in Figure 2.2d for films containing polyvinylpyrrolidone. The full width at half maximum (FWHM) of the obtained angular distribution is taken as a measure of the degree of misalignment of the anisotropic particles within the material (Figure 2.2e).

Alumina platelets coated with PVP exhibit a very good alignment in the cast films, as evidenced by the low FWHM values in the range 7.6-11.9°. These values are relatively close to those achieved with the better controlled, but more cumbersome and time-consuming, layer-by-layer approach (Figure 2.2e). This contrasts with the poor alignment observed for microplatelets coated with APTES molecules, which exhibit FWHM values ranging from 15.4° to 28.5°. For both surface modifiers, the degree of platelet alignment decreases for higher volume fraction of particles, as illustrated in Figure 2.2e.

2.4.2 Modeling the alignment of platelets during tape casting

Understanding the major factors controlling the alignment of non-spherical particles in a suspension under shear is crucial to assess the potential and limitations of tape casting as a means to control particle orientation and thus eventually reinforce the composite. According to early investigations by Jeffery, an ellipsoidal
Figure 2.2. a) Schematic drawing illustrating the shear field applied to the platelet-containing suspension during tape casting. b,c) SEM cross-sections of polyurethane-based composites containing (b) 7 vol% laponite and 20 vol% alumina microplatelets modified with APTES and (c) 7 vol% laponite and 17 vol% alumina microplatelets modified with PVP. d) Normalized angular distribution of alumina microplatelets obtained by applying the X-ray diffraction rocking technique to composites containing increasing volume fractions of PVP-modified platelets. e) Full width at half maximum (FWHM) values of the angular distribution curves obtained for the tape-cast composites investigated here as compared to other composites produced with a layer-by-layer technique. (19, 20) f) Theoretical normalized angular distribution expected from equation 2 for platelets of decreasing effective aspect ratio, seff. g) Volume fraction of microplatelets required for the formation of an ordered nematic phase as a function of the platelet effective aspect ratio.
particle immersed in a fluid subjected to shear displays a well-defined angle $\omega$ with respect to the shear plane (or flow direction) that changes in time according to the following relation: \(26, 27\)

$$
cot \omega = s_{\text{eff}} \tan \left( \frac{s_{\text{eff}} \dot{\gamma} t}{s_{\text{eff}}^2 + 1} \right), \quad (1)
$$

where $s_{\text{eff}}$ is the effective aspect ratio of the platelet (long axis length : short axis length), $\dot{\gamma}$ is the shear rate and $t$ is time.

Assuming that the probability of finding a particle within a given infinitesimal range of angles $d\omega$, $P(d\omega) \propto dt/d\omega$, we differentiate equation (1) with respect to time to obtain the following relation:

$$
\frac{dt}{d\omega} = - \frac{s_{\text{eff}}^2 + 1}{\dot{\gamma} \cos^2 \omega \left( s_{\text{eff}}^2 \tan^2 \omega + 1 \right)}. \quad (2)
$$

Although it has been derived for one single non-spherical particle in an infinite continuous fluid, equation (2) provides qualitative insights into the effect of surface modifiers on the agglomeration state and alignment of the alumina microplatelets. According to this equation, the angular distribution of an anisotropic particle immersed in a fluid subjected to shear depends solely on the particle effective aspect ratio, $s_{\text{eff}}$. Figure 2.2f shows that the angular distribution of the normalized ratio $dt/d\omega$ becomes broader for decreasing effective aspect ratios, $s_{\text{eff}}$. This implies that the alignment of reinforcing microparticles parallel to the shear stresses applied during tape casting requires anisotropic particles with high aspect ratio that are well dispersed within the suspension. Agglomeration of the individual microplatelets into larger clusters of lower effective aspect ratio should lead to poorer alignment under shear.

In addition to shear-induced alignment, ordering of the microplatelets into a lamellar phase is also expected to occur at high volume fractions due to packing entropic effects. \(28\) The transition from an isotropic to an ordered nematic phase is typically described by the dimensionless parameter $nD^3$, with $D$ being the diameter of the platelet and $n$ the critical number density of platelets. Assuming that coexisting isotropic and nematic phases are formed for $nD^3$ values between 6.8 and 7.7, \(29\) we estimated the minimum volume fraction of platelets $V_{p,\text{nem}}$ required to achieve nematic ordering due to the packing entropic effect. Considering that $n = 4s_{\text{eff}}V_{p,\text{nem}}/\left( \pi D^3 \right)$, one can show that $V_{p,\text{nem}}$ increases significantly with a decrease of the platelet effective aspect ratio, $s_{\text{eff}}$, as indicated in Figure 2.2g. Thus,
agglomeration is expected to decrease both the shear-induced and packing-induced alignment of microplatelets.

On the basis of this theoretical analysis, the lower FWHM values achieved using PVP as surface modifier suggests the presence of well dispersed platelets with high effective aspect ratio in these suspensions. The SEM image shown in Figure 2.2c clearly indicates the presence of individualized platelets in composites containing PVP. The efficient dispersion of alumina particles after surface modification with PVP was confirmed by sedimentation experiments on dilute suspensions containing various concentrations of the modifier (Figure 9.1, Appendix 1). Films containing 6.4-16.8 vol% of platelets covered with PVP exhibit FWHM values in the range 7.6 – 8.5°, which is not so far from the minimum value of 3° that can be theoretically achieved upon shearing a completely dispersed individual platelet with an aspect ratio of 37.5 (Figure 2.2f).

The wider angular distribution obtained for platelets coated with APTES is caused by their agglomeration into lamellar clusters, which exhibit a lower effective aspect ratio than the individual platelets. The formation of such lamellar clusters is confirmed by SEM images of films containing APTES-modified platelets (Figure 2.2b). Agglomeration in this case might have occurred during the deposition of the silane on the platelets’s surface during the silanization process.

2.4.3 Polyurethane reinforced with nanoplatelets alone

To understand the effect of inorganic platelets on the mechanical behavior of tape-cast films, we first investigate the properties of composites reinforced only with laponite nanoplatelets. The incorporation of laponite alone into polyurethane films leads to composites with yield strength and elastic modulus that are up to 4.3-fold and 10.7-fold higher than that of the pure polyurethane matrix (Figure 2.3). Most importantly, this remarkable reinforcing effect is obtained without compromising the high ductility of the polymer matrix, leading to annealed composites with strain at rupture as high as 147% upon addition of 10vol% nanoplatelets (Figure 2.3). The ability of laponite particles to reinforce polyurethanes without impairing their high initial ductility has been attributed to the spontaneous preferential segregation of the nanoplatelets into the hard crystalline domains of the polymer. (23) Laponite segregation into the hard domains is made possible by first completely exfoliating the nanoplatelets in a water/DMF solution followed by removal of the aqueous phase and incorporation of the polymer, as shown by Liff et al (Figure 2.1a). (23)
Due to the limited fraction of hard domains in the polymer, the amount of laponite platelets that can be incorporated into the crystalline domains without impairing the polymer ductility has an upper limit at concentrations around 10vol%. Above this critical concentration, laponite platelets start to accumulate in the soft domains of the polyurethane, eventually degrading the composite’s mechanical properties (squares in Figure 2.3).

Figure 2.3. The elastic modulus, yield strength and strain at rupture of thermoplastic polyurethane as a function of the volume fraction of reinforcing laponite nanoplatelets. Data obtained for as-cast (squares) and annealed samples (triangles) are shown. Note that composites containing 19 vol% laponite were extremely brittle and thus could not be mechanically characterized even after the annealing step. Theoretical estimates for the elastic modulus and yield strength of the composites based on simple rule of mixtures (30, 31) are shown as fitting curves. Gm is the shear modulus of the polymer matrix, whereas τy is either the interfacial shear strength or the shear strength of the continuous matrix (see text). The strain at rupture data are linked with lines to guide the eyes.
Interestingly, we found that such critical laponite concentration increases from 10 to 16 vol% upon annealing of the composite at 130°C for 3 hours (triangles in Figure 2.3). Differential scanning calorimetry indicates the appearance of an additional endothermic peak in composites subjected to the annealing step (Figure 9.2, Appendix 1). While further investigations are needed to identify the microstructural changes imparted by the annealing process, the new endothermic peak might be related to hard segment relaxation effects or to the crystallization of hard segments on the surface of the platelets (see Appendix A1). If confirmed, the formation of crystalline hard domains on the platelet surface would explain the higher concentration of polar laponite platelets that can be accommodated in the annealed composites without deteriorating their mechanical properties.

To understand the effect of laponite platelets on the yield strength \( \sigma_c \) and elastic modulus \( E_c \) of the resulting polyurethane-based composites, we use the following rule of mixtures equations put forward by Glavinchevski and Padawer-Beecher, respectively: \( (30, 31) \)

\[
\sigma_c = \alpha V_p \sigma_p + (1 - V_p) \sigma_m \quad (3)
\]

and

\[
E_c = \beta V_p E_p + (1 - V_p) E_m \quad (4)
\]

where

\[
\alpha = \frac{\tau_y s}{2 \sigma_p},
\]

\[
\beta = \frac{1}{\frac{\tanh \left( \frac{s \sqrt{G_m V_p / \left( E_m (1 - V_p) \right)}}{s \sqrt{G_m V_p / \left( E_m (1 - V_p) \right)}} \right)}},
\]

\( V_p \) is the volume fraction of platelets, \( \sigma \) is the strength, \( E \) is the elastic modulus, \( G \) is the shear modulus, \( s \) is the platelet aspect ratio, and \( \tau_y \) is either the interfacial shear strength (weak platelet/polymer interfaces) or the shear strength of the continuous matrix (strong platelet/polymer interfaces). The indices \( p \) and \( m \) refer to the platelets and to the continuous matrix, respectively. Note that since the aspect ratio, \( s \), of the platelets is lower than the critical aspect ratio, \( s_c = \sigma_p / \tau_y \), for all the investigated composites, we use a factor \( \alpha \) corresponding to the pull-out mode of fracture. \( (19, 20) \)

The shear strength \( \tau_y \) and the shear modulus \( G_m \) determine, through the factors \( \alpha \) and \( \beta \), the magnitude of stress that is eventually transferred from the soft continuous matrix to the stiff platelets at the matrix/platelet interface. Thus, estimating these parameters from the strength and elastic modulus experimental
data provides insightful information about the chemical environment in the vicinity of the reinforcing platelets.

By fitting equation (3) to the experimental yield strength data for laponite-reinforced composites, we obtain a shear strength, \( \tau_y \), in the range 17-24 MPa (Figure 2.3). \( s \) and \( \sigma_m \) values of, respectively, 25 and 12.9 MPa were assumed. In case of the elastic modulus, good agreement between the experimental data and theoretical predictions is obtained using a shear modulus, \( G_m \), of 0.7 GPa (Figure 2.3). Assuming a Poisson ratio, \( \nu \), of 0.40 for polyurethane, the shear modulus obtained corresponds to an elastic modulus, \( E_m \), of 1.96 GPa (\( E_m = 2G_m(1+\nu) \)).

The \( E_m \) and \( \tau_y \) values estimated from the experimental data (Figure 2.3) are, respectively, eight and four times higher than the elastic modulus and the shear strength of the macroscopic homogenous polyurethane film. Here, the shear strength, \( \tau_y \), is assumed to be half of the tensile strength, \( \sigma_m \), measured through uniaxial tests of polyurethane films (\( \sigma_m = 12.9 \) MPa). (32) These results suggest that stress transfer to the nanoplatelets is not governed by the properties of the macroscopic homogeneous polyurethane but rather by an eight times stiffer and four times stronger local phase in the platelet vicinity. This suggests that the platelets are surrounded by the stiffer and stronger polar segments of the polyurethane, which is in line with the observation by Liff et al that laponite preferentially segregates into the hard crystalline domains of polyurethanes. (23)

### 2.4.4 Interfacial bonding between polyurethane and inorganic microplatelets

The effective reinforcement of laponite-containing composites with alumina microplatelets at a second hierarchical level requires an optimum interfacial bonding between the inorganic microplatelets and the polyurethane matrix. Such bonding enables stress transfer from the polymeric continuous phase to the strong and stiff microplatelets during mechanical loading. Bonding is achieved using surface modifiers or coupling agents that connect the dispersed microplatelets to the surrounding polymer matrix through physical or chemical interactions.

Aminopropyltriethoxysilane (APTES), nitrodopamine (ND) and polyvinylpyrrolidone (PVP) were investigated as possible coupling agents between polyurethane and the alumina surfaces. APTES was attached to the platelet through condensation reactions between their hydrolysable \( \text{–OC}_2\text{H}_5 \) groups and the hydroxyl groups on the platelet surface. Due to the presence of three \( \text{–OC}_2\text{H}_5 \) groups per molecule, APTES molecules can also undergo self-condensation reactions,
eventually leading to the formation of multilayers on the platelet surface (Figure 9.3, Appendix A1). In contrast, nitrodopamine and related catechols/pyrogallols form well-defined monolayers on the surface of alumina particles through strong ligand exchange reactions between their –OH groups and the hydroxyl groups on the particle surface. (33-36) PVP molecules are expected to adsorb weakly on the platelet oxide surface through polar interactions between –OH surface groups and the pyrrolidone polar groups of the macromolecule. (37, 38) The adsorption of APTES and nitrodopamine on the platelet surface was confirmed by FTIR analyses (Figure 9.3, Appendix A1), whereas the adsorption of PVP was indirectly confirmed by the remarkably longer stability of platelets in suspensions containing this polymer (Figure 9.1, Appendix A1).

Despite the successful adsorption of the coupling agents on the platelet surface, the addition of 18.5vol% modified platelets to a polyurethane matrix did not lead to any significant reinforcing effect in as-cast composite films (Figure 2.4d). This is a clear evidence of a weak interfacial bonding between the modified platelets and the polymer matrix. Due to the predominantly polar nature of the functional groups present on the platelet surface upon adsorption of the coupling agents, a high interfacial bonding is only expected if the surface modified platelets are exposed to the polar hard segments of the polyurethane. Thus, our results suggest that the phase separation of hard and soft segments during processing does not lead to segregation of the hard segments near the surface of modified platelets.

The interfacial bonding between platelets and polymer matrix is markedly increased by annealing the composite at 130°C for 3 hours (Figure 2.4e). The strong interfacial bonding achieved through such heat treatment leads to a up to 145 and 130% increase in both the yield strength and elastic modulus of composites containing 18.5vol% platelets, regardless of the coupling agent used. This surprising increase in interfacial bonding probably results from microstructural changes in the polyurethane matrix during annealing. Our results indicate that the mobility of the PU macromolecules at 130°C is likely high enough to allow for molecular rearrangements that promote energetically favorable interactions between hard segments and the platelet surface. Because of the polar nature of the bare alumina surface, a strong interfacial bonding and reinforcing effect was observed even in composites containing unmodified platelets (Figure 2.4e). DSC experiments on such hierarchical composites (Figure 9.2, Appendix A1) also show an additional endothermic peak that might be an indication of such microstructural changes.
Hierarchical Reinforcement of Polyurethane-based Composites

Figure 2.4. Schematic drawing of the expected surface chemistry on the alumina platelets after modification with (a) aminopropyltriethoxysilane (APTES), (b) nitrodopamine (ND) and (c) polyvinylpyrrolidone (PVP). (d,e) Effect of these surface modifiers on the mechanical behavior of polyurethane-based composites containing 7.8 vol% laponite nanoplatelets (laponite:PU volume ratio of 1:9) and 18.5 vol% alumina microplatelets (d) before and (e) after annealing at 130°C for 3 hours. Stress versus strain results for pure polyurethane (PU) and polyurethane containing laponite (PU-Lap, laponite:PU volume ratio of 1:9) are also shown for comparison.

2.4.5 Stress transfer in hierarchically reinforced polyurethane

Hierarchically reinforced composites were obtained by incorporating increasing volume fractions of alumina microplatelets into polyurethane-based matrices containing 10 vol% of laponite nanoplatelets. At such laponite concentration the polyurethane is still sufficiently ductile to allow for the addition of up to 26.9 vol% of microplatelets before a significant decrease in the work of fracture takes place (Figure 2.5).

The elastic modulus, yield strength, work of fracture and strain at rupture of the resulting hierarchical composites are shown in Figure 2.5 for platelets coated with either APTES or PVP. The elastic modulus and yield strength data for volume fractions of microplatelets up to 20-25vol% can be reasonably described using the simple rule of mixture equations (3) and (4). The shear modulus \( G_m \) and the shear
strength \( \tau_y \) were used as fitting parameters to explain the dependence of \( E_c \) and \( \sigma_c \) on the volume fraction of microplatelets below 25vol% (Figure 2.5a,b,d,e).

Figure 2.5. Mechanical properties of annealed hierarchical composites containing laponite nanoplatelets (laponite:PU volume ratio of 1:9) and increasing volume fractions of alumina microplatelets modified with (a-c) APTES and (d-i) PVP. The PVP concentration was fixed at a PU:PVP:Laponite volume ratio of 9.5:2:1 in graphs (d-f) and a PVP:Alumina volume ratio of 1:1.27 in graphs (g-i). Theoretical estimates for the elastic modulus and yield strength of the composites based on simple rule of mixtures (30, 31) are shown as fitting curves in (a,b) and (d,e). \( G_m \) is the shear modulus of the polymer matrix, whereas \( \tau_y \) is either the interfacial shear strength or the shear strength of the continuous matrix (see text). The dotted lines in (c,f,g-i) are guides for the eyes.

To obtain these fittings, equations (3) and (4) were applied to the second level of hierarchy, assuming that the laponite-reinforced polymer behaves as the continuous matrix around the alumina microplatelets. Thus, the variables in equations (3) and (4) are defined as follows: \( V_p \) is the volume fraction of microplatelets, \( \sigma_p \) and \( E_p \) are respectively the strength and the elastic modulus of the microplatelets, \( \sigma_m \) and \( E_m \) are respectively the strength and the elastic modulus of the laponite-reinforced polyurethane, and \( s \) is the aspect ratio of the microplatelets.

The \( G_m \) and \( \tau_y \) parameters obtained by fitting the rule of mixture relations (eqs. 3 and 4) to the experimental data provide information about the stress transfer from
the laponite/polyurethane matrix to the alumina microplatelets. Stress transfer is determined by the phase in the close vicinity of the reinforcing microparticles, (39) which in this case could be the polyurethane hard crystalline domains or a mixture of hard crystalline domains and soft amorphous matrix, either in the presence or absence of intercalated laponite platelets.

Most of the shear modulus and shear strength values obtained from the fitting are relatively close to the $G_m$ and $\tau_y$ expected for bulk polyurethane or polyurethane-PVP blends (Table 2.1). The only exception is the $G_m$ value obtained for composites containing PVP-coated microplatelets, which is surprisingly almost 2-fold higher than the $G_m$ expected for the bulk polyurethane-PVP polymer blend (Figure 9.4, Appendix 1).

Despite the inconsistency observed in the more complex PVP-containing system, our theoretical analysis suggests that stress transfer to the microplatelets is governed by the shear properties of the bulk polymer matrix in the absence of laponite reinforcement. This indicates that the microscale platelets are likely surrounded by a mixture of unreinforced hard crystalline domains and soft amorphous matrix.

Table 2.1. Comparison between the shear modulus ($G_m$) and shear strength ($\tau_y$) obtained as fitting parameters in Figure 2.5 with that estimated from tensile tests in bulk polyurethane and polyurethane-PVP blends.

<table>
<thead>
<tr>
<th></th>
<th>$G_m$ (MPa)</th>
<th>$\tau_y$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>APTES-coated microplatelets</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>From fitting the experimental data</td>
<td>120</td>
<td>5</td>
</tr>
<tr>
<td>Estimated for bulk polyurethane</td>
<td>90 *</td>
<td>6.5 &quot;</td>
</tr>
<tr>
<td><strong>PVP-coated microplatelets</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>From fitting the experimental data</td>
<td>350</td>
<td>5 - 13</td>
</tr>
<tr>
<td>Estimated for bulk polyurethane-PVP blend</td>
<td>170 *</td>
<td>13.8 &quot;</td>
</tr>
</tbody>
</table>

* estimated from the experimental elastic modulus of bulk samples ($E_m$) using the relation $G_m = E_m/2(1 + \nu)$ and assuming a Poisson ratio $\nu = 0.4$.

*" estimated from the experimental tensile strength of bulk samples ($\sigma_m$) using the relation $\tau_y = \sigma_m/2$.
2.4.6 Hierarchical reinforcement of polyurethane with nano- and microplatelets

The hierarchical reinforcement of polyurethane with laponite nanoplatelets and alumina microplatelets modified with APTES leads to composites with maximum yield strength and elastic modulus of 56.3 MPa and 3.54 GPa, respectively (Figure 2.5a-c). These $\sigma_c$ and $E_c$ values are approximately 4-fold and 14-fold higher than those of the pure polymer matrix, respectively.

The incorporation of polyvinylpyrrolidone (PVP) into the system to improve the alignment of microplatelets and to form a stronger and stiffer polymer matrix further increases the absolute strength and the elastic modulus of the composites up to the remarkable values of 91.7 MPa and 6.97 GPa, respectively (Figure 2.5d,e,g,h). This corresponds to a 7-fold increase in yield strength and 29-fold increase in elastic modulus as compared to pure polyurethane. Such reinforcing effect is accompanied by a substantial decrease in the ductility of the composite, which is reduced from 500% in the pure polymer to only a few percent in the hierarchically reinforced film (Figure 2.5f,i). Similar decrease in the work of fracture has also been observed in other platelet-reinforced systems. (18-20)

The reinforcement of polyurethanes at two length scales allows us to achieve mechanical properties that could not be obtained using only one platelet size. This is illustrated in Figure 2.6, which compiles the different experimental series investigated in this study and the strength and elastic modulus of the resulting composites. The advantage of the hierarchical reinforcement concept is more evident in composites containing a PU-PVP blend as polymer matrix (Figure 2.6d,e). This probably results from the improved dispersion of the alumina microplatelets in the presence of PVP. The combination of nano- and microplatelets leads to a more effective reinforcement of the polymer blend because it allows for the addition of higher concentrations of the inorganic phase before a significant reduction in the work of fracture occurs. The selective segregation of the nanoplatelets into the PU hard domains is key to keep the laponite-reinforced PU-PVP matrix ductile and thus enable the further incorporation of alumina microplatelets at the next hierarchical level.
Figure 2.6. a) Quartenary phase diagram indicating the series of compositions investigated in this study. b,c) Mechanical properties of hierarchical composites (blue diamonds) consisting of pure polyurethane reinforced with APTES-modified alumina platelets at the microscale and laponite platelets at the nanoscale. d-e) Mechanical properties of hierarchical composites (green filled circles) consisting of PU-PVP polymer blends reinforced with PVP-modified alumina platelets at the microscale and laponite platelets at the nanoscale. Properties of the respective composites reinforced only at the nanoscale are indicated by the red squares in (b-e) for comparison.
Polyurethane-based composites covering a wide spectrum of mechanical properties, from soft and rubbery to strong and stiff, can be obtained by deliberately reinforcing the polymer matrix with inorganic nano- and microplatelets. This is illustrated in Figure 2.7, which displays all the experimental data obtained in this study in single plots of the major mechanical properties.

