# *In Situ* Polymerization Approach to Poly(ε-caprolactone)-Graphene Oxide Composites

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#### Abstract

The grafting of graphene oxide (GO) with a cyclic ether monomer,  $\varepsilon$ -caprolactone ( $\varepsilon$ -CL), directly affords graphene-PCL nanocomposites. The resulting nanocomposites show good solubility in the solvents of polymers, exfoliation of graphene in the polymer matrix and excellent mechanical properties and robustness under bending.

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#### Keywords

Graphene, composites, ring-opening polymerization

## 1. Introduction

Graphene, a monolayer of sp<sup>2</sup>-hybridized carbon atoms arranged in a twodimensional lattice, has attracted tremendous attention in recent years owing to its exceptional thermal, mechanical and electrical properties [1–3]. One of the most promising applications of this material is in polymer nanocomposites, polymer matrix composites which incorporate nanoscale filler materials [4]. Graphene-based hybrid materials have attracted a great deal of attention due to their promising applications in fields such as catalysis, biosensors and nanoelectronic devices [5, 6]. Up to date, diverse methods for the functionalization of graphene have been developed [7–9]. However, it is difficult to control and quantify the functionality, density, and thickness of grafted materials [10]. Thus, it is still a challenge to prepare graphene-based composite. Although graphene is functionalized when reduced from GO, the residual oxidized functional groups are not sufficient to sustain the high surface area necessary for long-term stable dispersion in solvents [11]. Therefore, for many applications, it is necessary to modify the surface of graphene in

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order to dissolve it in the required solvents, or to increase the interfacial interaction between the matrix and graphene. There are two main methods of functionalization: (i) non-covalent attachment of large/small aromatic-containing molecules through  $\pi-\pi$  stacking [12, 13]; (ii) covalent attachment of molecules through chemical bonding [14, 15]. The advantage of using non-covalent attachment is that it functionalizes the graphene surface without risking significant damage to it. However, the forces of physical interaction might be weak, making the load-transfer efficiency of the reinforcement of the composites quite low. In order to overcome these problems, covalent method above may offer a better way to functionalize graphene through chemical bonding.

In the study described herein, samples of covalently functionalized graphene were prepared by an *in situ* polymerization approach. Using the abundant oxygencontaining functional groups of GO as directly reactive sites, they are also the restorable sites for the construction of covalent bonding without any pretreatment. In our strategy, GO was synthesized by a modified Hummers and Offerman method [16]. Subsequently, the chemical grafting of poly( $\varepsilon$ -caprolactone) (PCL) onto the GO sheets was carried out by the grafting-from approach based on *in situ* ring-opening polymerization of  $\varepsilon$ -caprolactone ( $\varepsilon$ -CL) [17–19].

## 2. Experimental

## 2.1. Materials

Graphite powder (40 µm) was obtained from Qingdao Henglide Graphite. Concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), potassium permanganate (KMnO<sub>4</sub>), sodium nitrate (NaNO<sub>3</sub>) and methylene blue were purchased from Shanghai Reagents and used as received.  $\varepsilon$ -Caprolactone ( $\varepsilon$ -CL, 99%; Acros) was dried over CaH<sub>2</sub>, distilled under reduced pressure, and stored under a nitrogen atmosphere. Tin (II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>, 98%) purchased from East China Chemical and used as received. Other reagents were purchased from Shanghai Chemical Reagent and used as received.

## 2.2. Preparation of Hyperbranched Polymers-Graphene (HPG) Composites

First, GO was synthesized through graphite powder oxidation with sulfuric acid and potassium permanganate (H<sub>2</sub>SO<sub>4</sub>–KMnO<sub>4</sub>) [16, 20]. The chemical grafting of PCL onto the GO sheets was carried out by the grafting-from approach based on *in situ* ring-opening polymerization of  $\varepsilon$ -CL [17]. In a typical experiment, GO and  $\varepsilon$ -CL were added into a Schleich tube to form dispersion solution under sonication at room temperature for 1 h. And then, the catalyst tin (II) 2-ethylhexanoate, Sn(Oct)<sub>2</sub>, was added into the reaction tube. After reaction for the desired time, a homogeneous black solid (PCL-G) was obtained. The original solid was then dissolved in THF and precipitated in cold methanol.

