HIGH MECHANICAL PERFORMANCE OF GRAPHENE OXIDE-POLY(VINYL ALCOHOL) LAYERED NANOCOMPOSITES

Y. Gao1,2, L. Q. Liu1, D. Zhou1, B. H. Han1, Z. Zhang1*

1 National Center for Nanoscience and Technology, Beijing, China
2 Academy for Advanced Interdisciplinary Studies, Peking University, Beijing, China
*
* Corresponding author (zhong.zhang@nanoctr.cn)

Keywords: graphene oxide, polymer, nanocomposite, mechanical performance, load transfer

1. Introduction
During recent several years, great efforts have been applied to graphene-based nanocomposites to achieve high mechanical performance.[1,2] At low concentrations, graphene-based nanofillers have assuredly given rise to exceptional enhancements in mechanical properties. The factors referring to the significant improvements mainly include the well dispersion, the enhanced specific area and the two dimensional geometry of graphene, as well as the suitable interfacial adhesion. For example, a ~31% increase in tensile strength and a ~40% improvement of Young’s modulus were achieved by addition of only 0.1 wt% of graphene nanosheets into epoxy nanocomposites.[3] However, high concentration graphene-based nanofillers introduced into nanocomposites would lead to agglomerates, and thus restrain the further improvements of mechanical properties.[4] A great deal of researches have been attempted to effectively transfer the outstanding mechanical performance of graphene-based nanosheets at high loadings and realize the ultrastrong nanocomposite materials.[5-7] Layered PVA nanocomposite with high graphene oxide (GO) nanosheets loadings has been made by LBL technique, which exhibited a enhancement of mechanical properties.[8] In addition, by aqueous filtration, Park et al. proceed polyallylamine cross-linked GO layered nanocomposite with well mechanical performance.[9] However, up to now, the modulus and strength of these composites are still much lower than the theoretically predicted values. And the structural factors affecting mechanical behaviors of these layered nanocomposites still need deeply investigated.

Herein, GO-based paper-like nanocomposites with high mechanical performances were fabricated by vacuum-assisted self-assembly technique, in which the nanosheets component takes up the majority and acts as principal framework. To probe the structural factors, the effects of polymer molecular weight onto the mechanical properties of nanocomposites were carefully studied. Furthermore, based on the AFM analysis, we proposed two modes for the enhanced mechanical properties of GO-PVA nanocomposites.

2. Experimental
GO nano-sheets were synthesized from purified natural graphite by the modified Hummers method.[7] PVA powder with two different molecular weight (Mw=72000, 2000) was purchased from Alfa Aesar. The typical well-dispersed GO/PVA layered nanocomposite was fabricated as follows: 5 mg/ml PVA solution (12ml) was gradually added to the GO suspension (1.5 mg/ml, 40ml), and then the mixed solution was sonicated for 10 min with 400w power. Finally, by filtrating the homogeneous GO/PVA solution through a cellulose membrane filter (47 mm in diameter, 0.22 μm pore size), GO/PVA nanocomposite paper was fabricated following by air drying and peeling from the filter. Samples of nanocomposite paper prepared in this manner were cut into strips (30mm×2 mm) by a razor blade and then dried at 333 K over 12 h with a vacuum oven before further tests.

Typical tapping-mode AFM measurements were performed using Dimension 3100. Samples for AFM images were prepared by depositing a
dispersed GO or GO-PVA solution (20 μg/mL) onto a freshly cleaved mica surface and allowing them to dry in air. The cross section of nanocomposite paper was studied by field-emission SEM (HITACHI S-4800). X-ray diffraction (XRD) measurements for nanocomposite samples were performed at room temperature using specular reflection mode (Cu Kα radiation, XPert PRO, PANalytical, Holland). A dynamic mechanical analyzer (TA, DMA Q800) were employed to evaluate the mechanical performances of GO-PVA nanocomposite paper. The static tensile tests were conducted in displacement ramp mode with a pre-strain 0.01% and a ramp rate of 20 μm/min. Short time creep tests were performed in the tensile mode at room temperature with the applied stress about 40 MPa and the creep strain were determined as a function of time (t_{creep}=10 min, t_{discovery}=10 min).

3. Results and Discussion

Fig.1a shows the XRD patterns of GO-PVA nanocomposite paper, the sharp peak of nanocomposite paper indicates that the graphene oxide nanosheets had packed into well ordered architecture. Additionally, compared to GO paper, the intercalation of PVA chains between the nanosheets resulted in the increasing d-spacing from initial ~0.83nm to ~1.35nm. Based on the above analysis, we can infer the nacre-like structure of the GO-PVA nanocomposite where nanosheets and polymer chains alternately pile up (Fig.1b). Due to the hydroxyl groups of both alternant components, hydrogen bonds between the nanosheets and PVA polymer chains would largely form and consequently enhance the interactions. In this structured composite, PVA chains may work as the soft organic materials in natural nacre and GO nanosheets would be the oriented inorganic crystals. Accordingly, the nanocomposites provided with this architecture character are expected to transfer the exceptional mechanical properties of nanoscale materials to the macroscale properties of the bulk materials and behave excellent performance. As shown in Fig.1c, typical tensile curves of GO-PVA nanocomposite display ~4 times higher strength and ~2 times higher modulus when compared with GO papers produced by filtration. Concretely, the GO nanocomposite has an average modulus of 25.5 GPa and a strength of 256.3 MPa, while that of graphene oxide paper are 10.5 GPa and 63.6 MPa respectively. Deduced from the tensile results, the intercalation of PVA polymer definitely improved the load transfer of the adjacent graphene oxide platelets, resulting from the hydrogen bonds or twisted polymer chains. Although the soft polymer chains may weaken the mechanical properties, the enhanced load transfer between nanosheets effectively employ the nanosheets to undertake the stress and finally increased the modulus and strength of nanocomposites.

