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Hierarchical reinforcement of polyurethane-based composites with inorganic micro- and nanoplatelets

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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.

1. 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.

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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 polyvinylpirrolidone 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. Experimental procedure

2.1. 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 1,4-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 200 nm (Fig. 1e, Alusion®, aspect ratio: 37.5, Antaria Limited, Australia) and Laponite RD platelets with diameter of 25 nm and thickness of 1 nm (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 = 40,000 g/mol, Aldrich, Switzerland), 3-aminopropyltriethoxysilane (APTES, 98%, Aldrich, Switzerland), 6-nitrodopamine sulfate (ND, SuSoS, Switzerland) were of technical grade, unless otherwise stated.

2.2. 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 min at room temperature. The resulting powder was washed five times with THF and dried in vacuum (10 mbar) at room temperature for 24 h. 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 h. Next, the modified alumina platelets were washed five 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 h 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 h. Finally, the obtained mixture was directly used to prepare platelet/polymer suspensions for tape casting as described in the next sections.

2.3. 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 h. 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 250 mL 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.

2.4. 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 × 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 h. Before performing the mechanical tests, the dried composites were annealed at 130 °C for 3 h and kept in a desiccator for, at least, 24 h.

2.5. 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 [24]. In brief, a high-resolution scan is performed at high 2θ angles ($85° < 2\theta < 95°$) 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* ω curves was used as a measure of the platelet degree of misalignment. All XRD measurements were performed in a X'Pert PRO equipment (PANanalytical, The Netherlands).

2.6. Surface analyses

Covalent attachment of coupling agents (APTES and ND) was confirmed by Diffuse Reflectance Infrared Fourier Transform