



# Precisely controlled growth of poly(ethyl acrylate) chains on graphene oxide and the formation of layered structure with improved mechanical properties



Rui Cao<sup>a</sup>, Ze Chen<sup>a</sup>, Yanhong Wu<sup>a</sup>, Yingfeng Tu<sup>a</sup>, Gaoxiang Wu<sup>b</sup>, Xiaoming Yang<sup>a,\*</sup>

<sup>a</sup>State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Suzhou Key Laboratory of Macromolecular Design and Precision Synthesis, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, Department of Polymer Science and Engineering, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, PR China

<sup>b</sup>Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, PA 19104, USA

## ARTICLE INFO

### Article history:

Received 21 September 2016

Received in revised form 12 November 2016

Accepted 16 November 2016

Available online 17 November 2016

### Keywords:

Graphene oxide

Poly(ethyl acrylate)

Layered structure

Mechanical properties

## ABSTRACT

A biologically inspired, multilayer laminate structural design is realized by using hybrid films of poly(ethyl acrylate) (PEA) graft graphene oxide (GO) synthesized by Ce(IV)/HNO<sub>3</sub> redox system in aqueous solution. Due to the moderate activity of ethyl acrylate (EA) monomers, the added amount of monomers exhibits a linear relationship with the grafted content of PEA on the GO surface. This indicates that the grafting process of PEA chains on the GO surface is well-controlled. Then, hybrid films with layered structures are fabricated by the vacuum-assisted filtration macroscopic assembly method, and the mechanical properties of the formed hybrid structures are investigated. The fracture stress of the film are significant improved to 83.92 MPa with even a low content of PEA (3.46 wt%). The mechanism of the enhanced mechanical property is related to its unique composite microstructures similar to the brick-and-mortar system in natural nacre.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

After millions of year evolution in the nature, the hierarchical microstructured biocomposites composed of mineral particles and a protein matrix, such as bone, teeth, or nacre exhibit remarkable strength and toughness [1–4]. Nacre in particular, consisted of high content of aragonite calcium carbonate platelets and 5% organic biopolymer, has been found with incomparable strength and toughness. The remarkable mechanical properties are attributed to their unique structures, i.e. a highly ordered brick-and-mortar arrangement of hard and soft building blocks and interfacial interactions between layered inorganic platelets and organic proteins. The layered structure provides inspiration of designing high performance artificial composite materials, [5–9] with applications in a variety of fields, such as gas barriers [10], sensors [11], separator [12,13], electrical conductors [14,15], dielectric properties [16], and moisture permeability [17], superoleophobic materials [18].

For the mimic nacre materials, the inorganic components play a key role in promoting exceptional mechanical properties [19] such as aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) flake [20], carbon nanotubes [21], and nanoclay [22] have been used to successfully. Recently, graphene

oxide (GO) based 2D materials have been demonstrated with outstanding mechanical properties, making it a widely adopted component for fabricating the high performance free-standing layered materials [23–29]. The interfacial bonding between the GO and polymer have a huge influence to the GO-based artificial nacre. In generally, the GO were incorporated into the polymer was a sample method to functional the GO such as the Yuan Hu's work [30]. The GO was dispersed into the poly(vinyl alcohol) owing to their hydroxyl groups and various hydrogen bonds which make dispersion easy and obtain remarkable enhancements in mechanical properties. Meanwhile, the *in-situ* polymerization method was often used to functionalization of the GO. Example for the Jang-Kyo Kim's work, they used simultaneous *in-situ* reduction and self-alignment of GO sheets to synthesis GO/water-borne epoxy composites without the organic solvents and the reduction of GO have a highly stable dispersion in aqueous epoxy by the covalent bonding and Non-covalent bonding [31]. Inspired by the natural nacre, Cheng's group introduced the MoS<sub>2</sub> as the lubricant into the GO-based artificial nacre to improve the tensile strength and toughness [32]. At the same time, they introduced the PCDO polymer as the mortar and cross-linker of adjacent GO sheets by the covalent bond which could improve the artificial nacre tensile and toughness and higher conductive [33–37]. Anyway, the GO-based nanocomposites have been summarized at Table S2 [8]. In

\* Corresponding author.

E-mail address: [yangxiaoming@suda.edu.cn](mailto:yangxiaoming@suda.edu.cn) (X. Yang).

our previous works [38–40], polystyrene (PS) and poly(*n*-butyl acrylate) (PBA) grafted GO were synthesized by Ce(IV)/HNO<sub>3</sub> redox system in aqueous solution. The biomimetic layered materials were prepared by a “bottom-up” strategy from assembling flakes of polymer grafted GO as building blocks. Such a fabrication process can simultaneously avoid local phase separation and introduce strong interfacial interaction between GO layers. Our previous studies show that the layered structure formed by PS and PBA grafted GO had better mechanical properties than pure GO. And we summarized the mechanical properties of bioinspired graphene-based nanocomposites with different interface bonding or structure (Fig. S1). We can see the synergistic effect have a huge advantage than the single interfacial interaction and our method could obtain appropriately mechanical properties [8,41–47,37,34,40]. Meanwhile, the  $T_g$  (glass transition temperature) of the grafted polymers can strongly affect the mechanical properties of composite film. The PS grafted GO films show improved strength and modulus but lower strain to fracture and lower toughness [39,40]. The possible reason is that the polymer chains are confined strictly within the inter-lamellar space between the nanosheets due to high  $T_g$ . Thus, the polymer chains cannot uncoil, and the intermolecular slide is restricted. Meanwhile, the grafted contents of PS are low (12 wt%) due to the low activity of the monomers. So, later we introduced monomers with higher activity, i.e. *n*-BA. The weight fraction of PBA in the composite films can then cover a wide range from 3.5 to 77 wt% by adding increased amount of *n*-BA monomers [40]. Interestingly, by tuning the amount of grafted PBA, a wide range of mechanical properties (tensile strength from 20 to 180 MPa, Young's modulus from 0.1 to 7 GPa, toughness from 0.8 to 4.3 MJ/m<sup>3</sup>, elongation from 1.2% to 24.5%) were realized. PBA grafted GO shows larger fracture strain, higher modulus and toughness attributed to lower  $T_g$  of the PBA (−54.15 °C) [48], which allows the chain movement of PBA during tensile tests at the room temperature. Yet, the activity of BA monomers was found too high to control polymerization process. Chain transfer occurs in the process of polymerization, which results in large amount of non-grafted free polymers. These free polymers need to be removed, which lead to complicated experimental procedures. Here, another monomer system, i.e. ethyl acrylate (EA), known with moderate activity is investigated in this work. The results show that the improved controlling of the polymerization process can be realized. Furthermore, the poly(ethyl acrylate) (PEA) has a low  $T_g$  of −24 °C and thus is expected to achieve good mechanical properties similar to PBA-GO system [48].