![Figure 2.7](image.png)

**Figure 2.7.** Range of mechanical properties covered by the polyurethanes and polyurethane-based composites investigated in this study.

### 2.5 Conclusions

The hierarchical reinforcement of polyurethane with nano- and microplatelets leads to materials with remarkably high strength and stiffness because it partly circumvents the undesired reduction in work of fracture that typically results from the addition of high concentrations of reinforcement at one single length scale. We show that the incorporation of 5.3 vol% laponite nanoplatelets and 26.9 vol% alumina microplatelets into polyurethane-PVP blends leads to a 7-fold increase in yield strength and 29-fold increase in elastic modulus as compared to pure polyurethane, which is at least 60 and 170% higher than the values achieved using for example nanoplatelets alone. However, such strengthening effect still occurs at the expense of ductility, which is reduced from approximately 500% in pure polyurethane to 3-5% upon addition of the platelets. Due to the preferential segregation of laponite into the hard crystalline domains of the polyurethane, stress transfer to the nanoplatelets is enhanced by the presence of a strong and stiff domain surrounding the nano-reinforcement. In contrast, stress transfer to the alumina microplatelets seems to be primarily determined by the mechanical properties of bulk polyurethane, suggesting that no preferential segregation occurs at the microscale and that the presence of
Hierarchical Reinforcement of Polyurethane-based Composites

nanoplatelets in the surrounding matrix does not affect the transfer of stress to the microplatelets. Large-area polyurethane thick films and laminated bulk parts with tunable strength, stiffness and ductility were obtained using a simple, up-scalable tape casting process. The use of PVP as surface modifier resulted in less than 8° misalignment of the alumina microplatelets within the polymer matrix, which is not so far from the level of orientation that can theoretically be achieved with individual platelets of the same aspect ratio when subjected to shear. Annealing of the cast and dried composites at 130°C for 3 hours is needed to ensure efficient stress transfer from the polymer matrix to the hydrophilic reinforcing microplatelets, regardless of the hydrophilic molecules used as surface modifiers. The combination of nano- and micro- inorganic platelets as reinforcements of polymer matrices at different length scales significantly extends the range of strength and stiffness levels that can be achieved in polyurethane-based systems, indicating that the hierarchical reinforcing concept is a very promising approach to tailor the local mechanical properties of composites using a few number of reinforcing building blocks within the same polymer matrix.

2.6 Acknowledgements

We thank Prof. Markus Niederberger, Prof. Ludwig Gauckler and Prof. Paul Smith for providing access to equipment from their laboratories, Dr. Kyrill Feldman for his invaluable help in many of the experiments, Mr. Markus Müller for his technical assistance and Dr. Thomas Schweizer for performing the DSC experiments.

2.7 References


3.1 Abstract

Heterogeneous composite materials with variable local stiffness are widespread in nature, but are far less explored in engineering structural applications. The development of heterogeneous synthetic composites with locally tuned elastic properties would allow us to extend the lifetime of functional devices with mechanically-incompatible interfaces and to create new enabling materials for applications ranging from flexible electronics to regenerative medicine. Here, we show that heterogeneous composites with local elastic moduli tunable over five orders of magnitude can be prepared through the site-specific reinforcement of an entangled elastomeric matrix at progressively larger length scales. Using such a hierarchical reinforcement approach, we designed and produced composites exhibiting regions with extreme soft-to-hard transitions while still being reversibly stretchable up to 350%. The implementation of the proposed methodology in a mechanically challenging application is illustrated here with the development of locally stiff and globally stretchable substrates for flexible electronics.
3.2 Introduction

Integration of different synthetic materials, such as polymers, metals and ceramics, into functional devices often results in mismatches in mechanical and thermal properties that favor premature failure of the solid interfaces due to stress localization. Examples of functional devices whose durability is impaired by premature interfacial failure are numerous and range from biomedical implants in orthopedics \(^1\) to metal-composite joints in automotive and aerospace applications \(^2, 3\) to inorganic functional devices in high-performance flexible electronics. \(^4\) In some applications, this issue can be circumvented by developing functionally-graded heterogeneous materials (FGM) whose through-thickness chemical composition is gradually changed to reduce mismatches in the elastic and thermal properties of the homogeneous materials to be integrated. However, this approach has been limited to purely inorganic systems whose elastic moduli lie within the same order of magnitude, as is the case for example of ceramic thermal barrier coatings deposited on metals. \(^5, 6\)

Constructing heterogeneous composite materials with locally tuned mechanical properties in all three dimensions is a recurring strategy in nature to achieve unusual mechanical properties and to couple surfaces with very different elastic moduli. \(^7-14\) For instance, the biological tissue that connects tendons to bone exhibits locally tuned elastic moduli that can vary by as much as two orders of magnitude in order to match the stiff surface of bone with the soft tendon. \(^15-17\) This is achieved by changing the local concentration of hydroxyapatite reinforcing particles embedded within hierarchically structured collagen fibers. \(^15\) Likewise, the teeth of many vertebrates and invertebrates exhibit a 3D bilayer structure that combines a remarkable surface hardness to withstand mastication loads with a high toughness in the inner layer to resist crack propagation. Such properties are achieved by tailoring the concentration and orientation of reinforcing mineral particles across the material. \(^12, 18\) While a multitude of other heterogeneous natural composites with locally tuned elastic moduli exist, \(^9, 18-20\) the examples above well illustrate the ability of biological materials to deliberately control its mechanical properties by using an entangled continuous polymer matrix reinforced to different extents with a limited choice of inorganic reinforcing elements. \(^21, 22\) Such an interpenetrating polymer matrix is believed to be key in ensuring efficient stress transfer and in avoiding local failure between regions of different elastic moduli.
Despite the improved mechanical and thermal interfacial coupling offered by artificial FGMs, the three-dimensional nature and the unique local control of structure and properties observed in heterogeneous biological composites have not yet been achieved in synthetic systems. Obtaining such level of 3D control in artificial heterogeneous composites would allow us to not only extend the lifetime of existing functional devices prone to interfacial failure but also to develop new materials for mechanically challenging demands. These include for example dental restorations for prosthetic dentistry that more closely resemble the mechanical properties of natural tooth, (23) elastomeric substrates for flexible electronics that are bendable and stretchable but yet locally stiff, (24-29) and synthetic bio-scaffolds for the replacement of intervertebral discs (30) and for the regeneration of graded tendon/ligament-to-bone insertions. (31-33) In addition to addressing such mechanical challenges, the deliberate local reinforcement of weak regions achievable with such heterogeneous composites also represents an economical and environmental-friendly approach to attain the required mechanical performance while minimizing the use of limited and costly resources.

Here, we show that heterogeneous manufactured composites exhibiting elastic moduli spanning over several orders of magnitude can be obtained by tuning the local reinforcement of an entangled continuous polymer matrix using reinforcing elements at multiple hierarchical levels. To illustrate the unusual sets of properties that can be achieved with this approach, we create 3D polymer-based composites whose local elastic modulus on the surface can approach that of the hardest biological materials like bone and tooth enamel, while still being reversibly stretchable up to 350% strain on a global scale without failure.

3.3 Experimental procedure

3.3.1 Materials

All chemicals were purchased from Aldrich Co. and were of analytical grade, unless otherwise stated. N,N-dimethylformamide (DMF, dried over molecular sieves), 4,4'-methylenebis(cyclohexyl isocyanate) (H-MDI, 90%), 1,4-butandiol (BDO, ≥ 99%); poly(tetrahydrofuran) (T1000, M_w = 1000 g/mol), glycerol ethoxylate (EG, M_w = 1000 g/mol) and dibutyltin dilaurate (DBTL) were used for the synthesis of polyurethanes with different hard-to-soft segment ratios. Composites were prepared
using a commercial thermoplastic polyurethane (Elastollan C64D, BASF, Germany), N,N-dimethylformamide (DMF, ACS grade), polyvinylpyrrolidone (PVP, M<sub>w</sub> = 40000 g/mol), alumina platelets with average diameter of 7.5 µm and thickness of 200 nm (Alusion, Antaria Limited, Australia) and laponite platelets with diameter of 25 nm and thickness of 1 nm (Laponite RD, ProChem, Switzerland).

### 3.3.2 Polyurethane syntheses

Polyurethane syntheses were carried out under nitrogen atmosphere in a three-neck round bottom flask equipped with a reflux condenser. H-MDI and BDO were used as hard segments, T1000 as soft segment, and EG as cross-linker. The hard-to-soft segment ratio was adjusted by changing the proportion between T1000 and BDO. Firstly, the glassware was dried with a heating gun at 350°C to remove any adsorbed water. Then, a prepolymer was prepared by loading the flask with H-MDI followed by the dropwise addition of a solution of T1000 and EG in DMF under magnetic stirring (600 rpm). The resulting mixture was kept at 80°C for 3 hours. After formation of the prepolymer, the temperature was reduced to 60°C and a solution of BDO in DMF was added to the flask to proceed with the polymerization reaction for a time period of 1 hour. Finally, DBTL was added and stirred for additional 30 minutes. The reactant concentrations were adjusted to keep a constant NCO:OH molar ratio of 1:1 with a 5wt% excess of H-MDI. The final concentration of polyurethane in DMF was 0.2 g/mL. Polymer films were obtained by casting the solution onto silicone molds and dried at 60°C for 24 hours. Table 10.1 (Appendix 2) summarizes the amounts of chemicals used for the polyurethane syntheses.

### 3.3.3 Preparation of polyurethane-based composites

Composites reinforced with nano- and micro-platelets were prepared following the procedure previously described by Libanori et al. (34) In summary, alumina platelets were first dispersed in a solution of PVP in DMF and kept under stirring for 12 hours. Next, polyurethane pellets (Elastollan) and a suspension of laponite in DMF (obtained through solvent exchange method) (34, 35) were added to the alumina/PVP suspension. The resulting mixture was kept at room temperature and under stirring (600 rpm) until the polymer pellets were dissolved. The viscosity of the mixture was adjusted by removing DMF in an evaporator at 10 mbar and 60°C.
(R-215 Rotavapor, Buchi, Switzerland) before casting the fluid on polyethylene plates using a doctor blade (height = 1 mm). The remaining DMF was removed by placing the sample in a conventional oven (Memmert, UNE 200, Germany) at 60°C for 24 hours. The obtained composites were finally annealed at 130°C for 3h. Table 10.2 (Appendix 2) depicts the composition of the platelet-reinforced composites investigated in this study.

3.3.4 Preparation of patch-substrate composites

Patch-substrate modules for mechanical and electrical testing were prepared by first assembling individual films (M0550, M1600, M3600 and M7000) into multilayered 0.4 cm x 5 cm ribbons using the solvent welding technique. For that purpose, a small amount of DMF was first applied on the two surfaces to be welded using a cotton swab. Pressure was manually applied onto the multilayer stack by squeezing the sample in between glass slides. The patch layers were assembled from the hardest to the softest material and subsequently welded onto a 5 cm x 5 cm x 0.19 mm M0040 substrate. The composition and thickness of each individual layer is indicated in Table 10.3, Appendix 2. Finally, the samples were dried at 60°C for 12 hours in a vacuum oven. 2-mm wide dogbone samples were cut from the large M0040 substrate in the direction perpendicular to the multilayered ribbon to obtain patch-substrate modules with the architecture shown in Figure 3.2a-c. For the resistance measurements, a 50-nm thick gold layer was sputtered on the top of the stiffest layer (Figure 10.7, Appendix 2). Sputtering was carried out using a working distance of 50 mm, current of 40 mA and pressure of 2 x 10^{-5} mbar for 200 seconds. Electrical contacts were made by gluing 100 µm-diameter copper wires to the gold layer using silver paste and an epoxy resin.

3.3.5 Preparation of 3D heterogeneous composite

3D heterogeneous composites shown in Figure 3.1f was prepared by first solvent welding 5 cm x 5 cm individual layers of the compositions M0550, M1600, M3600, M7000, as described above. The resulting multilayered welded film was cut into 5 mm x 5 mm patches using a scalpel. Finally, the patches were welded onto a 190 µm-thick M0040 substrate by applying DMF on both surfaces and manually pressing them together using glass slides. Patches welded on the top of the
substrate were locally heated (60 °C) with a heating gun to ensure good adhesion between the materials and to remove the remaining solvent.

3.3.6 Characterizations

3.3.6.1 Tensile tests

Single layer materials were evaluated under tensile mode in a universal mechanical testing machine (Instron 4411, USA). A strain rate of 2.5 mm/min was applied to pure polyurethane samples (M0002 to M0550), whereas polyurethanes reinforced with nano- and/or microplatelets (M0330 to M7000) were tested at 10 mm/min. Control experiments showed that the elastic moduli of platelet-reinforced polyurethanes decrease approximately 10-20% by reducing the strain rate from 10 to 2.5 mm/min, indicating that the order of magnitude comparison shown in Figure 3.1a is still valid despite the different strain rates used for mechanical characterization. Standard dog bone samples with a rectangular central region of 12 mm x 2 mm were punched from the materials for the tensile tests. Elastic moduli were taken as the slope of the resulting stress-strain curves in the linear elastic regime. The reported values and standard deviations were calculated from a minimum of 3 specimens.

3.3.6.2 Local strain measurements on patch-substrate modules

A macroscope (Z16 APO, Leica, Switzerland) was used to track the local strain on patch-substrate modules while straining the materials at a constant rate of 2.5 mm/min. Image acquisition was synchronized with the global strain applied by the universal mechanical testing machine. Images were taken with time intervals of 10 seconds and were afterwards analyzed using the software ImageJ. The local strain was measured from images taken from the lateral cross-section of the sample in order to account for bending of the patch during stretching. Reproducibility was assessed by testing 3 specimens for each sample, which led to the results shown in Figure 10.8, Appendix 2.
3.3.6.3 Local strain measurements on 3D heterogeneous composites

To investigate the in-plane local elastic behavior of the 3D heterogeneous composite shown in Figure 3.1f, we measured the distance between consecutive patches on the sample surface \( l_{ij} \) before and after globally stretching the underlying substrate along the x-axis (Figure 10.9, Appendix 2). Samples were stretched up to 100% at a constant rate of 2.5 mm/min.

3.3.6.4 Electrical resistance measurements

The electrical resistance of a 50 nm-thick gold layer deposited on the surface of a graded patch (E-Grad in Figure 3.5) was determined by measuring the voltage across the layer for a constant current of 100 mA while straining the patch-substrate module in an universal mechanical testing machine. By synchronizing the electrical and mechanical measurements, we obtained the voltage across the film as a function of the externally applied strain. Samples were pulled at a strain rate of 2.5 mm/min.

3.3.6.5 Reinforced islands with reduced edge steps

Electrical interconnection between adjacent reinforced islands and integration of the proposed graded substrates into microelectronics can be facilitated if the height of the step between the reinforced patch and the underlying substrate would be smaller than the 250-500 \( \mu \text{m} \) used in the geometry investigated throughout our study (Figure 3.2 and 3.3). To demonstrate that it is possible to reduce the height of such step and electrically connect adjacent reinforced patches using standard deposition methods, we hot pressed 420-\( \mu \text{m} \) thick graded patches (M0550, M1600, M3600 and M7000 layers) against a 1100-\( \mu \text{m} \) thick elastomeric substrate (M0040) at 120 \( ^\circ \text{C} \) for 3 minutes using 700 \( \mu \text{m} \) spacers.

3.3.6.6 Cyclic testing of reinforced patches

Cyclic testing was performed using the same experimental apparatus used to measure the electrical resistance of gold layers deposited on the top of a graded patch. Samples were stretched to a nominal global strain of 80% and subsequently unloaded to the initial cross-head displacement position. A strain rate of 2.5 mm/min
was used in both loading and unloading curves. The patched substrates exhibited a high recoverability of about 75-85% after each cycle, despite the relatively high strain rate applied.

3.3.6.7 Stretching of substrates with functional LEDs deposited on reinforced graded patch

Light emitting diodes (LEDs, 1.8 mm diameter, Everlight Electronics CO., LTD.) were electrically contacted to two isolated 50nm-thick gold patterns using silver paste and subsequently fixed by applying a small amount of epoxy glue. 100 µm copper wires were fixed at the other end of the patch using the same technique (see Figure 10.10, Appendix 2). Samples were pulled at a strain rate of 2.5 mm/min, while keeping the LED switched on using an external 9V battery. Pictures were taken using a professional camera (Canon EOS 450D).

3.3.6.8 Finite element analysis (FEA)

FEA was carried out using the software Comsol Multiphysics (version 4.2a) to qualitatively analyze the effect of different elastic modulus profiles on the mechanical response of the patch-substrate modules (Figure 3.2). Ideal interfaces between the different layers of the patch and the substrate were assumed. The substrate and the patches were mechanically described using 2-term Mooney-Rivlin and linear elastic material models, respectively. For the Mooney-Rivlin model, the following relation for the strain energy density function of incompressible materials was used: (36)

\[
W = C_{10}(I_1 - 3) + C_{01}(I_2 - 3) \tag{1}
\]

where \(C_{10}\) and \(C_{01}\) are material constants and \(I_1\) and \(I_2\) are the first and the second strain invariants, respectively. For the simple case of uniaxial deformation, one can use the strain energy density \(W\) to obtain the engineering stress \(\sigma\) as a function of the stretch \(\lambda\) as follows:

\[
\sigma = (\lambda - \lambda^{-2}) \left(2C_{10} + \frac{2C_{01}}{\lambda} \right) \tag{2}
\]
where $\lambda=(\varepsilon+1)$. Equation (2) was fitted to the experimental stress versus stretch curve for the substrate M0040 to obtain the constants $C_{10}$ and $C_{01}$ (Figure 10.11, Appendix 2).

The shear modulus ($G$) and the bulk modulus ($K$) of the material were calculated using the relation $G = 2(C_{01} + C_{10})$ and $K = (2G(1 + \nu)) / (3(1 - 2\nu))$, respectively. In these calculations, a Poisson’s ratio of 0.49 was assumed for the M0040 material. The exact choice of the Poisson’s ratio was found to have little effect on the result of the simulation, with the stress and the strain throughout the patch decreasing by less than 12% when the Poisson ratio is changed from 0.49 to 0.40. The mechanical properties of individual compositions used for the simulations are listed in Table 10.5 (Appendix 2).

Simulations were performed by applying a prescribed longitudinal global strain ($\varepsilon_g$) along the long-axis of the module (y-axis in Figure 3.2), while keeping the other end of the substrate fixed (displacement equals to zero). The patch-substrate module was meshed using free tetrahedral elements (calibrated for general physics in Comsol). Maximum and minimum element sizes were set to 0.24 mm and 0.0024 mm, respectively (see Figure 10.12, Appendix 2). Other meshing parameters include: maximum element growth rate (1.3), resolution of the curvature (0.2) and resolution of narrow regions (0.1). Calculations were performed using Comsol’s structural mechanics package under stationary mode.

### 3.4 Results and discussion

#### 3.4.1 Hierarchical composites with extreme mechanical gradients

Composites with different elastic moduli were created by hierarchically reinforcing a polyurethane (PU) soft matrix with (1) PU hard segment domains, (2) inorganic nanoplatelets and (3) inorganic microplatelets at progressively larger length scales (Figure 3.1a). Reinforcement of the soft PU matrix with PU hard segments is accomplished by increasing the relative fraction of hard to soft segments (HS:SS) during polyurethane synthesis (Figure 3.1a). Further stiffening of polyurethane matrices is achieved through the selective reinforcement of the PU hard domains with laponite nanoplatelets, following the procedure developed by Liff et al. (34, 35) Alumina microplatelets are finally used to reinforce the laponite-containing polyurethane matrix at the next hierarchical level. Following this procedure, we
produce individual polyurethane films with elastic moduli that can be tuned between 4 MPa and 7 GPa. (34) In Figure 3.1a, the individual polyurethane compositions are indicated by the letter M followed by their elastic moduli in MPa.

Heterogeneous composites with deliberate local stiffness are prepared by solvent welding individual films with different levels of reinforcements into one single component, as schematically illustrated in Figure 3.1b. In the solvent welding process, two film surfaces are first wetted by a good solvent and pressed together to allow for polymer entanglement, which is then preserved upon solvent evaporation. Such entanglement eliminates the interfaces between individual films, leading to heterogeneous composites with efficient stress transfer throughout the structure. The upper limit in elastic modulus achieved with the hierarchical polymer-based composite (7 GPa) can be further increased on the surface through the deposition of a 100nm-thick layer of Al₂O₃ via atomic layer deposition (150 °C / 160 minutes). (37)

Figure 3.1. Hierarchical heterogeneous composites with locally tuned elastic properties. (a) Elastic modulus of polyurethane-based composites reinforced with different volume fractions of hard segments (left), laponite nanoplatelets (center) and

![Diagram of hierarchical heterogeneous composites with locally tuned elastic properties.](image)
alumina microplatelets (right) at increasing hierarchical levels. Arrows indicate the compositions of reinforced polyurethanes used in this study, which are identified by the letter M followed by their elastic moduli in MPa units. (b-d) Heterogeneous composite with extreme elastic gradient in the out-of-plane direction (d) prepared through solvent welding of individual layers with different reinforcement levels and atomic layer deposition of a 100nm-thick alumina layer (b). The solid black line in (d) indicates the in-plane elastic modulus as a function of the sample height $z$. (e-g) 3D heterogeneous composite with tunable elastic moduli in the out-of-plane and in the in-plane directions made by welding modular patches onto an elastomeric polyurethane film (e). Graph (g) shows the effective elastic modulus of the 3D composite in the in-plane direction (see Appendix A2). Scale bar in (c) is 5 mm.

