The Role of a Bifunctional Matrix Protein in a Biomimetic Graphene/Nanocellulose Composite

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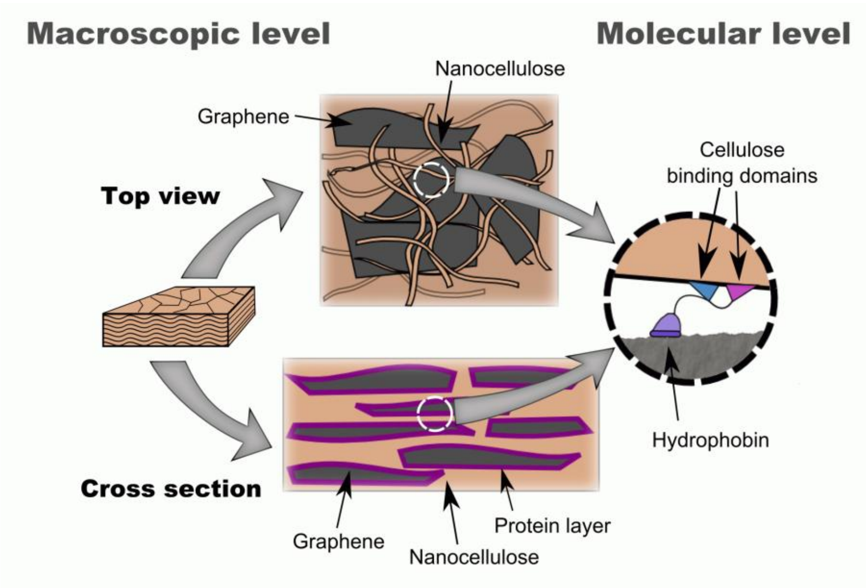
We present a truly biomimetic approach for building nanocomposites by using engineered biomolecules, nanocellulose and graphene flakes. Biomimetics is used as a tool for understanding how high performance materials can be built by the means of specifically binding matrix molecules. A significant reinforcement of cellulose film could be obtained when graphene, interfaced with a novel bi-functional protein HFBI-DCBD, was embedded in it. HFBI-DCBD is a recombinant protein where an amphiphilic hydrophobin molecule (HFBI) has been fused with two cellulose binding domains (CBD) as presented in Scheme 1. Due to the strong interactions that the proteins create between the components, nanocomposites prepared by this method showed excellent values for toughness (20.2 GPa), strength (278 MPa) and work-of-fracture (5.8 J/m^2). The method uses sustainable materials and is readily up-scalable.



Scheme 1. *A schematic presentation of the structure of the composite from macroscopic to molecular level. Top view: Graphene flakes are interlocked in the percolating network of cellulose, which provides structural rigidity. Cross section: Cellulose fibrils and protein-coated graphene form a layered structure where protein is facing both graphene and cellulose. The scheme on molecular level shows how the fusion protein HFBI-DCBD is oriented at the interface between cellulose and graphene. The violet part represents the amphiphilic hydrophobin (HFBI) which attaches to graphene. Blue and purple parts are two the cellulose-binding domains (CBDs).*

The studied composite matrix was formed from cellulose and graphene flakes [1], which were coated with a layer of fusion protein HFBI-DCBD. The two functional parts of the fusion protein appear in nature for totally different purposes compared to what we are now using them. Instead of breaking down materials, which is how the host organism (*Trichoderma reesei*) of these proteins operates, we use these molecules for building new materials. Hydrophobins are amphiphilic and assemble at interfaces [2], thus forming monolayers at surfaces of hydrophobic materials, such as graphene.[3] The second part of the molecule, CBD, originates from a cellulase,[4] which uses it for anchoring to cellulose surfaces. Functionalizing of nanofibrillar cellulose (NFC)[5] with CBD-containing molecules provides a soft non-destructive way to add function and to modify its properties. It was shown that exfoliation of graphene in a mixture of HFBI-DCBD and NFC resulted in suspension of graphene flakes attached to the cellulose nanofibrils. This suspension was then vacuum filtrated into films whose mechanical properties were characterized. The composite has excellent mechanical properties (See Figure 1), is light-weight and all its components are from sustainable sources.

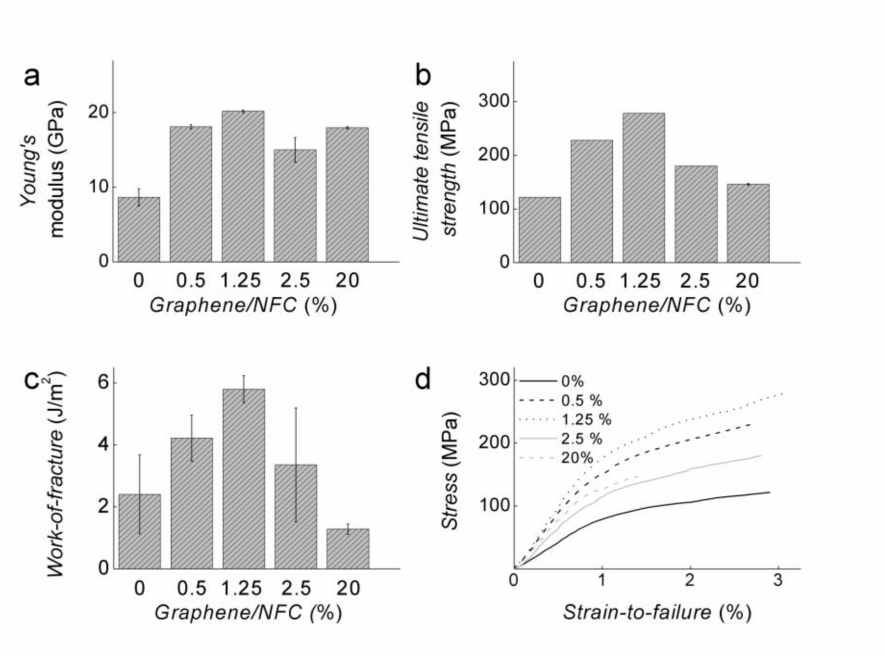


Figure 1. *Mechanical properties of composites consisting a varying amount of graphene. Amount of graphene is given as a w-% of graphene to nanocellulose. Stiffness (a) and ultimate tensile strength (b) and toughness (c) of the composite significantly increased when graphene content was increased and reached a maximum level at graphene content 1.25 %. d: Example stress vs. strain curves from samples containing different amounts of graphene. Graphene fraction is given as percentage to the mass of NFC.*

References

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