Here, we obtained PEA-grafted GO nanocomposites through an *in-situ* polymerization using Ce(IV)/HNO<sub>3</sub> redox system as initiator, a method with advantages of simple manufacturing techniques, low cost, and versatile choices of monomers [38,39]. More importantly, the polymerization process is well-controlled. The amount of PEA grafted onto the surface of GO can be controlled precisely. Furthermore, by adjusting the amount of EA, the mechanical properties and morphologies of the composite films can also be controlled. At lower content of PEA, during the vacuum-assisted filtration process, PEA-grafted GO sheets assembled into layered and “friction” structures. The mechanical properties of hybrids were investigated in this study. To further study the temperature effect, we introduced the dynamic mechanical analysis (DMA) to test the mechanical properties of hybrids at the different temperatures.

## 2. Experimental

### 2.1. Materials

Graphite was purchased from Uni-Chem. N,N-dimethylformamide (DMF), tetrahydrofuran (THF), sodium

hydroxide (NaOH), ethyl acrylate (EA), alcohol and nitric acid (65–68 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. EA was washed by 5 wt% NaOH aqueous solution and vacuum-distilled to remove the inhibitor prior to polymerization. Ceric ammonium nitrate (CAN) (Aldrich) was used without further purification. Stock solutions of Ce(IV) were prepared from CAN in aqueous nitric acid (1 mol/L).

### 2.2. Synthesis of PEA grafted GO

The well-dispersed GO was synthesized from graphite powder using a modified Hummers method [49,50], and stored in stock aqueous suspensions at 5–8 g/L. The synthesis of PEA grafted GO (GO-PEA) is similar to our previous reports [38–40]. A typical operation procedure of synthesis was carried out as follows: First, the GO was dispersed in water and sonicated in sonic bath for 30 min followed by introducing 20 mL of CAN in 1 mol/L nitric acid solution. The mixture was introduced under the protection of N<sub>2</sub> flow, and then the EA monomer was added to the solutions by drops under nitrogen atmosphere. The polymerization experiments were carried out at 60 °C for 4 h. After polymerization, the products were collected by vacuum filtration, washed by alcohol and DMF to get rid of the residual monomers and free polymers. The brown product was redispersed into DMF via stirring for 12 h. Finally, a dark red solution was obtained.

### 2.3. Preparation of GO-PEA hybrid films

By the vacuum filtered, the GO or GO-PEA solution become GO or GO-PEA hybrid film through a Millipore filter (47 mm in diameter and 0.45 μm in pore size). Subsequently, the filters supported GO or GO-PEA hybrid film was dried under vacuum. The thickness of the as-prepared free-standing GO or GO-PEA hybrid films was determined by the amount of solution.

### 2.4. Characterization

Mechanical properties at room temperature were tested by Instron-3365 with gauge length of 10 mm, and loading rate of 0.5 mm/min, and the relative humidity was 50% at the tensile test. Tensile tests at the different temperatures were conducted with a dynamic mechanical analysis (Q800 DMA, TA Instruments) where relative humidity was 48% at the test. The samples were gripped using film tension clamps with a clamp compliance and soaking at −10 °C, 40 °C for 5 min. All tensile tests were conducted in controlled force mode with a preload of 0.01 N and a force ramp rate of 0.2 N min<sup>−1</sup>.

All the tested rectangular strips were about 30 mm in length and 2 mm in width. The exact widths were measured by a slide caliper and the thicknesses were carefully determined by scanning electron microscopy (SEM). SEM images were obtained with a field emission scanning electron microscope (SEM, Quanta 400 FEG). Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Pyris 6 TGA instrument thermal analyzer at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 instrument (Thermo Electron) with Al K $\alpha$  radiation. X-ray diffraction (XRD) analysis was performed on X'Pert-Pro MPD diffractometer with a Cu K $\alpha$  radiation source at room temperature. Raman spectra were recorded from 800 to 2000 cm<sup>−1</sup> with a Renishaw spectrometer using a 514 nm argon ion laser. AFM characterization was carried out on the Dimension Icon AFM under tapping mode and the samples were prepared by spin-coating onto silica at 1000 rpm from sample solutions in DMF. Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) were obtained with Bruker Vertex 70.

Download English Version:

<https://daneshyari.com/en/article/5439661>

Download Persian Version:

<https://daneshyari.com/article/5439661>

[Daneshyari.com](https://daneshyari.com)