Using this approach, we obtained 2mm-thick heterogeneous composites with an out-of-plane gradient in elastic modulus spanning over five orders of magnitude (Figure 3.1c). The resulting composite is locally stiffer than tooth enamel on one side ($E_t \sim 10^2$ GPa), while being softer than skin on the other ($E_t \sim 1-5$ MPa, see Figure 3.1d). The extreme span in stiffness achievable within a single material free of macroscopic interfaces is far greater than that of other artificial graded composites (32) and is comparable to that of highly graded biological materials. (20) This opens numerous possibilities for the design of synthetic heterogeneous composites with deliberate local mechanics. For instance, modular patches with any pre-defined $E_t$ profile can be solvent welded at different pre-selected locations on the surface of a polymer substrate to create 3D composites with tunable elastic modulus profiles in the in-plane and out-of-plane directions (Figure 3.1e,f). In this example, not only the internal microstructure but also the shape of the composite is designed to effectively fulfill a mechanical function, alike the design strategy of many biological materials. The out-of-plane $E_t$-profile is determined by the local concentration of reinforcing elements throughout the cross-section of each modular patch at the microscale. The in-plane $E_t$-profile is controlled by the geometry and average elastic moduli of the patches and of the underlying substrate at the macroscale (Figure 3.1g and Appendix 2). All these parameters can be varied independently and in a modular fashion, providing a wide design space for tailoring the local elastic moduli of the heterogeneous composite in both the in-plane and out-of-plane directions.

3.4.2 Finite element analysis of model composite architectures

To further explore the unusual set of properties offered by 3D heterogeneous composites with tailored $E_t$ profiles, we investigated specific architectures that would combine high global stretchability with minimum local strains at specific surface sites.
The response of 3D composites with deliberate $E_i$ profiles to stretching is first evaluated by simulating the local mechanical stresses and strains across representative patch-substrate modules (Figure 3.2) using finite element analysis (FEA). Each module consists of a prismatic patch with designed $E_i$ profile deposited onto a ribbon of stretchable substrate. Four different patch-substrate module designs were investigated: two with a constant $E_i$ across the patch, one with a graded $E_i$ profile, and one control module with patch and substrate of same elastic modulus. These different hypothetical arrangements are shown in Figure 3.2a and referred to throughout the text using the letter S followed by the elastic modulus of the patch (except for the graded patch, which is named S-Grad).

Figure 3.2. Finite element analysis (FEA) of the local mechanics of representative patch-substrate modules with tunable elastic properties. (a) Elastic modulus profiles of the investigated modules, which are identified by the letter S followed by the assumed elastic moduli in MPa units. (b,c) Distribution of strains $\varepsilon_{yy}$ for the architectures S-0040 and S-Grad after applying a longitudinal global strain ($\varepsilon_g$) of 25% in the y-direction. (d) $\varepsilon_{yy}$ (left) and $\sigma_{yy}$ (right) profiles across the height of different patch-substrate architectures ($\varepsilon_g = 25\%$). The inset shows the variation of the local strain ($\varepsilon_{yy}$) at the center of the top surface of the patch as a function of the global strain ($\varepsilon_g$) applied to the substrate for the S-0040 and S-Grad modules.
FEA revealed that patches respond differently to the external tensile strain, depending on whether their average elastic moduli ($\bar{E}_{\text{pat}}$) are equal or higher than that of the underlying substrate ($E_{\text{sub}}$). For $\bar{E}_{\text{pat}} > E_{\text{sub}}$, patches undergo significant inwards bending during tensile stretching of the representative modules. This effect generates compressive (negative) strains on the patch surface and tensile (positive) strains across the substrate, as shown in Figure 3.2c. In contrast, the patch exhibiting the same elastic modulus as the substrate ($\bar{E}_{\text{pat}} = E_{\text{sub}}$, S-0040) experiences a combination of bending and stretching. This leads to curved surfaces at the edge of the patch and a stretched area with high tensile strains at its center (Figure 3.2b and Figure 10.1 in the Appendix 2). Among the patches with $\bar{E}_{\text{pat}} > E_{\text{sub}}$, we observe that bending becomes less pronounced as the average stiffness of the patch increases (higher $\bar{E}_{\text{pat}}$). The radius of curvature of the region that underwent bending was found to be 9.7, 17.2 and 63.2 mm for the specimens S-0550, S-Grad and S-7000, respectively. As a result, the stiffest patch (S-7000) offers the advantage of a lower compressive strain on the top surface and a lower tensile strain at the bottom of the underlying substrate (Figure 3.2d). Because of its stiff top layer, the graded patch (S-Grad) experiences surface compressive strains nearly as low as that of the stiffest patch (S-7000).

In addition to the strains at the surface, the elastic modulus profile of the patch also affects the mechanical stability and stretchability of the module, since local mismatches in $E_i$ may cause excessive stress concentrations within the structure and thus premature failure of the composite upon stretching. Analysis of the stress distribution throughout the cross-section of the simulated modules revealed the expected stress peaks at regions where the elastic modulus changes abruptly (Figure 3.2d). While the stress and strain indicated in Figure 3.2d refer only to the normal values at the center of the patch, similar trends were observed for the shear values at the edge of the simulated patches (see Figure 10.2 in the Appendix 2). The less abrupt changes in local elastic modulus throughout the architectures S-0550 and S-Grad lead to lower tensile stress peaks and thus a presumably higher resistance against local delamination during stretching. Because of its graded architecture, the module S-Grad better distributes the stress along the height of the patch, which contrasts to the sharp stress peak observed at the bottom of the stiffest homogeneous patch (S-7000, $z = z_{\text{int}}$). Overall, the FEA indicate that the graded architecture is the most suited to minimize the strain on the patch surface while
preventing premature failure of the stretched composites through reduced mechanical mismatches throughout the structure.

3.4.3 Combining ultra-stretchability with local surface stiffness

To experimentally investigate the surface strains and the failure resistance of composites exhibiting architecture similar to the S-Grad design, we fabricated graded modules using the hierarchical reinforcement approach described above (E-Grad, Figure 3.3). A highly stretchable, fully recoverable elastomeric substrate (Figure 3.3a) was produced by performing a two-step polymerization reaction of a 50:50 weight ratio mixture of hard and soft monomers in N,N-dimethylformamide (DMF), followed by casting in a silicone rubber mold (see details in Experimental Procedure, section 3.3.2). Mechanically graded patches were formed by solvent welding and hot pressing individual layers with progressively higher elastic modulus using DMF as solvent. The elastic modulus was tuned to gradually increase from the bottom to the top of the patch by changing the type and concentration of reinforcing elements, as depicted in Figure 3.3b. A freeze-fractured cross-section of the resulting graded sample exhibits a very smooth surface across the platelet-free polyurethane layers and no detectable interface between the platelet-reinforced layers (Figure 3.3c,d). This suggests that the macromolecules of the different original layers are effectively entangled and that a graded structure containing an interpenetrating polymer matrix was successfully created.
Figure 3.3. Mechanics and microstructure of synthetic heterogeneous composites with graded patch architecture. Materials are identified by the letter M followed by their elastic moduli in MPa units. (a) Stress-strain behavior for the elastomeric polyurethane containing 50% of hard segments used as underlying substrate (strain rate: 2.5 mm/min). The inset shows the full recoverability of the elastomer after a strain of 80% is released at room temperature. (b) In-plane elastic modulus profile across the height (z) of the graded patch. (c,d) SEM images of the graded patch highlighting the absence of macroscopic interfaces after solvent welding. Scale bars in (c) and (d) are 100 µm and 20 µm, respectively.

The effectiveness of the entangled polymeric matrix and the elastic modulus gradient in increasing the composite failure resistance was investigated by performing tensile tests on graded (E-Grad) and non-graded (E-7000) experimental samples prepared as described above. Remarkably, substrates containing the graded patch could be stretched by as much as 300% without failure due to localized internal stresses (Figure 3.4a). The high shear stresses developed at the interface between the substrate and the graded patch close to the patch edge (see Figure 10.2c in the Appendix 2) lead to partial detachment of the substrate for global tensile strains higher than 150% (see white arrow in Figure 3.4b). However, because of the lower stresses developed within the graded patch as compared to the non-graded stiff patch (S-Grad and S-7000 in Figure 10.2 in the Appendix 2), this partial detachment is limited to the edge of the graded patch and does not lead to complete delamination of the patch-substrate interface (Figure 3.4b and Figure 10.3 in the
Appendix 2). Instead, failure of the patch-substrate module typically occurs through the rupture of the elastomeric substrate material close to the patch edge at global strains higher than 350% without delamination (Figure 10.4 in the Appendix 2). This indicates that mechanical degradation in this system is controlled by the tensile strength of the substrate material rather than the strength of the patch-substrate interface, which allows us to take full advantage of the high stretchability of the elastomeric substrate. In contrast, composites exhibiting a homogeneous patch of the stiffest material (E-7000) delaminated completely at the interface between the patch and the substrate at strains between 150 and 200%. These results qualitatively agree with the FEA and can be explained by the lower stress concentration at the patch-substrate interface predicted for the graded composite (Figure 3.2d).

Tensile mechanical tests were conducted to experimentally assess the local strain on the surface of graded (E-Grad) and non-graded (E-0040) patches as a function of increasing global deformations. The local strain was obtained by measuring the length of the patch on lateral images acquired by a travelling microscope during mechanical deformation (Figure 3.4b). In line with the FEA predictions, local strains lower than 1% were detected on the surface of the graded patch for global strains as high as 300%. Conversely, samples consisting of both patch and substrate made of the same polyurethane (E-0120, $E_{\text{pat}} = E_{\text{sub}}$) displayed the predicted steady increase in local tensile strain for increasing global strains (Figure 3.4c and inset of Figure 3.2d). The inward bending effect observed in the simulation of the graded composite was confirmed by lateral recording of the specimen during the tensile test (Figure 3.4b). Interestingly, the as-prepared graded patch developed an outward curvature after solvent welding and hot pressing the individual composite layers. This initial outward bending presumably results from the higher shrinkage of the substrate and the softer bottom layers of the graded patch upon removal of the welding solvent and release of the load applied during hot pressing.
Figure 3.4. Failure resistance and local surface strain of synthetic graded composites in comparison to non-graded controls. The experimental samples are identified by the letter E followed by the elastic modulus of the patches in MPa. (a) Resistance of the graded architecture against interfacial failure under stretching as opposed to the complete delamination observed for the non-graded sample containing the stiffest patch. (b) Front and lateral views of graded specimens (E-Grad) under increasing global tensile strains, highlighting the inwards bending of the patch upon stretching. The white arrow indicates only partial detachment of the substrate at the edge of the graded patch. (c) Local strain lower than 1% on the surface of graded patches for increasing global tensile strains, as opposed to the increasing local deformations observed for the control sample. Scale bars in (a) and (b) are 2 mm.

3.4.4 Graded composites for stretchable electronics

To demonstrate the potential of such 3D graded composites in combining unusual functional properties, we deposited a 50-nm conductive gold layer on the top surface of the graded patch and measured its electrical response while stretching the
underlying elastomeric substrate (Figure 3.5a). Because of its small thickness and poor interfacial adhesion, the gold layer is expected to start deforming and to exhibit increasing electrical resistance at tensile strains of about 1%; (27) thus, much earlier than its strain-at-rupture of 20-30%. (27, 38) Since the strain of 1% is comparable to the failure tensile strain of high-performance semiconductor and dielectric layers (e.g. indium-gallium-zinc oxide and aluminum oxide), (4) the electrical response of the gold layer can be taken as a simple indicator of the effectiveness of the graded composites in protecting brittle electronic devices in stretchable electronic applications. The stretching experiments revealed that the 3D graded composite can be globally strained by as much as 200% without any detectable increase in the electrical resistance of the gold layer (Figure 3.5a). This is in strong contrast with the sharp increase in resistance at approximately 1-2% strain obtained for a control sample consisting of a gold layer deposited directly on the elastomeric substrate.

The protection of brittle electronic devices over prolonged periods of time requires substrates that are not only highly stretchable but that can also withstand extensive cyclic deformation. The resistance of the proposed 3D graded composites against cyclic strains was probed by following the electrical resistance of the conductive gold layer while subjecting the underlying elastomeric substrate to a cyclic triangular strain pattern with maximum engineering strain of 80%. In contrast to the sharp increase in resistivity observed in the first stretching cycle of a control sample, the 3D graded composite was able to keep the gold layer fully conductive and with no detectable increase in electrical resistance after more than 10 full cycles (Figure 3.5b).

The ability of the 3D graded architecture to protect brittle electronic devices was ultimately probed by assembling a light emitting diode (LED) on the surface of a graded patch and testing its function while increasing tensile strains was applied to the substrate beneath. By using silver paste, the diode was electrically contacted to two sputtered gold layers connected to a 9V external battery and finally fixed in place with epoxy glue. Upon stretching of the whole construct, the switched-on LED deposited on the graded patch remained functional up to 150% global strain, as opposed to the impaired functionality and delamination observed for control diodes assembled directly onto the elastomeric substrate (Figure 3.5c).
Figure 3.5. Electrical response of a conductive film and a functional electronic device assembled on the surface of graded patches while the underlying substrate was subjected to steady or cyclic tensile strains. (a) Normalized electrical resistance of a thin gold layer deposited on the surface of a graded patch (E-Grad) or directly on the elastomeric substrate (E-PU0040) as a function of steadily increasing global strains. The inset schematically shows the setup used for the simultaneous electrical and mechanical measurements. (b) Normalized electrical resistance of the gold layer deposited on the same specimens shown in (a) when subjecting the substrate to cyclic strains with a maximum amplitude of 80%. (c) Steady stretching of patch-substrate modules containing a switched-on LED assembled on the patch surface. The diode assembled on the graded patch (E-Grad) remains functional up to global strains as high as 150%, whereas it fails and eventually delaminates before 10% strain if deposited directly on the elastomeric substrate (E-PU0040).

Although elegant photolithographic approaches have been successful in locally increasing by a factor of 5 the elastic modulus of polydimethylsiloxane elastomers within the MPa range, (25, 39) the 100-fold reduction in the local-to-global strain ratio enabled by the graded architecture outperforms previous attempts to obtain locally stiff islands that protect brittle inorganic layers from failure in stretchable electronics. (25-29) Since the step at the patch edges might be undesired in flexible electronics, other geometries can be readily obtained using other approaches to assemble the
polyurethane compositions with different level of reinforcement, including hot-pressing, tape-casting, screen-printing and 3D rapid prototyping techniques. As an illustrative example, we produced a planar substrate with locally reinforced islands by simply hot-pressing graded patches into an elastomeric thick layer (Figure 10.5, Appendix 2). The step between the pressed patch and the elastomeric substrate is smaller than 15.2 µm, which enables sputtering of conductive metallic interconnectors between LEDs assembled onto adjacent islands (Figure 10.6, Appendix 2). Using this flat configuration, in-plane gradients at the edge of the patch can potentially be also introduced using individual layers of different size to eliminate the stress concentration leading to partial detachment of the substrate at the patch edge (Figure 3.4b and Figure 10.3 in the Appendix 2).

In addition to the macroscopic LEDs shown in Figure 3.5c, our recent demonstration that high-performance thin film transistors can be deposited and successfully operated on the surface of platelet-reinforced polymeric substrates (26) confirms the great potential of using such graded, hierarchical composites in stretchable electronics and other functional devices requiring extreme gradients in elastic modulus, including flexible solar cells, circuit boards, biological sensors and wearable electronic devices. The proposed methodology could be further improved by exploring approaches to increase the thickness and the smoothness of the purely inorganic layer deposited on the hard side of the reinforced composite.

3.5 Conclusions

In summary, we show that tuning of the local reinforcement level of a thermoplastic elastomer in 3D can lead to polymer-based heterogeneous composites with unique set of mechanical properties within the same material, including for example millimeter-thick profiled sheets with an out-of-plane soft-to-hard transition spanning 2 decades in elastic modulus combined with a global in-plane stretchability higher than 350%. Such properties are achieved by reinforcing the soft elastomeric polymer matrix with hard molecular domains, nanoplatelets and microplatelets at progressively higher hierarchical levels and at deliberate positions of the composite. Spatial control over the reinforcement level is possible by solvent welding individual layers with different concentrations of reinforcing elements. Our ability to create heterogeneous composites with locally tunable elastic modulus spanning over five orders of magnitude with a fully entangled polymer phase allows us to combine unusual functional properties that would not be achievable with homogeneous
materials. In addition to the locally stiff and globally stretchable substrates demonstrated here, this method can potentially be explored to produce artificial biomaterials with extreme mechanical gradients for cartilage, tendon and ligament repair in regenerative medicine, durable dental restorations that more closely match the flaw-tolerant architecture of natural tooth, and tougher graded adhesives that would reduce catastrophic failure of current fiber-reinforced composites. The approach may also be exploited to create bioinspired heterogeneous architectures that mimic the structural features of biological materials, allowing for the investigation of biological structure-function relationships of interest for reverse biomimetics. (40)

3.6 Acknowledgements

We thank Niko Münzenrieder, Thomas Kinkeldei and Dr. Emilio Gini for the experimental support; Prof. Gerhard Tröster, Dr. Kunigunde Cherenack and Dr. Davide Carnelli for fruitful discussions; and BASF (Germany), Antaria Limited (Australia) and ProChem (Switzerland) for kindly supplying some of the materials used in this study.

3.7 References


Chapter 4

COMPOSITES REINFORCED IN 3D USING LOW MAGNETIC FIELDS

Randall M. Erb, Rafael Libanori, Nuria Rothfuchs and André R. Studart

The results shown here are part of the paper published in:
Science 335, 199-204 (2012).

Supplementary material to this chapter is attached as Appendix 3.

4.1 Abstract

The orientation and distribution of reinforcing particles in artificial composites are key to enable effective reinforcement of the material in mechanically loaded directions, but remain poor if compared to the unique architectures present in natural structural composites like teeth, bone and seashells. We show that micron-sized reinforcing particles coated with minimal concentrations of superparamagnetic nanoparticles (0.01 – 1 vol%) can be controlled using ultra-low magnetic fields (1 - 10 milliTesla) to produce synthetic composites with tuned 3D orientation and distribution of reinforcements. A variety of structures can be achieved with this simple method, leading to composites with tailored local reinforcement and wear.
4.2 Introduction

The primary reason for the widespread use and increasing relevance of composite materials is their higher strength-to-weight ratio (specific strength) compared to metals, and higher toughness (flaw tolerance) compared to ceramics. Polymer-matrix composites are predominantly assembled with ceramic, metal or polymeric one-dimensional (1D) reinforcement such as glass, steel, aramide (Kevlar) or carbon long fibers. These fibers are typically tens of micrometers in diameter and increase the strength and stiffness along the long axis of the reinforcement because of the transfer of stress across the reinforcement-polymer interfaces parallel with the load. (1) However, 1D reinforcement makes manufactured materials weak in the other two dimensions, which can be overcome through laminating 1D layers at varied angles, weaving fibers into 2D arrays, using 2D reinforcement particles such as platelets or synthesizing lamellar structures. (1-9)

Few 3D reinforcement solutions have been proposed to reinforce man-made composites, including the insertion of out-of-plane fibers by mechanical punching, (10) the formation of special fiber arrays using textile processes like weaving, braiding, stitching and knitting, (11) and the growth of aligned carbon nanotubes on the surface of the reinforcing woven fibers. (12, 13) 3D reinforcement is also present in composites containing randomly oriented short fibers or platelets. However, these approaches either lead to a decrease in in-plane mechanical properties or do not allow for deliberate control over the distribution and 3D orientation of high concentrations of reinforcing nano- and microparticles. The lack of controlled reinforcement in the third dimension makes manufactured composites susceptible to impact damage, (2, 14) wear, (15) longitudinal microbuckling of fibers, (16) delamination (2) and long-term fatigue. (13, 17)

Structural biological composites tackle this problem by accurately controlling the orientation of anisotropic nano- and micro- building blocks so as to reinforce the material in specific directions to multi-directional external loads. (18-20) Examples include the spiral twisting of mineralized collagen fibrils in bone, (21) the out-of-plane oriented calcite prisms and in-plane oriented aragonite platelets in the outer and inner layers of seashells, respectively, (22) and the out-of-plane oriented hydroxypatite prisms and in-plane oriented mineralized collagen fibrils in tooth enamel and dentin, respectively. (23) Capturing some of the design principles underlying the exquisite architecture of such biological materials would allow us to overcome many of the mechanical limitations of current artificial composites.
Here, we propose a strategy to obtain microstructured artificial composites exhibiting 3D architectures and enhanced mechanical behavior. The approach relies on the application of external magnetic fields and field gradients to align and position anisotropic reinforcing microparticles within the composite matrix. As typical reinforcing particles are often diamagnetic requiring extremely high magnetic fields for alignment (∼ 10 Tesla) (24), we first coat them with superparamagnetic nanoparticles to make them more responsive to magnetic fields. Though a similar method has been previously employed (25) to align carbon nanotubes with fields in the range 0.2 -1 Tesla, we have discovered through experiments and theoretical energy models (26) that using the right geometry of reinforcement particles leads to an ultra high magnetic response (UHMR). In fact, the magnetic field required to align the reinforcement particles can be reduced to the value of 0.8 milliTesla (mT). This alignment field is only one order of magnitude above the earth’s natural magnetic field (∼0.05 mT) and is orders of magnitude below rare-earth magnets (∼200 mT), common solenoids (∼20 mT), and even cheap refrigerator magnets (∼10 mT).

4.3 Experimental methods:

4.3.1 Preparation of magnetically responsive alumina platelets

7.5 µm alumina platelets (Alusion®) were kindly supplied by Dr. John Robinson from Antaria Limited, Australia. To enable magnetic control of these particles, 8 g of alumina platelets were stirred in 200 mL of deionized water at pH=7 while 200 µL of EMG-705 ferrofluid (Ferrotec, Germany) was added dropwise. The 12 nm iron oxide particles in the ferrofluid are coated with anionic surfactant, which leads to electrostatic adsorption of the negatively charged magnetic nanoparticles onto the positively charged platelets. At these concentrations, 1 hour incubation is sufficient to coat the alumina platelets with all the iron oxide nanoparticles initially dispersed in the suspension. The coated platelets were washed three times with deionized water and then completely dried at 150°C for 24 hours. The platelets were stored in a dry environment until use.
4.3.2 Preparation of homogenous polyurethane composite films

Homogenous polyurethane samples were prepared using thermoplastic polyurethane (Elastollan® C64D, BASF, Germany), polyvinylpyrrolidone (PVP, Sigma-Aldrich, $M_w$ 360,000 g/mol), and the UHMR alumina platelets described above. In a typical composition, 2.4 grams of alumina platelets, 0.75 grams of PVP in powder form and 2.2 grams of polyurethane pellets were suspended in 150 mL of dimethylformamide (DMF, Sigma-Aldrich) and stirred at 60°C for 24 hours to fully dissolve the polyurethane. DMF was carefully removed in a R-125 Rotavapor (Büchi, Switzerland) at 60°C and 10 mbar until the suspension was sufficiently viscous for mold pouring (~500 mPa.s) and yet fluid enough to enable alignment of platelets under a magnetic field. The polymer suspension was then poured onto a 1cm x 3cm x 9cm polytetrafluoroethylene (PTFE) mold prepared in-house. For films with out-of-plane aligned platelets, a magnetic field was applied using a custom 20 cm x 10 cm rectangular solenoid (Magnetech Corporation, Michigan, USA) placed below the mold. Samples were heated with or without a field at 60°C for 24 hours to remove the DMF and consolidate the polyurethane. The films obtained after consolidation contained 20vol% alumina platelets, 20vol% PVP and 60vol% polyurethane. An annealing step at 130°C for 3 hours was conducted to ensure good adhesion between the alumina platelets and the polyurethane matrix. Cross-sections of the composites were also obtained using a focused ion beam scanning electron microscope (Zeiss NVision 40, EMEZ Facility at ETH-Zürich). These micrographs (Figure 11.1, Appendix 3) clearly show distinct out-of-plane alignment of the alumina reinforcement particles when a magnetic field is applied as opposed to the in-plane alignment achieved in the absence of the field.