![XRD patterns of GO paper and GO-PVA nanocomposite paper](image1)

![Schematic representation of the internal architecture of GO-PVA layered nanocomposites](image2)

![Mechanical performance of GO-based nanocomposite](image3)

Fig.1.(a) XRD patterns of GO paper and GO-PVA nanocomposite; (b) Schematic representation of the internal architecture of GO-PVA layered nanocomposites; (c) Mechanical performance of GO-based nanocomposite.

To study the effect of polymer molecules onto the mechanical properties of nanocomposites, we selected two different kinds of PVA with
HIGH MECHANICAL PERFORMANCE OF GRAPHENE OXIDE- POLY(VINYL ALCOHOL) LAYERED NANO COMPOSITES

Mw≈72000 (PVA I), and 2000 (PVA II) respectively. Keeping a constant amount of GO nanosheets, GO-PVA nanocomposite was fabricated by vacuum filtration. From the mass of these papers, the content of GO nanosheets in the fabricated nanocomposites is about 55 wt%. Fig.2 displays SEM characterization of cross-section of nanocomposite paper with well-packed layer structure. Compared with the pure GO paper, the thickness of the GO-PVA nanocomposite papers evidently increases to 14 μm from 7 μm due to the intercalation of PVA polymer.

Fig.2. SEM images of GO paper (a), GO-PVA I nanocomposite (b) and GO-PVA II nanocomposite (c), demonstrating increased thickness due to intercalation of PVA polymer.

Fig.3a presents the typical stress-strain curves of GO-PVA nanocomposite papers which the molecular weight of PVA polymers are 72000 (PVA I), and 2000 (PVA II) respectively. At least five samples were tested for each specimen as summarized in Figure 3b. From these results, the modulus of PVA I and PVA II based nanocomposites are similar in the range of 24~26 GPa. The tensile curves of these two specimens overlap with each other until the final break of GO-PVA II nanocomposite paper. As summarized in Fig.3b, the molecular weight of PVA polymer significantly affect the tensile strength of nanocomposite paper. With a larger molecular weight, GO-PVA I nanocomposite paper has a higher average strength of ~256.3MPa, while this value for GO-PVA II nanocomposite paper is ~201.6MPa.

Fig.3. Mechanical properties of the GO-PVA nanocomposite: (a) Typical stress-strain curves of
tensile tests; (b) Summary of modulus and strength for tested samples; (c) Typical creep and recovery curves.

On the basis of the above tensile tests, it could be inferred that hydrogen bonds between the nanosheets and PVA polymer chains can enhance the interactions of adjacent nanosheets and consequently improve the mechanical behaviors of nanocomposite paper. And additionally, with a larger molecular weight PVA, the mechanical improvement is more pronounced. Here the creep and recovery curves at 40MPa in Figure 3c further reflect the relative slippages of adjacent layers. Compared to pure GO paper, GO-PVA nanocomposite paper exhibits less creep strain and residual deformation after recovery, which implies that the enhanced interlayer interactions could effectively restrain the slippage of the neighboring nanosheets. Similar to the tensile results, larger molecular weight PVA favors better creep improvement of nanocomposite.

To further unveil the interactions between neighboring nanosheets, we analyzed the status variations before and after mixing with PVA polymer by AFM. As indicated in Fig.4a, the thickness of nanosheets is within a narrow range of 0.9-1.0 nm. In a same plane, GO nanosheets look like isolated island and the size of nanosheets is not so uniform due to the ultrasound effect. In Fig.4b, the state of GO sheets is totally different after mixing with PVA polymer. On one hand, because of the hydrogen bonds between the PVA chains and basal planes of GO nanosheets, polymer chains would easily coat the nanosheets and then the thickness increases to 1.8-2.4 nm. The coating PVA polymer would enhance the interlayer interactions and resist the applied loads due to the hydrogen bonds between the polymer and nanosheets. On the other hand, “isolated islands” are linked as networks, illustrating PVA polymer chains can bridge the adjacent nanosheets on the same plane. On tensile loading, the bridging PVA polymer can resist normal deformations between nanosheets that are on the same plane. Generally, both the coating polymer and bridging polymer would benefit the load transfer between the nanosheets and mechanical improvements.

4. Conclusion
In summary, we fabricated GO-PVA layered nanocomposite paper with high mechanical performance by vacuum-assisted self-assembly
HIGH MECHANICAL PERFORMANCE OF GRAPHENE OXIDE-POLY(VINYL ALCOHOL) LAYERED NANOCOMPOSITES

...technique, in which the nanosheets component takes up over 50 wt% and acts as the principal framework. Nacre-like structure of the nanocomposites was inferred with XRD tests, in which graphene oxide sheets and polymer chains alternately pile up. Tensile results demonstrated that GO-PVA nanocomposite displayed ~4 times higher strength and ~2 times higher modulus in compare with pure GO papers. In addition, polymer molecular weight evidently affected the mechanical properties of layered nanocomposites. Larger molecular weight PVA favored better mechanical improvements of nanocomposite. Furthermore, based on the AFM analysis, we proposed two modes for the enhanced mechanical properties of GO-PVA nanocomposites.

References


