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Multimodal and self-healable interfaces enable strong and tough graphene-derived materials

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ABSTRACT

Recent studies have shown that graphene-derived materials not only feature outstanding multifunctional properties, but also act as model materials to implant nanoscale structural engineering insights into their macroscopic performance optimization. In this work, we explore strengthening and toughening strategies of this class of materials by introducing multimodal crosslinks, including long, strong and short, self-healable ones. We identify two failure modes by fracturing functionalized graphene sheets or their crosslinks, and the role of brick-and-mortar hierarchy in mechanical enhancement. Theoretical analysis and atomistic simulation results show that multimodal crosslinks synergistically transfer tensile load to enhance the strength, whereas reversible rupture and formation of healable crosslinks improve the toughness. These findings lay the ground for future development of high-performance paper-, fiber- or film-like macroscopic materials from low-dimensional structures with engineerable interfaces.

1. Introduction

The synergetic excellence of mechanical, thermal and electronic properties of graphene has attracted immersed interests in, but not limited to, the materials community (Geim and Novoselov, 2007). Focus has been placed not only on utilization of its high intrinsic stiffness and strength up to 1 TPa and 120 GPa, ultimate strain to failure of 20%, but also how to transfer the strong and tough performances of graphene monolayer into macroscopic applications (Liu et al., 2012). Within this scenario, nanostructures such as graphene, graphite nanoplatelets and carbon nanotubes have been widely used as reinforcing phases in high-performance composites. Major advantages based on this approach include well-enhanced stiffness, strength, resilience, as well as the multifunctionality (Stankovich et al., 2006; Young et al., 2012). However, it is also widely recognized that the native interface between these nanostructures and matrices creates weak points in the mechanical sense. This issue critically prevents successful transfer of outstanding performance of graphene across multiple length scales up to the macroscopic level, in addition to other difficulties such as lack of efficient technique to uniformly disperse nanostructures into the matrix at a high volume fraction (Gong et al., 2010; Young et al., 2012).

Graphene-derived materials (papers, fibers, films etc.) usually feature layer-by-layer microstructures with single sheet spanning over hundreds of micrometers (An et al., 2011; Compton et al., 2011; Kotov et al., 1996; Qiu et al., 2012; Stankovich et al., 2006;

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Xu et al., 2013; Zhao et al., 2013). In comparison with particle or fiber-based reinforced composites, they demonstrate many advantages, such as the extreme exposure of graphene sheets to the environment for functionalization, enabling rich and tunable crosslinking mechanisms between them. Recently, a number of theoretical and experimental efforts have been made in predicting and optimizing mechanical performance of this class of materials. Similar structural hierarchy broadly appears in biological materials, such as bones, teeth and nacre, where brittle minerals and soft proteins are integrated for their superior strength and toughness (Cheng et al., 2013; Dimas et al., 2013; Finnemore et al., 2012; Gao, 2006; Yao et al., 2013; Zhang et al., 2010, 2011; Zhong et al., 2013; Zuo and Wei, 2007). Mechanical enhancement is achieved by the staggered arrangement of mineral platelets that distributes the tensile load, which is transferred across the material by shear in soft protein interphases. In this manner the high stiffness, strength of mineral platelets and toughness of proteins are integrated, yielding superior overall mechanical properties, as captured in the tension–shear chain model proposed by Ji and Gao (2004). Later works have also focused on the topological optimization and stabilization of the staggered layer-by-layer structures (Zhang et al., 2010, 2011).