4.3.3 Preparation of locally reinforced polyurethane composite films

Locally reinforced heterogeneous composites were prepared using the polyurethane and magnetized alumina platelets described above. 0.358 grams of alumina platelets in powder form were added to 3.61 grams of polyurethane pellets so that a volume fraction of alumina platelets of 3 vol% could be obtained in the final composite. These solids were suspended in 150 mL of DMF and stirred at 60°C for 24 hours to fully dissolve the polyurethane. The resulting suspension was then poured into a 5cm circular flexible silicon mold. A magnetic field gradient was applied using the edge of a 5cm x 5cm x 2cm rare earth magnet (Supermagnet,
Switzerland) placed below the mold. The magnetized alumina platelets were attracted to the linear region of magnetic field maximum nearest the edge of the magnet. The platelets were magnetically concentrated for 1 hour. Then the mold was placed in the oven at 80°C for 24 hours to remove the DMF and consolidate the polyurethane. An annealing step at 130°C for 3 hours was conducted to ensure good adhesion between the alumina platelets and the polyurethane matrix. The sample showed a clear gradient in the concentration of UHMR particles as shown in Figure 11.2a, Appendix 3. Dogbone samples for tensile testing were punched out of the reinforced and non-reinforced regions of the film.

4.3.4 Tensile testing of homogeneous and locally reinforced polyurethane composites

Tensile strength samples were produced from: (a) the homogeneous alumina-PVP-polyurethane composites (Table 11.1, Appendix 3) and (b) the locally reinforced alumina-polyurethane composites described above. Standard dog bone shapes were punched from the final material with the tested region being 12 mm x 2 mm. Thicknesses varied but were generally around 0.1mm. Tensile samples were tested with an Instron 4411 Universal Testing Machine. Samples were pulled at constant rates of 10 mm/minute. Force and displacement data were collected and converted into stress vs. strain plots. The slope of the stress vs. strain data in the linear elastic regime was measured to be the Young’s modulus of the material. At least five samples were tested in each case.

4.3.5 Hardness tests

Hardness tests were performed on acrylate-based composites reinforced with deliberately aligned alumina platelets. The polymer matrix is composed of the two monomers bisphenol A glycerolate dimethacrylate (Sigma-Aldrich) and triethylene glycol dimethacrylate (95%, Aldrich Chemistry) at concentrations of 50 and 49 wt%, respectively, in the final polymeric phase. A homogenous mixture of these monomers is obtained at 60°C through mechanical stirring with a glass stir bar. 1 wt% of the photoinitiator camphorcinone (97%, Sigma-Aldrich) with the co-initiator ethyl 4-dimethylaminobenzoate (99+, Sigma-Aldrich) in a 1:1 mole fraction was used. In addition, 10 vol% alumina platelets that were coated with magnetic nanoparticles as
described above were added to the polymer solution. Instead of 25 µl ferrofluid / g platelets, a concentration of 100µl / g was used.

Samples for the hardness test were prepared using a mold consisting of 0.5mm thick Teflon film spacers sandwiched between a top and bottom glass cover. The viscous resin was placed on a glass slide between two spacers and spread by pressing the other glass slide on top. In one planar direction the resin was confined by the spacers, in the other planar direction the resin was free to expand. The glass covers were kept together with tape and clamps. To achieve vertical aligned platelets within the polymer, a magnetic field of 160 mT was applied for 10 minutes. The shear flow of the resin within the glass slides was exploited to obtain samples with horizontally aligned platelets, which were afterwards kept in a horizontal position for 30 minutes. Polymerization was induced by irradiation with visible light through the top glass slide using a VIVADENT Bluephase 20i LED lamp for 40 seconds in case of the pure resin and for 2 minutes in case of the vertically and horizontally aligned samples.

The hardness tests were conducted in the Laboratory of Metal Physics and Technology of Prof. Dr. Jörg F. Löffler at ETH Zürich. A Wolpert Microhardness Tester MXT-α was used to measure Vickers hardness of the three samples: pure resin, composite with vertically and horizontally aligned alumina platelets. For each sample ten measurements were carried out using an HV0.5 indenter and a dwell time of 10 seconds. It was ensured that the indenter tip did not directly hit a platelet. Based on the arithmetic average length of the indent diagonals the value of the Vickers hardness was calculated.

4.3.6 Wear tests

Wear tests were performed in acrylate-based composites typically used as dental resins in restorative dentistry. Bisphenol A glycerolate dimethacrylate (Sigma-Aldrich) and triethylene glycol dimethacrylate (95%, Sigma-Aldrich) in a weight ratio of 50:49, respectively, were mixed with alumina platelets coated with magnetic nanoparticles prepared as described above. A commercial dental resin consisting of approximately 85wt% 5µm particles (Clearfil AP-X, Kuraray, Japan) was then added and mixed manually with a spatula. (27) The acrylate monomer mixture, alumina platelets and the commercial dental resin were mixed in such a ratio to obtain composites with final concentrations of 10.9, 1.1 and 87.9 vol%, respectively.
No additional photoinitiator was used. A 0.5mm thick Teflon film spacer with a quadratic hole sandwiched between two glass slides served as mold. The mold was filled with the pastelike resin, the two glass slides were pressed together and fixed by tape and clamps. In case of the vertical aligned platelets, a vertical field of 230 mT was applied for 10min. In case of the horizontally aligned platelets a horizontal field of 150 mT was applied for 10min. The polymerization was induced by irradiation with visible light using a VIVADENT Bluephase 20i LED lamp for 40 seconds. Typical samples are shown in Figure 11.4, Appendix 3.

The wear tests were conducted in the laboratory of Prof. Dr. Paul Smith at ETH-Zürich using a similar setup to that developed by Tervoort et al (28). Samples described above were glued to the wear testing substrate. A ball revolution of 500 rpm was used with a normal load of 1.98 N. Distilled water was dripped over the testing site to work as lubricating medium and to rinse away wear debris. Each test lasted approximately 8 hours. Ball penetration depth was measured with a laser. The raw data was noise-reduced by reporting averaged measurements for every 100 consecutive data points (100 seconds).

4.3.7 Preparation and testing of bilayer 3D reinforced epoxy composites

Bilayer 3D reinforced epoxy composites (Figure 4.3e and Figure 11.5a-d in the Appendix 3) were produced to study the effect of specific orientations of reinforcing particles on the flexural modulus and out-of-plane hardness of laminated rectangular bars. For composites with alumina platelets, 6.57 g of alumina platelets were stirred using a mechanical mixer at 1000 rpm into 9.38 g of Araldit GY250 and 8.44 g of Aradur 917 (Huntsmann Co, USA) for 1 hour. The mixture was then connected to a V-215 Büchi rotary evaporator and stirred at 15 rpm and 10 mBar for 30 minutes to remove air bubbles. 0.14 g of AGY070 polymerization catalyst was added to the solution, which was subsequently stirred again in the rotary evaporator for 15 minutes. The solution was then cast into 1 cm x 5 cm x 6 cm Teflon molds and positioned under the 5cm x 5cm x 2cm rare earth magnet that was connected to a small motor and was rotating vertically. The epoxy was allowed to sit in the field for 12 hours. The sample was then transferred to an oven at 60°C where it was placed for 4 hours within a vertically rotating field created by three temperature-rated computer programmed solenoids. One solenoid was positioned vertically below the sample, while the other two solenoids were positioned horizontally on either side of the sample. The current to the solenoids was driven using two 20-5M Bipolar
Operational Power Supplies (Kepco, USA) and regulated as two sinusoidal current waveforms offset by 90° using a LabView program controlling a CYDAS 1602HDP A/D board (CyberResearch, USA). Afterwards, the sample was removed from the rotating field and given a final heat treatment of 4 hours at 100°C. The sample was then cut into the appropriate slabs and assembled to produce the laminate structures schematically shown in Figure 4.3e. In all cases, the top and bottom layers were cut to be 1 mm and 2 mm thick, respectively, with a width of 5 mm and a length of 50 mm. The top and bottom layers were glued together using the same epoxy/alumina composition and pressed together using binder clips. The laminated structure was subjected to the same heat treatment to cure the epoxy. Resulting microstructures are shown in Figure 11.5a-d (Appendix 3) demonstrating successful orientation of the alumina platelets in the epoxy composites.

Samples were then tested in a 3-point bending apparatus hooked up to an Instron 4411 Universal Testing Machine (Figure 11.5e, Appendix 3). In all cases, the span of the test was 3 cm and the displacement rate was 5 mm/min. Force and displacement data were collected and converted into flexural modulus. At least three samples were tested in each case and found to have high reproducibility. Hardness tests, described above, were carried out in the out-of-plane direction of the top layer of the laminate structures.

4.3.8 Preparation of laminated polyurethane structures combining in- and out-plane reinforcement

Laminated polyurethane structures were made by first synthesizing two homogenous films with in-plane and out-of-plane platelet orientation via the methods described above. However, no annealing was conducted in these samples. Two equally sized substrates of each sample were cut from the materials. A thin layer of DMF was applied with a cotton swab to the top of the in-plane reinforced surface. The out-of-plane reinforced sample was then firmly pressed, by hand, against the wet substrate. The sample was then put in the oven for 3 hours at 130°C to remove the excess DMF. The sample was finally cut, dipped into liquid nitrogen, and freeze fractured. The fractured cross-section was imaged using a scanning electron microscope, which revealed a good bonding between the two laminated layers (Figure 4.2h).
4.3.9 Preparation of composites under a rotating magnetic field

A rotating field setup was employed identical to that described in an earlier study (29). Two orthogonal solenoids were placed in the oven, one aligned along the x axis (horizontal) and one along the z axis (vertical). Low frequency (1 Hz) sinusoidal current waveforms were run through the two solenoids with a 90° offset between them. This produced a circular rotating magnetic field. The current was adjusted until the point centered between the solenoids achieved a magnetic field of 10 mT as measured with a 410 Handheld Gaussmeter (Lakeshore, OH, USA). Viscous suspensions consisting of polyurethane and magnetized alumina platelets in DMF were prepared as detailed above and poured into a PTFE mold placed above one solenoid such that the substrate was in the x-y plane. The sample was then heated at 60°C under a continuously rotating magnetic field for 24 hours. The sample was removed and annealed at 130°C for 3 hours. Part of the sample was cut, dipped into liquid nitrogen, and freeze fractured to reveal the cross-section. The cross-section and the top surface of the sample were imaged using a scanning electron microscope (Figure 4.2j).

4.4 Results and discussion:

The magnetized surface coating is formed upon addition of the reinforcing particles to an aqueous suspension of 12nm iron oxide nanoparticle suspensions with oppositely charged surface at a specific pH. Under these conditions, adsorption is driven through electrostatic interactions and is further enhanced by short-range van der Waals attraction, eventually becoming irreversible. We investigate 7.5 µm-long, 200nm-thick alumina platelets (Alusion®, Antaria, Bentley, Australia) that exhibit respectively positive surface charge in water at pH=7. To coat such reinforcing elements we add 1 vol% platelets in aqueous suspensions of 0.0052 vol% oppositely charged iron oxide nanoparticle suspensions (anionic EMG-705, Ferrotec, Germany) until complete adsorption occurs (Figure 4.1a). The magnetized platelets are then aligned with a magnetic field as low as 1 mT (Figure 4.1b), confirming that it is possible to orient platelets of a few micrometers in length using very low magnetic fields. Changing the initial concentration of iron oxide nanoparticles in the suspension controls the magnetization of the platelets.
Figure 4.1. a) Example of 0.5 vol% (13% surface coverage) of iron oxide nanoparticles on an alumina platelet that leads to alignment at 1 mT. b) Iron-oxide coated alumina platelets with optimum sizes exhibit indeed ultra-high magnetic response (UHMR), aligning with the extremely low magnetic fields.

The ultra-high magnetic response of the coated anisotropic particles is of general interest in applications that require combined spatial and orientational control of suspended particles. (30) We exploit this effect to orient reinforcing particles in a polymer matrix and thus obtain artificial composites exhibiting unique mechanical reinforcing effects.

Reinforced composites with controlled orientation of reinforcements are prepared by dispersing UHMR anisotropic particles in a fluid, aligning and positioning them with a magnetic field, and finally consolidating the fluid to fix the oriented structure. Consolidation may occur through solvent evaporation if the fluid is a polymer solution, through temperature- or light-induced reactions if the fluid is a monomeric solution or by simply cooling down a molten polymeric matrix. We find that the higher viscosity of some of the polymer solutions and resins used for
Composite fabrication slows down the orientation process but does not change the minimum magnetic field required for alignment.

Examples of composites obtained by applying linear, uniform magnetic fields to fluid suspensions containing magnetite-coated alumina platelets, thermoplastic polyurethane elastomer (PU, Elastollan® C 64 D 53, BASF), and polyvinylpyrrolidone (PVP, Sigma-Aldrich, M_w 360,000 g/mol) are shown in Figure 4.2a,b,f,g,. In these examples, 2.4 g platelets, 2.2 g polyurethane and 0.75 g polyvinylpyrrolidone were suspended/dissolved in 150 mL of dimethylformamide (DMF, Sigma-Aldrich) and the end composites contained 60 vol% PU, 20 vol% PVP, and 20 vol% alumina. The orientation of the UHMR particles in the consolidated matrices directly reflects the direction of the magnetic field applied. Magnetic alignment and fixation of the UHMR platelets was also possible using epoxy and acrylate-based resins as polymeric matrix.

In addition to homogenously reinforced polymers, multi-layer composites are easily obtained by laminating together layers of reinforced polymer with specific orientations (Figure 4.2c,h). The resulting composites exhibit an external layer with out-of-plane oriented platelets and an internal layer with in-plane oriented platelets. This should lead to a highly structured artificial composite displaying the unusual and often desired combination of hardness and wear-resistance in the outer layer and strength and toughness in the inner layer using the same basic building blocks. Single batch synthesis composites with this architecture can also be prepared simply by mixing reinforcing particles with different magnetic nanoparticle coverage during processing and then applying a combination of magnetic fields. To demonstrate this, 4.025 g each of platelets with 13% and 1% surface coverage of iron oxide were added to 20 g polyurethane (RoPlasthan 2020R, resin-to-hardener weight ratio 3:1) and poured into a polyethylene mold. The sample was then subjected to an 80 mT horizontal field for 5 minutes followed by a 10 mT vertical field for 10 minutes. The resulting structure shows platelets in both configurations depending upon their surface coverage (Figure 4.2 d,i).
Figure 4.2. a,b) Schematic and f,g) top-view scanning electron micrographs of in-plane and out-of-plane reinforced composites, (20 vol% Al₂O₃ in polyurethane), made without and with an out-of-plane magnetic field, respectively. c) Schematic and h) scanning electron micrograph of cross-section of laminated layers of in- and out-of-plane reinforced composites, (20 vol% Al₂O₃ in polyurethane). d) Schematic and i) scanning electron micrograph of cross-section of mixed alignment using 5 vol% highly magnetized (1wt% Fe₃O₄/Al₂O₃) and 5 vol% weakly magnetized (0.1wt% Fe₃O₄/Al₂O₃) alumina platelets in polyurethane produced with sequential magnetic field applications. Arrows indicate platelets in the 2nd position of alignment. e) Schematic and j) scanning electron micrograph of cross-section of an alumina-polyurethane composite formed under rotating magnetic field that allows for ultra-high packing fractions. Inset shows top view of composite.
While the alignment of platelets using linear, static magnetic fields allows for the preparation of composites with unusual structures and properties, the concentration of platelets aligned in the out-of-plane direction is limited to about 20 vol% due to steric hindrance effects resulting from the lack of orientational control over the second axis of platelets. This issue can be circumvented using rotating, linear magnetic fields. A rotating field in the Y-Z plane will align the reinforcement platelets along this plane due to energy considerations, pinning two degrees of orientational freedom (Figure 4.2e,j). This alignment is contingent upon the frequency of the rotating field being high enough to produce a finite torque on misaligned platelets. Through such biaxial alignment of the reinforcement platelets, it is possible to reach very high concentrations of out-of-plane aligned platelets, even over 50 vol%.

Control of the orientation of reinforcing particles enables tailoring of properties in specific directions. The effect of the orientation of reinforcing particles on the mechanical behavior of homogeneously reinforced polymers was investigated by measuring the tensile mechanical properties of specimens containing reinforcement aligned parallel or perpendicular to the applied load (Figure 4.3a). The reinforced sample containing 20 vol% parallel-aligned platelets exhibits in average 63% and 86% higher yield strength as compared to the pure matrix and the perpendicular-aligned platelets, respectively. Likewise, the average elastic modulus of the composites with parallel-oriented platelets was 2.8-fold higher in comparison to the pure polyurethane matrix, whereas a moderate increase is observed if compared with composites with perpendicular-aligned platelets (Table 11.1, Appendix 3).

We use simple rules of mixtures (5) to obtain a quantitative relation between the aligned architecture and the resulting mechanical properties of the composites. Assuming pull-out mode of fracture, the yield strength, \( \sigma_c \), of the composite is given by:

\[
\sigma_c = \phi_p \frac{\tau_y s}{2} + (1-\phi_p) \sigma_m, \tag{2}
\]

where \( \tau_y \) is the shear strength of the lesser of either the polymer matrix or the platelet/polymer interface, \( s \) is the platelet aspect ratio, \( \sigma_m \) is the yield tensile strength of the matrix and \( \phi_p \) is the volume fraction of platelets. Taking \( \sigma_m = 28.6 \text{ MPa} \) (Figure 4.3a), we find that the yield strength of the composite with in-line reinforcement (\( \sigma_c = 46.8 \text{ MPa} \)) can be accurately described by equation (2) if the value of \( \tau_y \) is equal to 6.5 MPa. Such \( \tau_y \) is lower than the value of 14.3 MPa expected for the shear strength.
of the polymer matrix ($\sigma_m/2$), suggesting that fracture in this case is controlled by the weaker platelet/polymer interface. This indicates that further reinforcement with parallel-aligned platelets is possible by optimizing the platelet/polymer interfacial bonding in this system.

In addition to the tensile properties, hardness values were measured for homogeneous composites with 10 vol% UHMR platelets in methacrylate-based composites. Samples with reinforcement particles oriented parallel to the applied load showed increased hardness compared to perpendicular reinforcement and non-reinforced samples (Figure 4.3b). Composite films containing alumina platelets aligned out-of-plane also exhibit outstanding wear resistance. Wear was measured by sliding a zirconia ball subjected to a normal load of 1.98 N over acrylate-based composite films using double deionized water as lubricating medium. A commercial acrylate-based composite dental resin (Clearfil AP-X, Kuraray, Japan) with 85 wt% isotropic glass microparticles was subjected to wear testing (Figure 4.3c) and demonstrated a total wear volume of 0.001 mm$^3$. Instead, a nominal 1 vol% of UHMR platelets were added to the resin in both the in-plane and out-of-plane orientations. Orientation of only 1 vol% platelets normal to the wear ball (out-of-plane) decreases the maximum wear volume by 77% as compared to the samples with in-plane oriented reinforcement. Such wear volume is also 45% lower than that observed in the pure commercial resin. Observation of the worn area of tested films suggests that the out-of-plane oriented hard platelets remain strongly locked within the surrounding polymer matrix, effectively impeding the penetration of the zirconia ball into the material during sliding. In contrast, isotropic particles and in-plane aligned platelets can be more easily removed from the matrix by the shear stresses developed under the sliding ball, leading to more pronounced wear. In contrast to the tensile mechanical properties, a quantitative analysis of the effect of reinforcement orientation on the hardness and wear of such anisotropic structures is less straightforward due to the complicated stress states in these cases.
Composites Reinforced in 3D using Low Magnetic Fields

Figure 4.3. a) Representative increased tensile strength for polyurethane-based polymers with 20 vol% Al₂O₃ platelets parallel with applied force (red) versus perpendicular (blue) and non-reinforced (green) samples. b) Increased hardness for reinforced methacrylate resins with 10 vol% Al₂O₃ platelets parallel to the applied load versus perpendicular and non-reinforced samples. c) Increased wear resistance for acrylate-based composite films of dental resins with 1 vol% added out-of-plane aligned Al₂O₃ reinforcement. d) Localized stiffening in a polyurethane film using magnetically-induced spatial gradients in the 3 vol% Al₂O₃ particle reinforcement. e) Flexural modulus and out-of-plane hardness of bilayer rectangular bars (30×5×3mm³) with different combinations of reinforcement orientation. The schematic drawings show the cross-sections of the tested structures, with the bottom layer corresponding to the region subjected to tension in 3-point bending and the top layer corresponding to the region subjected to out-of-plane hardness measurements.
To demonstrate that concentrated UMHR particles can locally reinforce the polymer matrix, we conducted tensile tests on 2 mm by 12 mm by 0.1 mm polyurethane samples with a 5-mm stripe of reinforced area produced with a hand-held rare-earth magnet (Figure 4.3d). The highly heterogeneous composite obtained exhibit distinct local elastic moduli that can be estimated by using simple rules of mixtures (see Appendix 3). Local stiffening of 180% was estimated by evaluating the elastic modulus of the reinforced and non-reinforced areas in independent tensile tests (Figure 4.3d).

To illustrate the benefit of building composites with controlled 3D reinforcement, bilayer structures with tailored reinforcement architectures were produced by laminating together layers of 10 vol% alumina platelets in an epoxy resin (similar to Figure 4.2c, see SEM images in Appendix 3). The platelets in each individual layer were aligned both in-plane or out-of-plane using rotating linear magnetic fields, leading to the structures schematically shown in Figure 4.3e. Rectangular bars of the various created structures were evaluated with regards to out-of-plane hardness and flexure modulus under 3-point bending. Typically, structures containing platelets aligned in-plane exhibit high flexural modulus but low out-of-plane hardness. Conversely, composites containing only out-of-plane oriented platelets exhibit higher out-of-plane hardness but lower flexural modulus. Instead, by creating a laminate structure exhibiting out-of-plane alignment in the upper layer and in-plane orientation in the bottom layer, it becomes possible to produce a composite with both increased flexural modulus and increased out-of-plane hardness. Despite the much lower concentration of inorganic phase present in the synthetic composites, a similar architecture is found in seashells. (22)

4.5 Conclusions

The possible reinforcement orientations that can be achieved in these composites materials are in principle only limited by the magnetic field patterns that can be created. Given the possibility to precisely control the position and orientation of reinforcing particles within the matrix, the method outlined here offers a way to locally tailor the properties of composite materials using the same set of initial building blocks. The myriad of unusual properties including out-of-plane global or local increases in composite stiffness, strength, hardness and wear resistance achieved by simply controlling the orientation and position of reinforcing elements suggest the enormous potential of this approach.
4.6 Acknowledgments

We thank T. Tervoort, L. van Breemen, K. Feldman, B. Wegmann and M. Schinhammer for experimental assistance and Antaria, Huntsman Advance Materials, Rosen and BASF for supplying the alumina platelets, polymers and resins. We acknowledge internal funding from ETH Zurich and the Swiss National Science Foundation (grant 200021_135306/1), as well as support by the Electron Microscopy Center of ETH Zurich (EMEZ).

4.7 References


Chapter 5

MECHANICS OF PLATELET-REINFORCED COMPOSITES DIRECTED-ASSEMBLED VIA MECHANICAL AND MAGNETIC STIMULI

Rafael Libanori, Randall M. Erb and André R. Studart
To be submitted in 2013

5.1 Abstract:

Current fabrication technologies of structural composites based on the infiltration of fiber weaves with a polymeric resin offer good control over the orientation of long reinforcing fibers but remain too cumbersome and slow to enable cost-effective manufacturing. The development of processing routes that allow for fine control of the reinforcement orientation and that are also compatible with fast polymer processing technologies remains a major challenge. In this paper, we show that bulk platelet-reinforced composites with tailored reinforcement architectures and mechanical properties can be fabricated through the directed-assembly of inorganic platelets using combined magnetic and mechanical stimuli. The mechanical performance and fracture behavior of the resulting composites under compression and bending can be deliberately tuned by aligning the platelets into designed microstructures. By combining high alignment degree and relatively low volume fractions of reinforcement, we fabricated platelet-reinforced composites that can potentially be made with cost-effective polymer processing routes while still exhibiting properties that are comparable to those of state-of-the-art glass-fiber composites.
5.2 Introduction

Composite materials have been increasingly used in load-bearing applications mainly because of their high strength-to-weight ratio compared to their metallic counterparts. Despite their growing importance as structural material, the cost of conventional long-fiber composites remains prohibitive in many applications partly due to the fact that current manufacturing technologies do not allow for the production of high volume components at rapid rates and also incorporate costly steps, such as impregnation of the fiber mat with polymeric resins and curing under autoclave conditions.

In contrast to the more expensive and laborious manufacturing of long-fiber composites, processing of composites reinforced with discontinuous fibers and platelets can be much easier and cost-effective because it benefits from conventional methods used in the production of polymeric materials such as mold casting, injection molding and extrusion. However, to take full advantage of the reinforcing effect of fibers and platelets one needs to align them in specific directions or within a given plane of the composite. (1) Although flow-based processing techniques have been developed to fulfill this requirement, (2-5) shearing stresses inherent from the shaping process may also have undesired effects on the orientation and distribution of reinforcing elements throughout the polymeric matrix.

While deliberate control over the orientation of reinforcing particles has long been a challenge in synthetic composites, biological composites like mollusk shells, (6) bone (7, 8) and teeth (9) provide unique natural examples of accurate spatial and orientational distribution of reinforcing elements at multiple length scales. Inspired by such biological architectures, several synthetic routes have been proposed to obtain well-ordered microstructures in platelet-reinforced composites, including tape-casting, (10) layer-by-layer, (11) electrical fields (12) and gel casting combined with hot-pressing. (13, 14) These approaches usually yield composites exhibiting superior in-plane mechanical properties, but are often limited to thin films and/or require multiple processing steps. Bulk composites exhibiting a fairly high degree of platelet alignment or unique lamellar structures have also been obtained by hot-press assisted slip casting, (15) flow-induced alignment of fibers followed by filtration and polymer impregnation, (16, 17) and freeze-casting of particle suspensions followed by sintering and polymer infiltration. (18) Although lamellar composites with remarkable mechanical properties have been obtained, these approaches cannot be easily implemented in current polymer processing technologies to enable the
envisioned low-cost fabrication of composites reinforced with short fibers and platelets.

Conversely, the directed-assembly of anisotropic particles in polymer melts or in monomer solutions may be an effective means to deliberately control the reinforcement architecture of composites using conventional polymer processing methods. Recently, we proposed a strategy to align anisotropic reinforcing platelets and rods in specific orientations using very low external magnetic fields. (19) The approach relies on coating non-magnetic reinforcing microparticles with superparamagnetic iron oxide nanoparticles (SPIONs) to remotely control their orientation and position within a fluid using readily available magnets. Remarkably, SPION-coated microplatelets were found to exhibit ultrahigh magnetic response (UHMR), enabling full control over their alignment using magnetic fields as low as 0.8 milliTesla in low-viscosity suspending fluids. Such fluids can be then consolidated to fix the magnetically-imposed alignment and thus create composites with tailored reinforcement architectures. Earlier investigations have shown that the magnetic alignment of alumina platelets in the direction of externally applied mechanical load is an effective strategy to improve the mechanical properties of polymer-based composites. (19) Because of the remarkable increase in the viscosity of fluids containing platelet concentrations above a percolation threshold, the major challenge in this approach is to obtain a high degree of alignment in composites loaded with high volume fractions of reinforcing particles. A deeper understanding of the structure-property relationships of such magnetically structured composites should allow us to quantify and predict the level of reinforcement achievable in these directed-assembled composite architectures.

In this paper, we thoroughly investigate the mechanical properties of platelet-reinforced epoxy-based composites exhibiting well-controlled reinforcement architectures obtained by the directed-assembly of UHMR alumina platelets using mechanical vibration and magnetic fields. The mechanical properties of as-cast and aligned composites are compared and explained in light of their underlying microstructure. We show how the simultaneous use of mechanical and magnetic stimuli can be effective in obtaining composites with high degree of platelet orientation and improved mechanical performance.
5.3 Experimental procedure

5.3.1 Materials

The epoxy system used throughout this work was kindly supplied by Huntsman Co, USA. It is comprised of a bisphenol A-based resin (Araldite GY250), an anhydride-based hardener (Aradur 917) and a tertiary amine-based catalyst (Accelerator DY070). Micron-sized alumina platelets (AlPearl, 7.5 µm length and 0.2 µm thickness) were provided by Antaria, Australia. The aqueous-based anionic ferrofluid (EMG 705) used to magnetize the alumina platelets was purchased from Ferrotec Co., USA.

5.3.2 Magnetization of alumina platelets

Alumina platelets were magnetized by the electrostatic adsorption of superparamagnetic iron oxide nanoparticles in deionized water. In a typical procedure, 0.375 mL of ferrofluid EMG 705 were diluted in 200 mL of water and the resulting dispersion was added slowly to a suspension of 10 g of alumina platelets in 300 mL of water. Adsorption was carried out at room temperature and under magnetic stirring for at least 1 day or until the supernatant was clear. Magnetized platelets were removed from the suspension by vacuum filtration and washed with 1.5 L of water before a rinsing step with 200 mL of ethanol. Finally, the platelets were dried in an oven at 70 °C for 2h.

5.3.3 Preparation of platelet-reinforced composites

Figure 5.1 depicts the processing route used to prepare composites with deliberate reinforcement architectures using mechanical and magnetic stimuli. Prior to the preparation of the composites, magnetized platelets were dried in a vacuum oven under 30 mbar at 150 °C for 12h. Next, the total amount of dried platelets was divided into three portions that were added sequentially in three separate steps into the stoichiometric mixture of Araldite GY250 resin and Aradur 917 hardener. For each addition, the resulting mixture was mechanically stirred with a mechanical mixer for 30 minutes at a speed of 2000 rpm. The bubbles introduced during the mixing step were removed by applying alternating cycles of vacuum (10 mbar; 60 °C) and...
ultrasonication. After the addition of all the platelets, the catalyst was added into the degassed mixture and mixed manually with a spatula in order to prevent the incorporation of additional bubbles. Finally, the mixture was degassed again and poured into a Teflon mold with dimensions of 3.5 x 4.5 x 1.0 cm³.

Figure 5.1. a) Processing route for the production of platelet-reinforced composites with tailored architectures using mechanical and magnetic stimuli. Scheme (b) and picture (c) show the experimental setup used to keep the alignment of the UHMR-platelets while curing the composites inside an oven at 60 °C.

5.3.4 Directed-assembly of platelets and curing of the composites

The Teflon mold containing the composite mixture was placed onto a vibrating table (Fritsch, type 03 502) and positioned under a 5.0 x 5.0 x 2.0 cm³ rare earth magnet (Supermagnete, Switzerland), connected to a small motor (Figure 5.1a). The north-south axis of the permanent magnet was rotated at a frequency of 4 Hz within the x-z plane of the coordinate system shown in Figure 5.1a while a continuous mechanical vibration was applied on the sample at the maximum power of the vibrating table (500 W) for 10 minutes. Platelet alignment takes place during the first 2 minutes and can be observed by changes of the surface color of the composite mixture. Afterwards, the epoxy composite was allowed to rest under the rotating field for 12 hours. The sample was then transferred to an oven and exposed to a static and an alternating magnetic fields applied along the z- and x-axes, respectively. The magnetic fields were generated by three computer-programmed solenoids, as depicted in Figure 5.1b. Two solenoids were connected in series and
positioned horizontally on either side of the sample while the other was positioned vertically below the specimen (Figure 5.1c). The current passing through the solenoids was provided by two Bipolar Operational Power Supplies (20-5M, Kepco, USA) and controlled via a A/D board (CYDAS 1602HDP, CyberResearch, USA) using a LabView program. A sinusoidal waveform with frequency of 3Hz was set to control the amplitude of the current in the horizontal solenoids whereas a static current was driven to the vertical solenoid. This setup provided a vertical static and a horizontal alternating magnetic fields with amplitudes of about 300 and 200 Gauss at the center of the sample, respectively. After being heat treated at 60 °C for 4 hours, the sample was removed from the magnetic field setup and subjected to a final heat treatment of 4 hours at 100 °C. Composites designated in this study as “as-cast” were subjected only to mechanical vibration during casting but not to the magnetic fields.

5.3.5 Characterization

The microstructure of the platelet-reinforced composites was assessed by imaging polished or freshly fractured surfaces of the specimens under a scanning electron microscope (SEM, LEO 1530, Zeiss). To obtain smooth surfaces, samples were cold embedded into low viscosity epoxy resin, grinded with silicon carbide foils (grits: 600, 1200, 2400 and 4000) and finally polished with diamond suspension (grain size: 3 µm and 1 µm) and colloidal alumina suspension (particle size: 50 nm). Fractured surfaces were obtained from samples cleaved during the flexural tests.

The alignment of alumina platelets within the x-axis (Figure 5.1a) was measured by X-ray diffraction (XRD) using the rocking curve technique. (20) In this method, a high resolution scan along the x-axis of the sample is first acquired at high 2θ angles (88°>2θ>92°) and the most intense diffraction peak is selected. The 2θ angle corresponding to the maximum intensity of the selected diffraction peak is then fixed and the sample is slowly rocked by an angle ω while acquiring the data. The data is then corrected for tilt-defocusing and absorption effects using the software TexturePlus, which was kindly supplied by Mark Vaudin (NIST, Gaithersburg). All XRD measurements were performed in an Empyrean diffractometer (PANalytical).

Compression tests were performed on cylindrical samples with a diameter of 5 mm and a height of 10 mm using a Zwick universal mechanical testing machine (model Z250) at a displacement rate of 1 mm/min. Flexural tests were carried out on bars measuring 3 mm x 5 mm x 4.5 mm, which were machined from larger blocks
and polished with 600, 1200, 2400 and 4000 grit SiC foils. An Instron 4411 universal mechanical testing machine equipped with a three-point bending rig was used for the bending tests. Bending was applied using a load line displacement rate of 5 mm/min with a span of 30 mm between the static supports. Load-displacement curves were corrected for machine compliance. At least three samples were measured to obtain the reported average and standard deviation values.

A Wolpert Microhardness Tester (MXT-α) was used to measure Vickers hardness. Samples were cold embedded in epoxy resin and polished according to the procedure described above. A thin layer of platinum (20 nm) was sputtered on the surface of the samples to increase light reflectivity and improve the accuracy of the measurement. For each sample, five measurements were carried out using a pyramidal indenter pushed into the sample surface with a force of 0.05 kgf for 15 seconds. Vickers hardness was calculated based on the arithmetic average length of the indent diagonals. (21)

The composite’s resistance against crack initiation (Kic) was measured on an Instron 8562 universal mechanical testing machine equipped with a strain gage to accurately measure the deflection of single-edge notched beams during mechanical loading. A span of 20 mm was used to test all samples. The thicknesses of the samples varied within the range 2.5-3.0 mm and the width was accurately adjusted to obtain a span-to-width ratio of 4. Notches were prepared by first cutting the sample in a wire saw machine with wire diameter of 0.3 mm (Well model 3242) followed by continuously sliding a fresh razor blade with a custom-build machine. Calculations of the fracture toughness values were performed according to the ASTM standard D5045-99 (22) and the reported values are the average of at least 3 samples.

5.4 Results and Discussion

5.4.1 Directed-assembly of platelets

The ability to direct the assembly of UHMR alumina platelets into long-range well-ordered structures using magnetic fields is influenced by the volume fraction of platelets suspended in the fluid. Platelets with aspect ratio around 40 can be easily manipulated with external magnetic fields if their volume fraction is lower than approximately 10vol%. For this reason, magnetically-structured advanced composites have been often processed using diluting solvents that reduce the concentration of platelets in the suspension. (19) Alignment of high volume fractions
of platelets in the solvent-free systems utilized in polymer processing technologies is hindered by steric interactions between the particles, which prevent the system from reaching its most thermodynamically stable aligned configuration.

We found that the application of mechanical vibration during the magnetic alignment process can provide additional energy to overcome steric interactions between adjacent platelets and thus favor their alignment along the direction of the applied magnetic field. Figure 5.2 depicts the effect of mechanical vibration on the microstructure of a composite containing 11 vol% of UHMR platelets. When a rotating magnetic field is applied alone (Figure 5.2a), steric hindrance between neighbor platelets limits their movement and thus impedes full alignment of their long axis along the plane of the applied magnetic field. Remarkably, the simultaneous use of mechanical vibration and magnetic fields leads to microstructures exhibiting a much higher degree of alignment, as shown in Figure 5.2b. The effect becomes more significant as the volume fraction of the platelets is increased, since this further limits platelet movement in the suspension.

![Figure 5.2. Effect of the mechanical vibration on the microstructure of composites with 11 vol% of UHMR alumina platelets aligned by a rotating magnetic field. Scale bars: 40 µm.](image)

By applying simultaneously mechanical and magnetic stimuli, we are able to direct the assembly of platelets into highly ordered structures with platelet volume fractions as high as 27% (Figure 5.3d-f). The direction in which the long-axis of the platelets are aligned is solely controlled by the rotation axis and the frequency of the applied dynamic magnetic field. (23) In our experiments, the north-south magnetic axis of a rare-earth magnet is rotated within the x-z plane of the coordinate system shown in Figures 5.1 and 5.3. A frequency of 3 - 4 Hz is applied in order to ensure biaxial alignment of the UHMR platelets within the x-z plane (Figure 5.1a). At such a frequency, the drag force exerted on the platelets is too high to allow them to roll with
the rotating magnetic fields, which is the typical response observed for lower rotational speeds. The critical frequency required for such biaxial alignment can be analytically determined from a torque balance on the edge of the platelets. (23, 24)

In the absence of magnetic fields, packing entropic effects induce self-ordering of the platelets into nematic domains. (25-27) Alike the suspensions subjected to magnetic fields, the thermodynamically favorable nematic state can only be achieved by supplying additional energy to the system. This is due to the high suspension viscosity and the lack of thermal motion in micron-sized platelets, which eventually leads to arresting of the system in a disordered structure. We observed that supplying the system with additional energy in the form of mechanical vibration favors the formation of nematic domains, where platelets present similar orientation. The assembly of particles into nematic domains occurs when the volume fraction of platelets surpass the critical concentration expected for the isotropic-nematic phase transition. For the 7.5 μm platelets with an aspect ratio of 37.5 used in this study, we expect this phase transition to take place when the platelet volume fraction approaches 14-16 vol%. (10) In agreement with such prediction, domains of about 100-200 μm exhibiting platelets oriented in the same direction are observed in the fractured surfaces of composites containing 20 and 27 vol% platelets (Figure 5.3a-c). Despite such local ordering of platelets within each nematic domain, the structure does not show long-range ordering as the domains with different platelet orientations are randomly distributed throughout the matrix.
Figure 5.3. SEM images showing the fractured surfaces of (a-c) as-cast and (d-f) aligned samples at different volume fractions. Scale bars in a-c and in d-f are 40 µm 20 µm, respectively.

The long-range ordering and the degree of platelet alignment within the x-axis of the composites were experimentally assessed through an X-Ray diffraction technique called rocking curve or omega-scan (see experimental procedure). (20) The results revealed no defined diffraction peak in the omega-scan for the as-cast specimens, suggesting that no long-range preferential alignment of the platelets exists in samples that were not exposed to magnetic fields (Figure 5.4a, red lines). Conversely, samples subjected to mechanical vibration and rotating magnetic fields (Figure 5.4a, black lines) exhibit a well-defined peak at an omega angle of about 0°, indicating preferential alignment of the platelets within the x-axis of the composite. The degree of misalignment of the anisotropic platelets was quantitatively described by the full width at half maximum (FWHM) of the obtained angular distribution, which is shown as a function of the volume fraction in Figure 5.4b. Samples with volume fractions lower than 25 vol% exhibit reasonably high degree of platelet alignment within the x-axis, as revealed by the FWHM values below 10.1°. However, stronger
misalignment (FWHM = 14.65°) is observed for the sample containing 27.2 vol% of alumina platelets. This is probably caused by the strong steric interactions between platelets and the very high viscosity of the platelet-epoxy resin mixtures at such high concentrations of inorganic particles.

Surprisingly, the degree of alignment achieved for composites processed through the directed-assembly route is not so far from that typically obtained by the laborious and cumbersome layer-by-layer approach ([11, 28]) (blue regions in Figure 5.4b) and is even comparable to that observed in composite films produced by tape casting (yellow region in Figure 5.4b). ([10]) In addition to such high control over platelet alignment, the method proposed here allows for the fabrication of bulk samples with platelets oriented in any deliberately chosen direction and its directed-assembly nature makes it compatible with technologies currently used in the production of polymers and composites.

Figure 5.4. a) Corrected rocking curves comparing the long-range structural order of samples prepared with magnetic and mechanical stimuli (black lines) and only mechanical vibration (red lines). b) Full width at half maximum (FWHM) of the angular distribution curve as a function of the volume fraction of platelets in samples exhibiting long-range structural order (aligned). The blue and yellow regions show the FWHM values previously obtained for platelet-reinforced composites produced by tape-casting and a layer-by-layer approach. ([11, 28])

5.4.2 Structure-property relationships in tailored reinforcement architectures

Control over the orientation of reinforcing platelets is crucial for tailoring the mechanical response of the composites. To investigate the correlation between reinforcement architecture and the mechanical properties of the epoxy-based composites, we designed and assembled the series of model microstructures
schematically shown in Figure 5.5. In addition to the as-cast samples, three different aligned architectures containing 11.5 vol% of platelets were created. In one of the aligned configurations, platelets were oriented uniaxially along the z direction using a static magnetic field. In this case, platelets are free to rotate around their long axis. This increases steric interactions between neighbor particles, limiting the platelet volume fraction in the system. The other two aligned configurations were obtained using a rotating magnetic field that enables biaxial orientation of the platelets within a specific plane of the composite, namely the x-y or the x-z planes. Such model composites were mechanically tested under compression and bending.

Representative stress-strain curves obtained for composites tested under compression are depicted in Figure 5.5b. Composite architectures with platelets aligned uniaxially (z-axis) or biaxially (x-z plane) along the loading direction exhibited the highest averaged increase in elastic modulus ($E$) and yield strength ($\sigma_y$). The $E$ and $\sigma_y$ values for such composites were approximately 120% and 30% higher than those for the neat epoxy, respectively. While no significant difference in elastic modulus and yield strength was observed between samples reinforced in the loading direction, biaxially oriented platelets (x-z plane) were found to reduce significantly the overall strain at rupture as compared to uniaxially aligned particles (z axis). The lower strain at rupture (~35%) results from the preferential reinforcement of only one of the planes parallel to the loading direction (x-z plane). This stronger reinforcement in one specific plane leads to premature failure of the material at lower compressive strains because the expected deformation of the polymer matrix in the radial direction is significantly constrained within that reinforced plane, limiting ultimately the compressive strain at rupture of the whole composite. Conversely, composites biaxially reinforced perpendicular to the loading axis (x-y plane) allow for a much larger shear deformation of the matrix in the radial direction. As a result, these composites exhibit strain at rupture nearly as high as those achieved with the neat epoxy (44.5%), despite reaching $E$ and $\sigma_y$ values comparable to those of the as-cast specimens. As-cast composites were significantly stronger and stiffer than the neat epoxy, showing a relative increase in elastic modulus and yield strength of 79% and 55%, respectively, as compared to the pure polymer. Additional experiments showed that the presence of magnetic nanoparticles on the alumina surface do not affect the mechanical properties of as-cast composites (results not shown).