Besides of these elegant insights into rational design of high-performance materials, a whole new dimension is added in graphene-derived materials by engineering crosslinks in the interlayer gallery, through covalent, dative, ionic, hydrogen bonds or van der Waals interactions (Compton et al., 2011; Gao et al., 2011; Park et al., 2008). As the aspect ratio of a functionalized graphene sheet (the lateral size divided by its thickness) is usually very high ($>10^4$), there is enough space between the sheets for nanoscale structural engineering. By further considering the intralayer deformation of functionalized graphene sheets, a deformable tension–shear (DTS) model was proposed to describe the mechanical properties of graphene-derived materials (Liu et al., 2012), which predicts that giant graphene oxide (GO) sheets can be used to build ultrastrong materials, as achieved in recent experimental work (Xu et al., 2013). Beyond these points, recent progresses in functionalizing graphene sheets with various chemical groups (An et al., 2011; Bekyarova et al., 2013; Compton et al., 2011; Gao et al., 2011; Liu et al., 2011, 2012, 2013; Park et al., 2008; Xu et al., 2013), and improved understanding of crosslinking mechanisms in complex materials, such as multimodality, sacrificial bonds and self-healing behaviors (Hartmann and Fratzl, 2009; Liu et al., 2011; Mark and Erman, 2007; Wojtecki et al., 2011; Xu, 2013), could further enable optimal design in a new direction by tuning material interfaces at the molecular level. For example, gels with enhanced toughness were synthesized with multimodal crosslinks (Sun et al., 2012, 2013). The synergy of crack bridging by covalent crosslinks and hysteresis by unzipping ionic crosslinks allows synthesized polymer hydrogels to be stretched beyond 20 times their initial length, and have fracture energies of ~ 9000 J/m^2. In this regime, covalent crosslinks preserves the memory of the initial state, so that much of the large deformation is removed on unloading, while unzipped ionic crosslinks cause internal damage that is healed by re-zipping (Sun et al., 2012). Polyampholytes, polymers bearing randomly dispersed cationic and anionic repeat groups, form tough and viscoelastic hydrogels, where strong ionic bonds serve as permanent links holding the structure integrity under loading, while weak and reversible ionic bonds play a sacrificial role in mechanical energy dissipation, offering toughening and mechanical recovery, to heal the damage and fatigue thus being created (Sun et al., 2013). It is worth noting that, mechanical responses of polymeric gels are usually weak and delayed due to their entropic elasticity and random network structures, while layered materials derived from functionalized graphene sheets allow more intensive and prompt responses to external cues, and thus become ideal candidates to implement ideas of mechanical enhancement by introducing multimodal and self-healable crosslinks.

In this article, we first clarify failure modes of graphene-derived materials, and develop an analytical model to describe the failure propagation in Section 2. In Section 3, we introduce the concepts of multimodal and self-healable crosslinks based on atomistic simulation results, followed by discussions on strengthening and toughening effects of the material in Section 4.

2. Failure of graphene-derived materials

Graphene-derived materials with layer-by-layer microstructures may experience two distinct failure modes when subjecting to in-plane tensile loads, i.e. fracture of functionalized graphene sheets (by breaking covalent bonds) or interlayer crosslinks (also known as the 'pull-out' mode). Their mechanical performance is critically defined by the selection of failure modes. Thus in order to achieve enhancement by engineering their interlayer crosslinks, we need to identify the failure criteria of these two contrastive modes first.

2.1. Characterization of the failure mode

The mechanical behaviors of graphene-derived materials under tension can be captured in the DTS model by considering both intralayer elasticity of the functionalized graphene sheet and interlayer crosslinks as continuum phases (Liu et al., 2012). The unidirectional load applied is transferred along a path consisting of both the sheets under tension and interlayer crosslinks under shear. Based on a representative volume element (RVE) illustrated in Fig. 1a, we consider a tension force F_0 applied on the RVE in the DTS model. The tensile strain ε in the sheet along its in-plane direction and shear strain γ in crosslinks are (Liu et al., 2012)

$$\varepsilon(x) = \partial u_1/\partial x = \frac{F_0}{D}\left[\frac{1}{2} - \frac{\cosh(x/l_0)}{2} + \frac{1+c}{2s}\sinh(x/l_0)\right] \tag{1a}$$