The effect of platelet alignment on the mechanical properties of epoxy-based composites under three-point bending is shown in Figure 5.5b. Strong reinforcement and clear inelastic deformation is observed for composites containing platelets
oriented longitudinally with respect to the long-axis of the bending sample (x-y plane). In such configuration, the plane containing aligned platelets coincides with the plane of the sample where the highest normal stresses are expected. For the 3-point bending configuration used in these experiments, the maximum normal tensile stresses occur under the loading line at the bottom of the sample. At the microscale, reinforcement takes place through the development of shear forces at the platelet-matrix interface, which ultimately lead to stress transfer from the more stretchy polymer matrix to the stiffer and stronger inorganic platelets. As a result of such reinforcing effect, samples with longitudinally aligned platelets (x-y plane) exhibited an average increase in flexural modulus and maximum strength of 124% and 10% as compared to the pure polymeric matrix, respectively. These values are about 2.6-fold and 2.4-fold higher than those shown by as-cast composites. In contrast to such strong reinforcement, composites with random microstructure (as-cast) or containing platelets aligned transversely (x-z plane) exhibit brittle failure and rupture at much lower stresses than even the neat epoxy polymer (Figure 5.5c). These results indicate that the presence of platelets aligned perpendicular to the plane of maximum tensile stresses significantly degrades the mechanical properties of polymer matrices exhibiting limited ductility as the epoxy studied in this work. Although this degrading effect is stronger in the fully aligned sample (x-z plane), the very low strength of the as-cast composites suggests that the presence of even a small fraction of transversely oriented platelets in a random microstructure is already enough to significantly reduce the ultimate strength of the composite.

Overall, these results show a strong effect of the microstructure on the mechanical behavior of the composite. This makes it possible to achieve the mechanical response required in specific applications, by simply tuning the microstructure of the composite without changing the concentration of reinforcing particles and the overall chemistry of the material. Under compressive loads, applications requiring the highest stiffness and strength but with minimum reduction in strain at rupture would be best served if the composite contains platelets uniaxially aligned in the compressive loading direction (z-axis aligned in Figure 5.5). In contrast, situations requiring the highest strain at rupture but yet significant reinforcement would make the composites biaxially reinforced in the x-y plane a better choice. Under bending, the best performing microstructure is the one exhibiting platelets aligned in the plane where the normal stresses are developed during loading (x-y plane). This configuration leads to enhanced flexural modulus, maximum strength and strain at rupture. Microstructures containing random or fully aligned platelets in the x-z plane improve the flexural modulus but seriously degrade the maximum
strength and strain at rupture. This comparative analysis is valid for composites containing low concentrations of platelets (11.5vol%). Because the processability and resulting degree of alignment within the composites are affected by the volume fraction of platelets (Figure 5.4), different trends may prevail for materials obtained with higher concentrations of reinforcing particles. To understand how the volume fraction of platelets may change this comparative analysis, the effect of platelet concentration on the mechanical response of such composites in specific loading conditions is investigated below.

Figure 5.5. (a) Schematics of the investigated model composite architectures. Blue and red colors represent bare and magnetized platelets, respectively. (b,c) Effect of the microstructure on the mechanical response of composites containing 11.5vol% of platelets subjected to (b) compression and (c) bending.

5.4.3 Flexural properties

In addition to the effect of platelet orientation, we also investigated the flexural properties of as-cast and aligned composites (x-y plane) with increasing volume fractions. As depicted in Figure 5.6a, both as-cast and aligned composites showed improved flexural modulus \( E \) for increasing volume fractions of platelets. In agreement with the results presented above, composites containing platelets aligned in the x-y plane exhibited higher \( E \) values. Remarkably, flexural modulus as high as
16.6 GPa is obtained by the aligned composite with 27.2 vol% of platelets, which is 1.4-fold and 4.7-fold higher than those exhibited by the equivalent as-cast and pure polymeric matrix, respectively. These results were compared to predictions of the Halpin-Tsai model, which provides quantitative estimates of the elastic modulus of composites displaying random and aligned platelet architectures. (29, 30) Despite the reinforcing effect observed for both composites, their elastic moduli are far below the values predicted by the Halpin-Tsai model. This difference may arise from the deviations of the idealized composite microstructure assumed in the theoretical model. For instance, the model assumes that the matrix and the reinforcing platelet are linearly elastic, isotropic and perfectly bonded. The usual difficulties in achieving the theoretical perfect bonding in real systems might be one of the reasons for the observed inconsistency between theory and experiments. Moreover, the platelets in the model are considered perfectly aligned with a uniform size distribution and shape and the interactions between adjacent platelets at high volume fractions are neglected. All these idealized conditions, particularly the perfect alignment of platelets, are not representative of the actual microstructure of the investigated composites.

Although the stiffness of the aligned composites improved with increasing volume fractions of reinforcement, their maximum strength values were only marginally affected by the concentration of platelets (Figure 5.6b). The values obtained for the aligned composites lie within ± 10% of the value exhibited by the neat epoxy. The relatively low interfacial adhesion between the bare platelets and the matrix, (31) the incorporation of voids during composite fabrication (14) and the low ductility of the polymer matrix might be the main causes for limiting the increase in maximum strength expected for the aligned composites. In fact, literature data show that significant strengthening of epoxy polymers using stiff particles is often a challenge. Several studies actually report unchanged or even lower strength values upon addition of discontinuous stiff reinforcements. (31-35) A deleterious effect on the composite strength was also observed in the as-cast specimens, which showed maximum strength of approximately half of those of the pure epoxy matrix and of the aligned composites. These strength data for aligned and as-cast specimens are in good agreement with the results obtained for the series of composites with different architectures under three-point bending (Figure 5.5b). As discussed earlier, the low fraction of misaligned platelets in the as-cast specimen is sufficient to significantly degrade the mechanical strength of the composite under bending. This strength-degrading effect occurs because misaligned platelets work as stress concentrators, which locally increase the tensile stresses developed at the bottom of the bending
specimen. Such stress concentration is expected to be more pronounced in polymer matrices of low ductility like the epoxy investigated here. The ultimate ductility of the composite is also impaired by the stress concentration around misaligned platelets, as evidenced in Figure 5.6c by the lower strain at rupture of the as-cast specimens.

![Figure 5.6](image)

Figure 5.6. Effect of the volume fraction of platelets on the (a) flexural modulus, (b) flexural strength and (c) strain at rupture of as-cast and aligned composites.

### 5.4.4 Hardness

Surface hardness of the as-cast and aligned composites was also assessed by loading the samples with a pyramidal diamond indenter in different directions with respect to the reinforced plane. The results revealed that the surface hardness
enhances with increasing volume fractions of platelets for both aligned and as-cast composites (Figure 5.7). Specimens containing platelets preferentially aligned in the loading direction exhibit surface hardness significantly higher than those of as-cast composites, especially at volume fractions higher than 20% (Figure 5.7a). Conversely, aligned composites loaded perpendicular to the reinforced plane show surface hardness only slightly lower than those of as-cast composites (Figure 5.7b). The lack of preferential alignment in as-cast composites results in values of surface hardness that do not strongly depend on the loading direction. The larger error bars exhibited by the as-cast composites probably derive from the fact that the size of the indented area is at a similar length scale as the individual nematic domains found in these specimens (Figure 5.3b,c). This leads to a larger data spread, since individual indentations might probe one nematic domain alone, which can vary widely in orientation for the as-cast microstructures.

Overall, our ability to control the microstructure of platelet-reinforced composites allows us to reach values of surface hardness that would not be possible to obtain otherwise for the same set of initial building blocks. The surface hardness of aligned composites loaded parallel to the platelet orientation reached a value as high as 42.2 kgf.mm$^2$, which is 115% and 11% higher than those of the pure matrix and the equivalent as-cast composite, respectively. Despite the complex multiaxial stress state developed under the indenter during the measurement, the alignment of platelets parallel to the loading direction is clearly an effective approach to increase the composite’s hardness.

![Figure 5.7. Vickers hardness as a function of the volume fraction of alumina platelets in as-cast and aligned composites indented (a) parallel and (b) perpendicular to the platelet orientation in aligned specimens.](image-url)
5.4.5 Fracture toughness

To further illustrate the benefit of controlling the microstructure of platelet-reinforced composites, we compared the resistance against crack initiation ($K_{IC}$) of a series of specimens exhibiting the as-cast and aligned platelet architectures (Figure 5.8). As opposed to the fracture strength (Figure 5.6b), the $K_{IC}$ is an intrinsic property of the material that does not depend on processing surface flaws. Thus, the determination of the $K_{IC}$ values of as-cast and aligned composites eliminates the possible masking effect of surface defects, allowing for a direct comparison of the different microstructures. To ensure strong stress concentration at the crack initiation site, notches with root radius of around 2-3 $\mu$m were prepared (Figure 5.8a) by first cutting one edge of the beam using a wire saw and then sliding continuously a fresh razor blade over the notch to sharpen the crack tip.

Similarly to the orientation effect observed under bending mode (Figure 5.6b), composites containing platelets in the plane perpendicular to the crack propagation direction (x-y plane) result in better resistance against crack initiation as compared to conventional as-cast composites. For platelets volume fractions between 10 and 25vol%, the $K_{IC}$ values of aligned samples were 24 – 56 % higher than those obtained for the as-cast composites. This clearly shows the property enhancement possible by controlling the composite microstructure. Composites containing 24.3 vol% of platelets aligned in the x-y plane presented fracture toughness of 2.56 MPa.m$^{1/2}$, which is 4.7-fold higher than pure epoxy alone. The unexpected low value observed for the composite with 27.2 vol% of aligned alumina platelets might be due to the high degree of platelet misalignment revealed by the texture measurements (Figure 5.4b). Surprisingly, the as-cast composite with 27.0 vol% of platelets showed a relatively high $K_{IC}$ value of 2.37 MPa.m$^{1/2}$, even though its mechanical performance under bending was significantly lower compared to the aligned composites. Overall, the alignment of platelets in the direction of the highest tensile stresses enables an increase in the material’s resistance against crack initiation at much lower reinforcement volume fractions than those required with conventional as-cast microstructures (Figure 5.4b).
In addition to enhancing the resistance against crack initiation, anisotropic reinforcing particles are expected to enable multiple toughening mechanisms during crack propagation throughout the composite. Indeed, ex-situ SEM images of partially fractured notched specimens containing 20 vol% of Al₂O₃ platelets suggest that several toughening mechanisms occur when the crack propagates through the microstructures with randomly oriented nematic domains (as-cast, Figure 5.9a) and with long-range aligned platelets (aligned, Figure 5.9b).

We observe that the crack interacts differently with the microstructure depending on the local orientation of platelets. Platelets aligned perpendicular to the direction of crack propagation provide fracture resistance by multiple crack deflection events at the platelet-matrix interface (Region I, IV, V and VI, Figure 5.9). In contrast, little interaction with the microstructure is found when the crack advances through nematic domains of the as-cast samples containing platelets aligned parallel to the propagation direction (Region II, Figure 5.9b). Despite the absence of crack deflection events, the lower elastic modulus of such parallel-aligned domains decreases the stress intensity factor at the crack tip enabling local arresting of the crack. We observe that such arresting effect at parallel-aligned domains sometimes induces crack initiation at another position of higher local elastic modulus and thus higher stress concentration within perpendicular-aligned domains (Region III). This leads to the formation of unbroken ligaments that increase the material’s crack growth resistance through crack bridging (Region III). Other crack bridging and intrinsic toughening mechanisms are likely to occur but cannot be precisely identified.
in such ex-situ images due to the advanced stage of the fracture process. These results suggest that the composites presented in this study might exhibit crack growth resistance that increases with the crack length, namely a rising R-curve behavior. Overall, the combination of crack deflection events within aligned nematic domains at the length scale of individual platelets (intra-domain toughening, Region I) and crack bridging due to local differences in elastic modulus between domains at larger length scales (inter-domain toughening, Region III) indicate the rich set of multiscale toughening mechanisms that can occur in such platelet-reinforced composites.

Figure 5.9. Visualization of the crack path in (a) as-cast and (b) long-range aligned composites after partial fracture of the notched specimens under bending. The regions I-VI depict some of the toughening mechanisms that take place during crack propagation. Scale bars: 200 µm in (a) and (b); 20 µm and 5 µm in the insets (a) and (b), respectively.
5.4.6 Comparison with other short fiber- and platelet-reinforced composites

The mechanical performance of the composites reported in this study are compared in Figure 5.10 with data from a series of short fiber- and platelet-reinforced epoxy composites reported in the literature. (15-17, 31) Remarkably, the composites fabricated by the directed-assembly approach described here exhibit mechanical properties comparable to those reinforced with long- and short- glass fibers and micron-sized alumina platelets, with the advantage of being highly compatible with current polymer processing technologies.

Mechanical properties such as elastic modulus, fracture strength and hardness were all found to lie in between the extreme values expected for pure epoxy and pure alumina. A more detailed analysis shows that even though the composites prepared in this study (Families II and III) contain relatively low volume fraction of reinforcing platelets (< 28%), their elastic modulus and strength reach values that are comparable to those typically obtained for conventional composites reinforced with long glass fibers (GFRC, Figure 5.10a). This is a promising result, since it indicates that the directed-assembly route can potentially increase fabrication rates and cost-effectiveness while maintaining the same level of mechanical properties as those of current long-fiber composites.

The design lines shown in the elastic modulus versus density diagram (Figure 5.10b) also reveals that the directed-assembled composites perform particularly well in comparison with other materials if their weight-normalized specific elastic moduli are considered. This is especially important for the design of stiffness-driven structures with minimum weight. As far as surface hardness is concerned, we find that the presence of intrinsically stiffer and harder alumina platelets partially or fully aligned within the epoxy matrix results in composites with surface hardness significantly higher than those obtained with conventional long glass (GFRC) or carbon fiber-reinforced composites (CFRC) (Figure 5.10c).

Although the aligned composites described here exhibit crack-initiation fracture toughness significantly lower than that of conventional GFRC and CFRC, the $K_{IC}$ values achieved were found to be unusually high for their low reinforcement volume fraction and elastic modulus $E$ (Figure 5.10d). This combination of high $K_{IC}$ and low $E$ leads to fracture energy levels $G_C$ that surpass those observed for epoxy and pure alumina ($G_C = K_{IC}^2/E$). Design lines showing different $G_C$ levels are included in Figure 5.10d to facilitate this comparison. Overall, this comparative study demonstrates the huge potential of tailoring the microstructure of platelet-reinforced
composites to fulfill specific mechanical demands of targeted load-bearing applications.

Figure 5.10. Ashby diagrams correlating the properties of the as-cast and aligned composites fabricated in this study with a wide range of materials and other similar composites published in the literature. (15-17, 31) Diagrams (a), (b) and (d) adapted from ref. (36) Diagram (c) adapted from the database of the software Granta CES. (37)

5.5 Conclusions

The directed-assembly of reinforcing alumina platelets into ordered architectures using magnetic and mechanical stimuli leads to epoxy-based composites exhibiting enhanced mechanical response. We show that the use of
Mechanical vibration during magnetic alignment is crucial to overcome steric hindrances between platelets and thus improve their degree of alignment, especially at higher volume fractions. The mechanical properties of the resulting composites under bending and compressive loads can be tuned following simple microstructural design rules without changing the concentration of reinforcing elements. In general, effective reinforcement against bending and compression is achieved by aligning the platelets in the direction where the highest normal tensile and compressive stresses are developed, respectively. Under the multiaxial stress state imposed by sharp indenters, we find that the alignment of platelets parallel to the loading direction is most efficient in increasing the surface hardness of the composite. With regards to the fracture process of the composites, our results suggest that several energy dissipation mechanisms take place during crack propagation throughout the platelet-reinforced microstructures. The directed-assembled composites exhibit mechanical performance comparable to those of long glass fiber-reinforced composites widely used as structural materials. Because of its easier scalability and compatibility with fast polymer processing technologies, the proposed directed-assembly approach should enable faster and more cost-effective processing of composite materials without compromising their unique mechanical properties.

5.6 Acknowledgements

We thank Prof. Jörg Löffler and Prof. Ludwig Gauckler for granting access to equipment from their laboratories; Dr. Kyrill Feldman, Simon Bachmann and Benjamin Hartmeier for their invaluable experimental support; and Peter Kocher, Beatrice Wegmann, Martin Elsener and Christian Roth for their technical assistance.

5.7 References


MAGNETICALLY RESPONSIVE FLUORESCENT MICROPLATELETS WITH TUNABLE OPTICAL EMISSION

Rafael Libanori, Frieder B. Reusch, Randall M. Erb and André R. Studart
To be submitted in 2013

6.1 Abstract:

Tuning the optical properties of suspensions by controlling the orientation and spatial distribution of suspended particles with magnetic fields is an interesting approach to create switchable optical devices. However, the relatively high concentration of magnetic material required to manipulate these particles very often reduce the optical transmittance of the system. In this study, we describe a simple method to generate microplatelets with magnetically-tunable optical properties via the deposition and functionalization of a continuous layer of silica on ultrahigh magnetically responsive (UHMR) alumina platelets. UHMR fluorescent microplatelets that can be manipulated with external magnetic fields as low as 13 Gauss are obtained by covalently attaching an organic fluorescent dye on the silica surface. Because of the anisotropic shape of the particles, control of their orientation and distribution using low magnetic fields and field gradients enables easy tuning of the optical properties of the suspension. This strategy allows us to gain both spatial and temporal control over the fluorescent emission from the particle surface, making the multifunctional platelets an interesting building block for the manipulation of light in colloid-based smart optical displays.
6.2 Introduction

Magnetically responsive particles have been explored in many applications, ranging from mechanical sensing (1, 2) to microrobotics (3-5) to cancer treatment. (6, 7) By tailoring the surface chemistry of such particles, multifunctional systems that combine magnetic response with other mechanical, chemical or optical properties have been proposed in a variety of different fields. This has led for example to the development of magnetic systems to transport and release drugs in specific sites of the human body, (8, 9) to catalyze chemical reactions with minimum loss of catalysts, (10, 11) to trace fluid flow in extracorporeal blood purification (12) and to optically monitor chemical concentrations and temperatures of fluids at the microscale. (1, 13)

While magnetic fields enable high penetration depth and are harmless to the human body, the high field strengths and the high concentrations of magnetic material often required for particle manipulation remains a limiting factor in several applications. (14) The use of anisotropic microparticles partially coated with superparamagnetic nanoparticles (SPIONs) was recently shown to be an effective strategy to circumvent these limiting issues by enhancing the magnetic response and minimizing the undesired effects of gravity and thermal motion on the position and orientation of the magnetically-responsive particles. (15, 16) In this approach, coating of the non-magnetic microparticles with SPIONs can be easily performed by dispersing the two types of particles in water at a pH that leads to opposite electrical charges on their surfaces. The resulting SPION-coated microparticles were found to respond to magnetic fields as low as 1 milliTesla (10 Gauss) at surface coverage of less than 1%. Such Ultra-High Magnetic Response (UHMR) allows for a major reduction in the amount of magnetic material required for remote manipulation. For instance, UHMR alumina platelets can be made responsive to a magnetic field of only 20 milliTesla (200 Gauss) using SPION concentrations as low as 0.01wt% relative to the mass of platelets. Such SPION content is low enough to maintain the high reflectivity of the Al₂O₃ platelets, enabling the potential utilization of such system in optical applications in which the dark color arising from the magnetic material has so far been a major limitation.

Alumina platelets exhibiting ultra-high magnetic response have been used for the assembly of advanced composites with deliberately reinforced microstructures,(15) for the creation of swellable bilayered composites with programmable shape-changing effects (17) or for the preparation of injectable cementitious materials with in situ oriented macroporosity. (18) However, the combination of high reflectivity and magnetic control offered by such microparticles
are yet to be explored for the development of colloidal systems with switchable optical properties.

Previous work has shown that magnetic fields provide an effective means to control the optical reflectivity of suspensions containing aluminum microplatelets dispersed in a ferrofluid. (19) In this case, aligning the highly reflective metallic platelets perpendicular to the direction of light through negative magnetophoresis significantly hampers the optical transmission of an otherwise translucent suspension. However, the relatively high concentration of SPIONs present in the ferrofluid reduces the overall optical transmittance of the system even in the translucent state.

Here, we report a simple and up-scalable procedure to obtain multifunctional alumina platelets exhibiting both magnetic response and fluorescent emission. Magnetic nanoparticles adsorbed on the alumina surface are protected by a continuous silica shell deposited through a modified Stöber method, (20) which can be further functionalized with a fluorescent dye to emit light. (21) Manipulation of such multifunctional platelets with low magnetic fields allows for both spatial and temporal control over the fluorescent emission from the particle surface, offering a straightforward mechanism to control light in smart optical devices.

6.3 Experimental section

6.3.1 Materials

The following chemicals were used in the study: tetraethylorthosilicate (TEOS, Merck), ethanol absolute (EtOH, Scharlau, 99.9%), ammonium hydroxide (NH₄OH, Merck, 25%), N,N-dimethylformamide (DMF, Honeywell, 99.8%), anionic ferrofluid (EMG 705, Ferrotec), poly(vinylpyrrolidone) (PVP, Sigma-Aldrich, 360 kg/mol), rhodamine B isothiocyanate (RBICT, Sigma-Aldrich) and 3-aminopropyltriethoxysilane (APTES, Acros, 99%). All chemicals are of technical grade unless otherwise stated. The aluminum oxide platelets (Al Pearl) with average long-axis size of 7.5 µm and thickness of 200nm were kindly supplied by Antaria, Australia. Deionized water was used in all experiments.
6.3.2 Magnetization of alumina platelets

Two different suspensions were initially prepared by suspending 10g of alumina platelets in 300 mL of water and 0.375 mL of the ferrofluid EMG 705 in 200 mL of water. The latter was then slowly added to the platelet suspension and the resulting mixture was stirred at room temperature for 2 hours. Finally, the Ultra-High Magnetically Responsive (UHMR) platelets were removed by filtration, washed with 1500 mL of water and dried at 60°C for 4h.

6.3.3 Silica coating of alumina platelets

The surface modification of UHMR alumina platelets with silica was performed by a modified Stöber method described elsewhere. (20) The complete surface modification process is schematically shown in Figure 6.1. In summary, UHMR platelets are first functionalized with the non-ionic, amphiphilic polymer polyvinylpyrrolidone (PVP, $M_w = 360$ kg.mol$^{-1}$) in water and subsequently transferred to 140 mL of an ammonia/ethanol solution containing 0.56 mol/L of ammonia. Next, the silica coating is formed by slowly adding tetraethyl orthosilicate (TEOS) with a syringe pump at specific flow rates to control the extent of secondary precipitation of SiO$_2$ particles. In a typical synthesis, 1.6 g of UHMR platelets are dispersed into 200 mL of an aqueous solution containing 0.35 g.L$^{-1}$ of PVP, which is kept stirring overnight. The platelets are then filtered and washed with 100 mL of ethanol. After drying at room temperature for approximately one hour, the platelets are transferred to 140 mL of an ammonia/ethanol solution containing 0.56 mol.L$^{-1}$ of ammonia and stirred for 30 min at 600 rpm. For a nominal SiO$_2$ thickness of 20 nm, 20 mL of a 2.65 vol% TEOS solution in ethanol absolute were added by a syringe pump operated at a flow rate of 800 µL.h$^{-1}$. Finally, the silica-coated platelets (SiO$_2$@UHMR-Al$_2$O$_3$) are filtered, washed with approximately 1L of ethanol and dried at 70°C for 4 hours.

Since the above synthetic route typically resulted in less than 1.6 grams of modified platelets, an alternative similar procedure was also developed to upscale the production of SiO$_2$@UHMR-Al$_2$O$_3$ platelets. For the PVP surface modification of such larger batch, 10 g of UHMR alumina platelets were suspended in a 1 L solution of water containing 4.375 g.L$^{-1}$ of PVP. Next, platelets were filtered and suspended in 800 mL of an ammonia/ethanol solution with an ammonia concentration of 0.56 mol.L$^{-1}$. The silica coating step was then performed through the controlled addition of 40 mL of a 8.3 vol% TEOS solution in EtOH at a flow rate of 800 µL.h$^{-1}$. The
concentration of TEOS was increased to carry out the reaction in less than 50 hours. However, platelets were more prone to the formation of small agglomerates when processed following this up-scaled route.

![Diagram of the modified Stöber method used to coat magnetized alumina platelets with silica.](image)

**Figure 6.1.** a) Modified Stöber method used to coat magnetized alumina platelets with silica. b) Syringe pump utilized to adjust the injection rate of TEOS solution and thus control the extent of secondary precipitation of silica nanoparticles.

### 6.3.4 Functionalization of silica-coated platelets

Fluorescent silica-coated platelets were prepared by adding a previously synthesized fluorescent silane during the silica coating process described above. The synthesis of the fluorescent silane was carried out by adding 0.0855 mL of APTES into 9.2 mL of an EtOH solution containing 7.6 mg.mL⁻¹ of the RBITC dye. The mixture was allowed to react at room temperature and in the dark for 12h under continuous magnetic stirring. 6 mL of the resulting solution was directly added to a suspension of alumina platelets freshly coated with a silica layer as described above for the small batch synthesis procedure. The suspension was stirred for 48h at room temperature, before the platelets were finally filtered and washed with 500 mL of deionized water.

### 6.3.5 Structural, chemical and magnetic characterization

SEM images were acquired in a Zeiss LEO 1530 electron microscope using an operating voltage of 5 kV. Specimens were prepared by adding a small amount of powder onto a sample holder covered with carbon tape. Compressed air was used to
remove the excess of powder. Samples were coated with a 5 nm layer of platinum following a standard sputtering procedure.

Infrared spectra were obtained in diffuse reflectance mode between 4000–370 cm$^{-1}$ with 64 scans at a resolution of 4 cm$^{-1}$ (DRIFT, System 2000 FT-IR, Perkin Elmer). A mixture of 5 wt% platelets in KBr powder was initially ground in an agata mortar and subsequently milled in a vibration mill for 1 minute to generate FT-IR samples after powder compaction. A spectrum obtained for pure KBr was used to set the background reflectance.

A FEI Quanta 200 FEG electron microscope was used to acquire qualitative Energy Dispersive X-Ray (EDX) spectra in low vacuum mode. Samples were prepared as described for the SEM analysis but without the sputtering step. Local EDX data was collected during 100 s using an acceleration voltage of 5 kV.

The magnetic response of SiO$_2$@UHMR-Al$_2$O$_3$ platelets was evaluated by first sonicating a suspension of 0.01 g modified platelets in 10 mL of a 5wt% PVP aqueous solution. To enable observation in an optical microscope, a droplet of such suspension was added to a microscope glass slide covered with a transparent Teflon foil. A magnetic field was applied by setting up a solenoid next to the optical microscope. The amplitude of the magnetic field was adjusted by controlling the electrical current running through the solenoid. The minimum magnetic field required to align the platelets was defined as the amplitude at which at least 50% of the platelets were aligned parallel to the applied field.

6.4 Results and discussion

Chemical and structural analysis of the surface of the alumina platelets after each modification step allowed us to identify the most important parameters involved in the controlled synthesis of multifunctional platelets combining fluorescence and magnetic response. The formation of a silica layer on the platelet surface is particularly critical because it requires tight control over the nucleation process of hydrolyzed TEOS molecules. Therefore, such reaction was first investigated on bare alumina surfaces. The uniformity and the roughness of the silica layer deposited on the surface of alumina platelets were found to be strongly affected by the saturation level of the silica precursor solution and by the colloidal stability of the alumina microplatelets in the ammonia/ethanol mixture.

Stabilization of the platelets in the reaction medium is crucial to reduce agglomeration and ensure complete exposure of the particle surface during the
coating procedure. In agreement with earlier studies, (20) we observed that the as-received alumina platelets could be effectively suspended in water using the non-ionic amphiphilic polymer poly(vinylpyrrolidone) (PVP). Since the as-received platelets were found to be slightly hydrophobic, the amphiphilic PVP molecules likely adsorb through hydrophobic interactions with the alumina surface. This enables anchoring of the macromolecule on the particle surface while allowing its more hydrophilic moieties to extend towards the aqueous phase and thus provide the steric layer needed for effective particle stabilization.

Coating PVP-stabilized platelets with silica resulted in either uniform and smooth or non-uniform and rough layers depending on the saturation level of the initial TEOS solution. Control over the silica saturation level was achieved by adjusting the injection rate of TEOS into the reaction medium. (22) To obtain a more uniform and smooth coating, the concentration of TEOS \( C \) must be sufficiently low to suppress homogeneous nucleation in the bulk liquid, but high enough to enable the deposition of a continuous silica film through heterogeneous nucleation on the surface of the seeding platelets. For the micron-sized alumina platelets used here, we found that an addition rate of 800 \( \mu \text{L} / \text{h} \) of a 2.65 vol% solution of TEOS in EtOH yields a homogeneous, smooth silica coating and reduces drastically the agglomeration of platelets (Figure 6.2a). This flow rate corresponds to the addition of about 21 molecules.nm\(^{-2}\).h\(^{-1}\). Our results indicate that such addition rate lies within the optimum window in which the concentration of hydrolyzed silica precursor falls between the critical values needed to induce surface heterogeneous and bulk homogeneous nucleation \( C_{\text{hetero}} < C < C_{\text{homo}} \). Despite the microscopically smooth surface of the coated platelets, closer observation shows that the coating exhibits a granular texture with numerous asperities approaching a few tens of nanometers in size (Figure 6.2b). Such asperities increase the effective surface area of the platelet, providing more room for the later attachment of functional molecules.

In contrast, non-uniform and rougher coatings are obtained when TEOS reaches concentrations beyond the critical value needed for homogeneous nucleation \( C > C_{\text{homo}} \), Figure 6.2c,d). The rougher surface probably results from the deposition of silica nanoparticles that initially formed via homogeneous nucleation in the bulk solution and only afterwards adsorbed on the platelet surface. Such conditions were met by adding individual 1 mL aliquots of a 2.65 vol% solution of TEOS in EtOH per hour using a pipette. The rougher platelets were also more prone to agglomeration, as shown in Figure 6.2c, Spherical silica particles with diameter as large as 400 nm were observed on the surface of the alumina platelets coated by adding the TEOS precursor at a higher rate (Figure 6.2d).
The controlled precipitation procedure using low TEOS addition rate is also an effective means to obtain a monolayer of silica on the surface of alumina platelets initially pre-labeled with magnetic nanoparticles (UHMR-\(\text{Al}_2\text{O}_3\)). Fourier Transform Infrared Spectroscopy (FT-IR, DRIFT mode) and Energy Dispersive X-ray Spectroscopy (EDX) confirmed the presence of the continuous silica layer on the surface of treated UHMR-\(\text{Al}_2\text{O}_3\) platelets. The spectrum of SiO\(_2@\text{UHMR-}\text{Al}_2\text{O}_3\) platelets exhibits typical infrared absorptions bands of SiO\(_2\), such as stretching of free (3660 cm\(^{-1}\)) and associated –O–H groups (2800-3500 cm\(^{-1}\)) and asymmetric (1186 cm\(^{-1}\)) and symmetric (1067 cm\(^{-1}\)) bending of Si-O-Si groups, as displayed in Figure 6.3a. The absorption band at 1655 cm\(^{-1}\) is assigned to the stretching of carboxyl groups of the pyrrolidone moiety, (23) suggesting that PVP remains adsorbed on platelets’ surface after the coating step. SEM investigation employing a back scattered electron detector reveals the presence of iron oxide nanoparticles adsorbed on the platelet surface, shown as brighter spots in Figure 6.3b. Semi-quantitative analysis using EDX on selected regions of the UHMR-\(\text{Al}_2\text{O}_3\) surface
indicates that SiO$_2$ is present both on the platelet surface itself (red curve in Figure 6.3b) and at the brighter spots corresponding to the iron oxide particles (blue curve in Figure 6.3b). These results suggest that the continuous silica coating was deposited on top of the initially adsorbed magnetic nanoparticles, providing a new hydroxylated surface for further functionalization with silane coupling agents.

Figure 6.3. a) FT-IR spectra of bare (black) and silica-coated (red) platelets. b) EDX analysis on the surface of the silica-coated platelets indicating the presence of silica alone (red square) and silica combined with iron oxide (blue square).

Magnetic alignment tests show that the silica coating does not reduce the magnetic response of the UHMR platelets. The magnetic field in the range of 10-20
Gauss needed to align the SiO$_2$@UHMR-Al$_2$O$_3$ platelets is in good agreement with the experimental observations and theoretical predictions of the minimum field required to align bare alumina platelets. (15, 16)

Figure 6.4. Optical microscope images showing the alignment of SiO$_2$@UHMR-Al$_2$O$_3$ platelets under low magnetic fields (H).

To further explore the potential of the SiO$_2$@UHMR-Al$_2$O$_3$ system, we covalently attached an organic dye to the silica coating to provide a light-emitting molecule on the platelet surface. In fact, the attachment of chromophore groups onto silica surfaces rather than directly on magnetic particles has been shown to reduce significantly the quenching of the dye for sufficiently thick silica shells. (24, 25) To produce fluorescent platelets, a solution of rhodamine B thioisocyanate (RBTIC) coupled with 3-aminopropyltriethoxysilane (APTES) was added to a suspension of freshly-coated alumina platelets in a ammonia/ethanol mixture. Silanol groups (Si-OH) of the hydrolyzed RBTIC-APTES react with the hydroxyl groups present on the surface of the silica coating, as schematically shown in Figure 6.5a. Infrared spectroscopy confirmed the formation of the thiourea group (shown in blue in Figure 6.5a) expected from the reaction between RBTIC and APTES, as indicated by the absorption band at 1390 cm$^{-1}$ in Figure 6.5b. (26) The covalent coupling of the fluorescent silane on the silica surface through the formation of Si-O-Si bridges (green bonds in Figure 6.5a) was also confirmed by absorption bands at 1208 cm$^{-1}$ and 1155 cm$^{-1}$. Although not exploited here, other silane coupling agents carrying different functional groups can also be covalently attached to the SiO$_2$@UHMR-Al$_2$O$_3$ platelets using similar procedures. Another possible surface modification was demonstrated in a previous work, in which the surface of the same silica-coated platelets was modified with a hydrophobic silane to enable reinforcement of a polydimethylsiloxane (PDMS) matrix through efficient stress transfer at the platelet-matrix interface. (27)
Magnetically Responsive Fluorescent Microplatelets

Figure 6.5. a) Scheme showing the covalent attachment of a fluorescent dye molecule on the surface of a silica-coated platelet. b) FT-IR spectra of the SiO$_2$@UHMR-Al$_2$O$_3$ (black line) and fluorescent RBTIC-SiO$_2$@UHMR-Al$_2$O$_3$ (red line) platelets. c) Spatial control of the magnetic fluorescent platelets on the surface of a low-coercivity magnetic stripe. d) Temporal control of the fluorescent emission of RBTIC-SiO$_2$@UHMR-Al$_2$O$_3$ platelets in a fluid under rotating magnetic field.

The multifunctional nature of the resulting platelets allows us to gain both spatial and temporal control over the fluorescent emission from the modified particle. As an example of spatially-localized fluorescence, Figure 6.5c shows the accumulation of fluorescent RBTIC-SiO$_2$@UHMR-Al$_2$O$_3$ platelets onto the magnetic domains of low-coercivity magnetic stripes. Besides such static configuration, the emitted fluorescence can also be dynamically controlled to exhibit any arbitrary temporal pattern by exposing the multifunctional platelets to changing magnetic fields. To illustrate our ability to dynamically control the emission intensity using magnetic fields, we performed platelet alignment tests using a rotating magnetic field at a frequency of 30 Hz under an optical microscope (Figure 6.5d). At such a high frequency, the platelet experiences phase ejection and aligns its long axes parallel to
the plane of the rotating magnetic field. (16, 28) This configuration exposes a lower surface area to the detector, resulting in the reduced fluorescent emission shown in Figure 6.5d (position 1). By switching off the magnetic field, the platelet is subjected to gravitational forces alone and slowly returns to the horizontal position, which corresponds to position 3 in Figure 6.5d. This configuration exposes a higher surface area and maximizes the fluorescence intensity reaching the detector. As observed in previous studies, (16, 28) platelet orientation along the plane of the rotating magnetic field occurs much faster (Position 4 in Figure 6.5d) than its return to the resting position on the glass substrate (Position 2 in Figure 6.5d). In applications where faster response times are required, such as in light-emitting displays, the transition from out-of-plane to in-plane position can be greatly accelerated by using a competing field applied orthogonally to the direction of the initial rotating magnetic field. (19) Alternatively, lower frequencies can be applied to circumvent the effect of gravity and enable fast rolling of the platelets at the same speed of the rotating magnetic fields.

6.5 Conclusions

Silica-coated platelets exhibiting Ultra-High Magnetic Response (SiO₂@UHMRA₂O₃) were successfully synthesized by electrostatically adsorbing SPIONs on the platelets followed by a controlled precipitation of silica on their surfaces. The magnetic nanoparticles were completely incorporated in the silica coating and the Si-OH groups introduced allowed for the addition of new functionalities to the platelets through standard silica modification methods. The magnetic response of the SiO₂@UHMRA₂O₃ platelets was not affected by the presence of the silica coating and can be tailored by the surface coverage with SPIONs. Furthermore, fluorescent dyes were covalently attached to the silica surface to yield fluorescent platelets that can be manipulated using magnetic fields as low as 13 Gauss. The orientation and position of the magnetically responsive fluorescent microplatelets could be deliberately tuned to gain spatial and temporal control over the fluorescent emission from the particles, making them potential building blocks for the creation of smart light emitting displays.
6.6 Acknowledgements

We thank Prof. Markus Niederberger and Prof. Ludwig Gauckler for allowing access to their equipment and Jonathan Sander for the experimental assistance on the fluorescent microscope.

6.7 References


CONCLUSIONS

Biological composites are a great source of inspiration to guide materials scientists in the development of high-performance materials. A thorough analysis of their intricate microstructures reveals design principles that can be used in the fabrication of artificial composites exhibiting unique set of mechanical properties. In this thesis, we focused on developing innovative processing techniques to produce bioinspired platelet-reinforced composites that replicate at least two main design principles found in natural layered composites, namely the control of the local orientation and local concentration of reinforcing elements.

Living organisms are able to build hierarchical composite materials exhibiting a wide range of mechanical properties by just controlling the concentration and distribution of a few types of building blocks within the same continuous matrix. Inspired by this design principle, we fabricated artificial hierarchical composites by tape casting a suspension of nanoplatelets, microplatelets and polyurethane in dimethylformamide. This technique allows for the fabrication of large and homogenous composite films with a high degree of platelet alignment, which approaches the level of alignment achieved with more laborious techniques, such as layer-by-layer. Our investigations suggest that the shear-thinning behavior of the suspension and the use of polyvinylpirroliodone as a dispersing agent for the micron-sized platelets play an important role in avoiding segregation and sedimentation of the large alumina platelets during the consolidation of the polymeric matrix. The preferential reinforcement of the hard domains of polyurethanes with nanoplatelets is key to allow for the addition of high concentrations of microplatelets. The development of a synthetic framework to fabricate hierarchical materials with a wide range of mechanical properties allowed us to assemble mechanically graded composites with different layers of polyurethane-based materials. A solvent-welding technique was applied to achieve an effective mechanical coupling between the
different layers. Microstructural and mechanical characterization of these composites indicate that the graded structure is held by a fully interpenetrating polymer network. In addition, uniaxial mechanical tests reveal that the graded heterogeneous composites can be stretched by as much as 350% in-plane while strains below 1% are detected on the top of the stiffest layer. In fact, the mechanical behavior of the heterogeneous stretchable composites is in very good agreement with results obtained by finite element analysis. This strain minimization mechanism is also shown to effectively protect brittle electronic devices that are attached on the surface of the top layer of the graded composite. Our ability to create materials with locally tunable elastic modulus spanning 5 orders of magnitude with a fully entangle polymer phase allowed us to achieve an unusual set of mechanical properties that would not be possible with isotropic materials. This approach is highly compatible with current polymer and composite processing technologies.

The remarkable mechanical performance exhibited by structural biological composites also arise from the accurate control over the local orientation of anisotropic nano- and micro-sized building blocks. Unlike natural composites, state-of-the art approaches to fabricate platelet-reinforced composites lack the ability to fully control the local alignment of the building blocks and tailor their architectures according to the external loads exerted on the material. To gain control over the local orientation and arrangement of anisotropic reinforcing platelets, we coated micrometer-sized reinforcing platelets with minimal concentrations of superparamagnetic nanoparticles. These magnetically responsive platelets can be manipulated by using ultralow magnetic fields to produce synthetic composites with unprecedented three-dimensional orientation and distribution of reinforcements across the polymeric matrix. In contrast to the methods currently used to assemble platelet-reinforced composites, we show that magnetic manipulation of ultrahigh magnetic responsive platelets leads to a new generation of artificial composites, whose architectures are in principle only limited by the magnetic field patterns that can be created. To overcome the steric hindrances experienced by adjacent platelets in highly loaded polymeric resins, we supply an additional source of energy in the form of mechanical vibration simultaneously with their magnetic alignment. This approach improves significantly their alignment degree in the resulting composite. Platelet-reinforced composites produced through this method exhibit outstanding mechanical performance and outperform their isotropic counterparts. This technique is fast, robust and can be easily adapted to fabricate composites with several different polymeric matrices and reinforcing building blocks aligned in any given direction.
Magnetic manipulation of micron-sized anisotropic particles was also taken beyond the scope of mechanical reinforcement in synthetic composite materials. Deposition of a thin silica layer on the ultrahigh magnetically responsive platelets allows for functionalization of their surfaces with silane coupling agents containing fluorescent dye moieties. As the fluorescent emission from the platelet surface is proportional to its exposed surface area, this functionalization makes it possible to adjust both the spatial and temporal optical properties of platelet suspensions by just controlling the local position and orientation of such magnetic-fluorescent platelets. These multifunctional platelets can be potentially employed to fabricate smart light-emitting devices and composites with tailored optical properties.
Chapter 8

OUTLOOK

The concepts for mechanical design of graded composites presented in this work could be extended to other fabrication techniques to enable finer control over the material’s microstructure in all three dimensions. Although the solvent-welding technique allows for the manufacturing of large heterogeneous composites exhibiting a good control over the local concentration of reinforcing building blocks, it still presents several disadvantages. Since it is mostly based on the assembly of micrometer-thick layers, fabrication of 3D objects is quite limited. In addition, the production rate is very low as it involves multiple steps including the fabrication of the individual layers, assembling, hot-pressing and drying. In fact, 3D printing seems to be a potential technique to overcome these limitations. Designing the products with Computer-Aided Design software (CAD) and feeding the extrusion nozzles with different materials might provide a more accurate control of the spatial distribution of the reinforcing building blocks within the polymeric matrix. The manufacturing of 3D components with tailored local mechanical properties might enable this technology to be used in the fabrication of heterogeneous biomedical implants and more durable dental restorations. Also, in-plane gradients could also be obtained without having the unleveled surfaces of the patch-substrate configuration presented here. This would facilitate the implementation of electronic components that are more prone to mechanical failure, such as Thin Film Transistors (TFTs).

The magnetic manipulation of reinforcing particles presented in this work enables the production of high-performance composites with unprecedented control of their architectures. Our investigations demonstrate the enormous potential exhibited by these composites in terms of mechanical properties. To improve even further their mechanical properties, the methods described here must be adapted to yield composites with higher volume fraction of platelets while still keeping a high alignment degree. This goal could be achieved by performing the magnetic assembly
of platelets in uncured low viscosity polymeric resins followed by a hot-press assisted slip casting. Although layered composites containing up to 60vol% of alumina platelets have already been prepared through this method, the magnetic alignment might improve the packing degree of the platelets during the compaction and removal of the polymeric resin. Alternatively, highly loaded composites could also be obtained by impregnating ceramic scaffolds previously fabricated with aligned alumina platelets. Here, the magnetic platelets could be aligned in a sacrificial phase containing either monomers that are converted into ceramic materials; or silica nanoparticles dispersed in a cross-linked polymeric matrix. Upon calcination, the organic phase is converted into a porous ceramic matrix that would hold together the aligned platelets. Subsequently, the ceramic scaffold can be impregnated with a polymeric phase. Further research on the mechanical behavior of these platelet-reinforced composites should also be focused on quantifying the toughening mechanisms that occur as the crack propagates throughout the sample during fracture. It is expected that composites exhibiting such layered structure present rather high resistance against crack propagation. These mechanisms were already observed in the composites fabricated in this thesis through ex-situ SEM analysis of partially fractured surfaces.

Besides adjusting local concentration and orientation of anisotropic reinforcing building blocks, other design principles can also be implemented in platelet-reinforced composites. The unusual strain hardening observed in nacre is believed to have its origin in a mechanical interlocking mechanism resulting from the surface roughness and waviness of the aragonite platelets. Therefore, we expect that providing nanoasperities onto the surface of the bare alumina platelets will result in a more effective stress transfer from the matrix. Preliminary experiments (results not included in this thesis) show that silica nanoparticles can be adsorbed and sintered onto the alumina surface. The size and the density of these nanoasperities can be easily adjusted by using different sizes of nanoparticles and concentrations during the adsorption process. These roughened platelets can also be labeled with superparamagnetic nanoparticles and manipulated with ultralow magnetic fields. As the preliminary results are quite promising, I will follow up on this project after defending my PhD thesis.

Adding new functionalities to the magnetic platelets broadens the range of applications where magnetic assembly can be used to fabricate smart materials. Fabrication of multifunctional platelets exhibiting fluorescent and magnetic properties might allow us to incorporate special optical properties in polymer composites. By aligning the multifunctional platelets in transparent polymeric matrices, one could
possibly control the light emission intensity originating from any specific direction in the resulting material. Combination of platelets with different magnetic response and fluorescent dyes attached on the surface could generate interesting optical properties in the composite material. These principles might also be used to adjust the spatial and temporal emission of multifunctional platelets suspended in liquids for the development of smart light-emitting displays.
Appendix 1: Supplementary material to Hierarchical reinforcement of polyurethane-based composites with inorganic micro- and nano-platelets

Polyvinylpyrrolidone (PVP) as dispersant

Simple sedimentation tests were performed to evaluate the efficiency of PVP as dispersant of the alumina platelets in DMF. Figure 9.1 shows that platelet suspensions containing PVP exhibit improved stability in comparison to a reference suspension in the absence of the polymer. This is indicated by the slower sedimentation rate and lower volume of sediment (better particle packing) of PVP-containing suspensions. The high dispersion efficiency of PVP explains the better homogeneity and improved alignment of platelets in the as-cast hierarchical composites containing this polymer.

Figure 9.1. The effect of PVP (PVP 40, $M_w = 40000$ g/mol) on the stability of suspensions of alumina platelets in DMF.
Annealing of as-cast composites at 130°C for 3 hours was observed to enhance the reinforcing effect of the inorganic platelets. Although the possible morphological changes resulting from this annealing step on the polyurethane matrix are still unclear, we observed that this heat treatment is crucial to ensure a good interfacial adhesion between the platelets and the surrounding polymer. Figure 9.2 shows DSC curves obtained for composites reinforced with 12.9 vol% laponite and hierarchical composites reinforced with 7 vol% laponite and 16.8 vol% PVP-modified alumina platelets (alumina:PVP constant series). A new endotherm at approximately 160°C (indicated by an arrow) can be identified after annealing both laponite-reinforced and hierarchically reinforced composites. This endotherm might result from relaxation effects of the hard segments of the polymeric chain due to physical ageing of the sample when subjected to annealing. (1, 2) Alternatively, it might indicate the formation of crystalline domains on the surface of the reinforcing particles, which would explain the strong strengthening effect achieved after annealing (Figure 2.4 in Chapter 2). Additional DSC measurements will be carried out to better elucidate the nature of the endotherms exhibited by this system.

Figure 9.2. Differential scanning calorimetry (DSC) curves before and after annealing for a) polyurethane reinforced with 12.9 vol% laponite nanoplatelets and b) polyurethane hierarchically reinforced with 7 vol% laponite nanoplatelets, 16.8 vol% PVP-modified alumina platelets and 13 vol% PVP. The arrows indicate the endotherm peak that appears after annealing.
Surface modification of the alumina platelets with silane and nitrodopamine

Alumina microplatelets were surface modified to improve their adhesion to the polymeric matrix. By using either aminopropyltriethoxysilane or nitrodopamine the strategy was to introduce amine groups onto the surface of the reinforcing particles to favor polar interactions with the urethane groups. An acid-catalyzed silanization reaction was performed to covalently bind 3-aminopropyltriethoxysilane (APTES) to the alumina surface (see main manuscript). A multilayered coating is expected to form onto the platelet’s surface due to the self-condensation of the silane’s silanol groups. The adsorption of the catechol-derived molecule 6-nitrodopamine sulphate occurs through a ligand exchange reaction onto alumina surface by simply adding the modifier to a suspension of platelets in DMF. (3-6)

Both FT-IR and TGA measurements confirmed the surface modification of the alumina platelets using the aforementioned coupling agents. Figure 9.3a shows the FT-IR spectra in DRIFT mode of the modified alumina with the respective band assignments. Typical band absorptions of the surface modifiers could be identified, confirming the modification of the platelets. TGA thermograms (Figure 9.3b) show a weight loss of 0.35% and 5.35% for the alumina platelets modified with nitrodopamine (alumina-ND) and APTES (alumina-APTES), respectively. The weight loss at temperatures lower than 200°C was attributed to the evaporation of solvent remaining from the silanization reactions. Such TGA results are in line with the hypotheses that APTES and nitrodopamine form, respectively, multilayers and a monolayer on the alumina surface.

![FT-IR spectra and TGA thermograms](image-url)

Figure 9.3. a) FT-IR spectra of alumina platelets with the respective band assignments after surface modification with i) nitrodopamine (ND) and ii) APTES. b) Thermogravimetric analysis (TGA) of the alumina platelets modified with ND and APTES.
Molecular reinforcement of polyurethane with PVP

We found that PVP not only ensures an efficient dispersion of the alumina microplatelets in DMF but also increases the yield strength and elastic modulus of the PU matrix at the expense of ductility. To quantify this effect, polymer blends containing different amounts of PVP in PU were prepared and their mechanical properties in tensile mode were evaluated. Figure 9.4 shows the elastic modulus, the yield strength and the strain at rupture of such polymer blends as a function of the volume fraction of PVP. By applying a rule of mixtures to the system, we estimate an elastic modulus of 1.59 GPa and a yield strength of 98 MPa for pure PVP.

![Figure 9.4](image)

Figure 9.4. a) Elastic modulus, b) yield strength and c) strain at rupture of PU-PVP polymer blends as a function of the volume fraction of PVP.

Supplementary references


Figure 10.1. Strain distribution throughout the cross-section of the different patch-substrate modules investigated by FEA. The investigated modules are identified by the letter S followed by the assumed elastic modulus of the patch in MPa units. In addition to the stresses at the patch-substrate interface, the FEA also provided important insights into the strain distribution throughout the investigated patch-substrate modules. The overall response of the modules to external uniaxial stretching differed considerably depending on the average elastic modulus of the patch ($\bar{E}_{\text{pat}}$) relative to the elastic modulus of the underlying substrate ($E_{\text{sub}}$). For $\bar{E}_{\text{pat}} = E_{\text{sub}}$, the patch experiences a combination of bending at the edges and stretching at its center. In contrast, patches with $\bar{E}_{\text{pat}} > E_{\text{sub}}$ exhibited predominantly inwards bending upon uniaxial stretching. The implications of these different responses to the strain distribution within the patch are discussed in the main text.
Figure 10.2. Stress distribution at the interface between the patch and the elastomeric substrate for the different investigated systems. The investigated modules are identified by the letter S followed by the assumed elastic modulus of the patch in MPa units. The FEA for patch-substrates elongated by 25% in the y direction (Figure 3.2 in Chapter 3) revealed that the highest stresses occur at the interface between the patch and the elastomeric substrate. The shear stress $\tau_{yz}$ is particularly high at the edge of the patch, whereas the normal stress $\sigma_{yy}$ increases from the edge towards the center of the patch (c and a, respectively). This analysis suggests that the edges and the center of the patch-substrate interface are the most probable sites for yielding and fracture initiation. Among the simulated architectures, the highest $\tau_{yz}$ values at the interface were found to be 8.4 MPa, 10.4 MPa and 8.4 MPa for the S-0550, S-7000 and S-Grad samples, respectively. The highest normal stresses $\sigma_{yy}$ at the interface were found to follow the same trend, with values of 22.5 MPa, 31.3 MPa and 23.6 MPa for the S-0550, S-7000 and S-Grad specimens, respectively. Our experimental results confirmed that the edges were more prone to initial failure while elongating the patch-substrate in the y-direction (see Figure 3.4b in Chapter 3). Such edge delamination was found to propagate further across the interface in samples containing the stiffest homogeneous patch (E-7000), eventually causing full interfacial delamination (Figure 3.4a in Chapter 3). In contrast, the lower interfacial stress peaks of the graded architecture prevent further propagation of the delaminated edge for strains as high as 300%.
Figure 10.3. Snapshot of a graded patch connected to an elastomeric substrate subjected to 340% global tensile strain. Imaging the patch-substrate module from the substrate side reveals the partial detachment of the substrate close to the patch edge (indicated by the arrow).

Figure 10.4. Snapshots of a stretched patch-substrate module (E-Grad). In this exceptional case, failure initiated at a defect within the substrate material away from the patch edge at a global strain of 280%. While this particular sample does not represent the typical failure mode close to the edge, rupture was sufficiently slow to enable detection of the propagating crack.
Figure 10.5. Quasi-planar heterogeneous composites. Specimen exhibiting four circular graded patches that were hot pressed against an elastomeric substrate to produce reinforced islands with smaller steps between the patch and the substrate. Images (a) and (b) show, respectively, top and side views of the sample, whereas (c) depicts an SEM image of a gold-coated specimen highlighting the step between the patch (left) and the elastomeric substrate (right). Using contact profilometry (model Dektak XT Advanced, Bruker), we found that pressing reduced the step height to values within the range 3.7 – 15.2 µm. Scale bars: (a) and (b) 4 mm; (c) 5 µm.
Figure 10.6. Integration of electrical components onto quasi-planar heterogeneous composites. (a) Series of four graded patches that were hot-pressed into the elastomeric substrate and electrically connected by two parallel stripes of sputtered gold. (b) Top and (c) side views of functional LEDs placed on the surface of the graded patch and electrically connected to the metallic stripes. LEDs were switched on by contacting the ends of the metallic stripes (white arrows) to a 9V battery. The successful lighting of the LEDs confirms that the small edge step obtained after the hot pressing procedure enables the deposition of electrically conductive patterns between adjacent islands. In combination with well-adhered, (1) wavy, (2, 3) or non-coplanar electrically conductive patterns/wires, (4) this approach should allow for the creation of highly stretchable substrates with large-area arrays of interconnected functional devices. Scale bars: (a) and (b) 10 mm; (c) 5 mm.
Figure 10.7. Patch-substrate module used for measuring the electrical resistance of a gold layer sputtered on top of a graded patch. Scale bar: 5 mm.

Figure 10.8. Reproducibility of the mechanical response of patch-substrate modules. Local strain measured on the patch surface as a function of the global tensile strain applied to the underlying substrate for three different specimens of the same patch-substrate configuration. Red and blue curves correspond to configurations E-0040 and E-Grad, respectively.
Figure 10.9. Schematic top view of the 2D array of patches on the surface of the elastomeric substrate. The scheme depicts the distances experimentally measured before and after stretching to determine the local in-plane mechanics of the 3D heterogeneous composite (Figure 3.1f in Chapter 3).

Figure 10.10. Picture showing the assembly of the LED and electric contacts on top of a graded patch. Scale bar: 4 mm.
Figure 10.11. Modeling the mechanical properties of the elastomeric substrate. Engineering stress as a function of stretch ($\varepsilon + 1$) for the substrate M0040 and the corresponding Mooney-Rivlin fit. The non-linear regression was performed up to a stretch of 2.3.

Fitting parameters:
- $C_0 = 1 \times 10^{-14}$ MPa
- $C_1 = 3.7$ MPa
- $R^2 = 0.92$

Figure 10.12. Mesh model of the patch-substrate modules used in the finite element analysis (FEA). The Figure depicts the free tetrahedral elements used for meshing.
### Supplementary Tables

Table 10.1. Quantities used for the synthesis of polyurethanes with different hard-to-soft segment ratio.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastic modulus (MPa)</th>
<th>% hard segments</th>
<th>H-MDI (mL)</th>
<th>T1000 (g)</th>
<th>EG (g)</th>
<th>BDO (mL)</th>
<th>DBTL (µL)</th>
<th>DMF (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0002</td>
<td>1.8</td>
<td>30</td>
<td>2.070</td>
<td>4.8294</td>
<td>0.0706</td>
<td>0.205</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>M0004</td>
<td>4.5</td>
<td>40</td>
<td>2.590</td>
<td>4.1307</td>
<td>0.0693</td>
<td>0.430</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>M0040</td>
<td>41.5</td>
<td>50</td>
<td>3.108</td>
<td>3.4300</td>
<td>0.0703</td>
<td>0.650</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>M0110</td>
<td>108.0</td>
<td>60</td>
<td>3.627</td>
<td>2.7300</td>
<td>0.0705</td>
<td>0.872</td>
<td>70</td>
<td>35</td>
</tr>
<tr>
<td>M0550</td>
<td>554.1</td>
<td>70</td>
<td>4.146</td>
<td>2.0307</td>
<td>0.0698</td>
<td>1.095</td>
<td>70</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 10.2. Quantities used for the preparation of platelet-reinforced composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elastollan (g)</th>
<th>PVP (g)</th>
<th>Laponite (g)</th>
<th>Alumina (g)</th>
<th>DMF (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1600</td>
<td>2.4</td>
<td>-</td>
<td>0.6</td>
<td>-</td>
<td>160</td>
</tr>
<tr>
<td>M3600</td>
<td>2.4</td>
<td>0.353</td>
<td>0.6</td>
<td>1.518</td>
<td>160</td>
</tr>
<tr>
<td>M7000</td>
<td>2.4</td>
<td>1.080</td>
<td>0.6</td>
<td>4.633</td>
<td>160</td>
</tr>
</tbody>
</table>

Table 10.3. Compositions and thicknesses of individual layers used to obtained graded and non-graded patches.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer 1 (thickness/µm)</th>
<th>Layer 2 (thickness/µm)</th>
<th>Layer 3 (thickness/µm)</th>
<th>Layer 4 (thickness/µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-0040</td>
<td>M0040 (186 ± 23)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>E-7000</td>
<td>M7000 (71 ± 6)</td>
<td>M7000 (71 ± 6)</td>
<td>M7000 (71 ± 6)</td>
<td>M7000 (71 ± 6)</td>
</tr>
<tr>
<td>E-Grad</td>
<td>M0550 (91 ± 9)</td>
<td>M1600 (47 ± 7)</td>
<td>M3600 (48 ± 12)</td>
<td>M7000 (71 ± 6)</td>
</tr>
</tbody>
</table>
Table 10.4. Experimental average distances measured at different positions \((x_i)\) of the 3D composite before \((l_0)\) and after \((l_{100})\) applying 100% tensile strain along the x-axis (Figure 10.9). The distances \(l_0\) and \(l_{100}\) correspond to averages obtained from \(l_i\) data for patches within the entire row \(i\). \(\varepsilon_l\) and \(E_l\) correspond to the calculated average local strain and effective elastic modulus, respectively. Local distances within regions comprising solely the elastomeric substrate were also measured \((l_{s,i})\) in Figure 10.9 and were used to estimate the local strain of the substrate alone. Such strain \((\varepsilon_s)\) was found to be approximately constant at a value of 180 ± 17% throughout the entire sample. From this averaged \(\varepsilon_s\) value and the stress-strain curve of the elastomeric substrate (Figure 3.3a in Chapter 3), we estimate that the polymer region between patches is subjected to a local stress, \(\sigma_s\), of 8.1 MPa during stretching. Assuming the modular 3D composite to behave like elastic elements connected in series (Reuss model), we use the local stress \(\sigma_s\) as a good approximation of the global stress \(\sigma_g\) applied to the composite under 100% global strain. Dividing the estimated \(\sigma_g\) by the measured local deformation \(\varepsilon_l\), we obtained a local effective elastic modulus of the composite for different positions along its surface.

<table>
<thead>
<tr>
<th>Position, (i)</th>
<th>(x_i) (cm)</th>
<th>(l_0) (cm)</th>
<th>(l_{100}) (cm)</th>
<th>(\varepsilon_l) (%)</th>
<th>(E_l) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.56</td>
<td>1.14</td>
<td>1.21</td>
<td>6.34</td>
<td>127.7</td>
</tr>
<tr>
<td>2</td>
<td>1.23</td>
<td>1.20</td>
<td>1.41</td>
<td>17.73</td>
<td>45.7</td>
</tr>
<tr>
<td>3</td>
<td>1.98</td>
<td>1.30</td>
<td>1.72</td>
<td>32.33</td>
<td>25.1</td>
</tr>
<tr>
<td>4</td>
<td>2.80</td>
<td>1.38</td>
<td>1.96</td>
<td>42.37</td>
<td>19.1</td>
</tr>
<tr>
<td>5</td>
<td>3.70</td>
<td>1.46</td>
<td>2.24</td>
<td>53.35</td>
<td>15.2</td>
</tr>
<tr>
<td>6</td>
<td>4.71</td>
<td>1.51</td>
<td>2.50</td>
<td>65.49</td>
<td>12.4</td>
</tr>
</tbody>
</table>

Table 10.5. Mechanical properties of the individual layers of the patch-substrate modules used in the finite element analysis.

<table>
<thead>
<tr>
<th>Properties</th>
<th>S-M0040</th>
<th>S-M0550</th>
<th>S-M1600</th>
<th>S-M3600</th>
<th>S-M7000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical model</td>
<td>Mooney-Rivlin</td>
<td>Linear elastic</td>
<td>Linear elastic</td>
<td>Linear elastic</td>
<td>Linear elastic</td>
</tr>
<tr>
<td>Density (kg.m(^{-3}))</td>
<td>1200</td>
<td>1200</td>
<td>1330</td>
<td>1650</td>
<td>2010</td>
</tr>
<tr>
<td>Elastic modulus (MPa)</td>
<td>-</td>
<td>550</td>
<td>1600</td>
<td>3600</td>
<td>7000</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>0.49</td>
<td>0.40</td>
<td>0.35</td>
<td>0.32</td>
<td>0.30</td>
</tr>
<tr>
<td>Model parameter, (C_{01}) (MPa)</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Model parameter, (C_{10}) (MPa)</td>
<td>(10^{-14})</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bulk modulus, (K) (MPa)</td>
<td>367.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Supplementary References


Appendix 3: Supplementary material to Composites reinforced in 3D using low magnetic fields

Theoretical estimate for the elastic modulus of the locally reinforced composites

Stress versus strain curves for the reinforced and non-reinforced regions of locally reinforced composites were obtained as described above. The Young’s modulus, $E$, was found to be 310 MPa for the reinforced region compared with 250 MPa for the pure polyurethane. SEM analysis showed that the reinforced region exhibits a clear bilayer structure (Figure 11.2b). Bilayer composite theory is thus employed to estimate the stiffness of the thin reinforced layer responsible for the increase in the Young’s modulus. The Young’s modulus of the bilayer, $E_{net}$, can be determined with a rule of mixtures as:

$$E_{net} = \phi_a E_a + (1-\phi_a) E_b, \quad (S14)$$

where $\phi$ is volume fraction, $a$ refers to the thin reinforced layer containing the UHMR particles, and $b$ refers to the pure polymer layer. To accurately determine the volume fraction of the thin reinforced region, scanning electron micrographs similar to that shown in Figure 11.2b were analyzed. It was found that $\phi_a = 0.3$. Assuming an elastic modulus, $E_b$, equal to 250 MPa for the non-reinforced polyurethane layer, we obtain a Young’s modulus, $E_{a}$, of 450 MPa for the thin reinforced layer.
Supplementary Figures

Figure 11.1. Focused-Ion Beam Scanning Electron Micrographs of alumina-polyurethane composites showing clear orientational preference of UHMR particles: a) with no field and b) under an external magnetic field.

Figure 11.2. a) Photograph of the locally reinforced alumina-polyurethane composite synthesized through concentrating the UHMR particles into a thin region of the film (dark brown). b) Scanning electron micrograph of cross-section of same film depicting clear bi-layer structure in these samples.
Figure 11.4 – Dental resin composites containing 1 vol% of UHMR alumina platelets in a) in-plane and b) out-of-plane configurations.

Figure 11.5. a-d) Epoxy composite laminates containing 10 vol% of UHMR alumina platelets in the different configurations schematically shown in Figure 4.3e (Chapter 4). e) Picture of the three-point bending apparatus used to test the flexural properties of these samples.
# Supplementary Tables

Table 11.1. Tensile testing results for the homogeneous polyurethane composites described above.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Young’s Modulus</th>
<th>Tensile Strength</th>
<th>Strain at Rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyurethane + 20% PVP</td>
<td>523 ± 148 MPa</td>
<td>28.64 ± 4.59 MPa</td>
<td>246.6 ± 74.4%</td>
</tr>
<tr>
<td>Polyurethane + 20% PVP+ 20%Al2O3 (Parallel)</td>
<td>1471 ± 104 MPa</td>
<td>46.82 ± 2.30 MPa</td>
<td>4.83 ± 0.75%</td>
</tr>
<tr>
<td>Polyurethane + 20% PVP+ 20%Al2O3 (Perpendicular)</td>
<td>1313 ± 200 MPa</td>
<td>25.21 ± 1.58 MPa</td>
<td>2.68 ± 0.38%</td>
</tr>
</tbody>
</table>
CURRICULUM VITAE

Rafael Libanori
Wolfgang-Pauli-Strasse 10
HCI G533
8093 Zürich, Switzerland
Citizenship: Brazilian

Education

2009-now  Ph.D. candidate in Materials Science
Swiss Federal Institute of Technology (ETH), Zürich
**Doctoral Thesis:** Bioinspired Composite with Controlled Alignment and Distribution of Anisotropic Reinforcing Particles
**Advisor:** Prof. Dr. André R. Studart

2007-2009  Master of Science (M.Sc.) in Materials Science and Engineering
Federal University of São Carlos (UFSCar), Brazil
**Master thesis:** Synthesis and characterization of polyurethane-based molecular composites
**Advisor:** Prof. Dr. Edson Roberto Leite

2003-2006  Bachelor of Science (B.Sc.): Chemistry
Federal University of São Carlos (UFSCar), Brazil
**Bachelor thesis:** Effect of TiO₂ surface modification on Rhodamine B photodegradation
**Advisor:** Prof. Dr. Edson Roberto Leite

1999-2002  High School and technical education in Civil Construction
Technical School of Limeira (Cotil/UNICAMP), Brazil

Publications and Patents


Teaching Experience


**Awards**

2013 *Spark Award* for the most promising invention of 2012, ETH, Zürich, Switzerland.


2011 2nd poster prize at *Euro BioMat*, Jena, Germany.

2009 Distinguished Master’s Thesis Award, São Carlos, Brazil.

**Conference presentations**

**Oral Presentations**

8. Third International Conference on Multifunctional, Hybrid and Nanomaterials 2013, Sorrento, Italy.


6. Materials Research Society Fall Meeting 2012, Boston, USA.

5. BASF Construction Chemicals 2012, Trostberg, Germany (invited talk).

4. Brazilian Agricultural Research Corporation 2012, São Carlos, Brazil (invited talk).

3. European Symposium and Exhibition on Biomaterials and Related Areas (Euro BioMat) 2011, Jena, Germany.


1. Materials Research Society Fall Meeting 2010, Boston, USA (2 presentations).

**Poster presentations**

5. Third International Conference on Multifunctional, Hybrid and Nanomaterials 2013, Sorrento, Italy.

3. European Symposium and Exhibition on Biomaterials and Related Areas (Euro BioMat) 2011, Jena, Germany.

2. Third International NanoBio Conference 2010, Zürich, Switzerland.

1. Materials Research Graduate Symposium 2010, 2011 and 2012, Zürich, Switzerland