### 2.3. Characterization

The <sup>1</sup>H-NMR spectra were recorded on an Avance AV 400 MHz Digital FT-NMR spectrometer operating at 400 MHz using deuterated CDCl<sub>3</sub> as a solvent. The sizes and morphologies of the resultant samples were characterized by JSM-2100 transmission electron microscopy (TEM) at an accelerating voltage of 200 kV, whereby a small drop of sample solution was deposited onto a carbon-coated copper EM grid (200 mesh) and dried at room temperature at atmospheric pressure. Thermogravimetric analysis (TGA) was performed on a Pyris Diamond 1 instrument at a heating rate of 20°C/min from 25 to 550°C in a flow of nitrogen. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5700 spectrophotometer using a KBr pellets for samples. The XRD pattern was analyzed by using a X-ray diffractometer (Siemens Diffraktometer D5000) using a  $CuK_{\alpha}$  radiation source at 35 kV, with a scan rate of  $0.02^{\circ}$ . AFM samples were prepared by drop-casting modified graphene on Mica surface. AFM images were obtained by a Molecular Imaging Picoscan II instrument in tapping mode. The mechanical properties of nanocomposites were measured using a universal testing machine (CMT-4102, SANS Group) at room temperature. A load cell of 500 N was employed and the tensile rate imposed was 1 mm/min. All samples were cut into the dumbbell shape with a razor blade. More than five tests were conducted for each sample, from which the mean values and standard deviations were derived.

#### 3. Results and Discussion

The synthesis of PCL-G is schematically shown in Fig. 1A. The first step is to synthesize GO sheets by completely oxidizing natural graphite with aid of ultrasonication. The FT-IR spectra of GO and natural graphite (Fig. 2) show that the characteristic peaks of the GO include the C=O carbonyl stretching vibration at 1720 cm<sup>-1</sup>, the –O–H deformation vibration at 1400 cm<sup>-1</sup>, the –OH stretching at 1230 cm<sup>-1</sup> and the C–O stretching at 1060 cm<sup>-1</sup> [9]. The resultant GO can be easily dissolved in water without dispersants, as shown in Fig. 1B. The X-ray diffraction (XRD) pattern of GO and natural graphite further confirm the efficient oxidation of graphite [21]. SEM and TEM images of the GO sheets show that the graphene oxide are slightly wrinkled and folded, and their sizes are >1 µm.

After successful grafting, the covalently grafted chains of PCL change the surface properties of graphene sheets and impact good solubility to the modified graphene in the good solvents of PCL. The resultant PCL-G are dissolved homogenously in CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, DMF, THF, toluene and ethyl acetate, without aggregation of graphene sheets for half a month, implying the high efficiency of polymer grafting, as shown in Fig. 1B. To confirm the successful grafting effect on the graphene sheets, we recorded the <sup>1</sup>H-NMR sprectrum; the protons from PCL can be observed (Fig. 3A) [17, 22].

As shown in Fig. 3B, TGA traces of pristine graphite show a negligible weight loss, while GO shows much lower thermal stability. The major weight loss of GO



**Figure 1.** (A) Scheme of grafting of poly( $\varepsilon$ -caprolactone) (PCL) onto graphene sheets. (B) Solubility of GO in H<sub>2</sub>O and PCL-G in different solvents.



Figure 2. FT-IR spectra of natural graphite and graphene oxide sheets.

occurs at  $180^{\circ}$ C, which can be assigned to the pyrolysis of the labile oxygencontaining functional groups, yielding CO, CO<sub>2</sub> and steam [21, 23]. However, PCL-G is more stable than GO and PCL. The increased thermal stability of the hybrid nanostructures could be attributed to the chemical grafting of PCL onto the GO surface.

The morphological properties of the GO and PCL-G were studied by atomic force microscopy (AFM). AFM is commonly used to study the surface morphology of a material in nanometer scale. It provides high-resolution imaging and measure-



**Figure 3.** <sup>1</sup>H-NMR spectrum of PCL-G composites in CDCl<sub>3</sub> at room temperature and TGA curves of natural graphite (A), GO (B), pure PCL (C) and PCL-G (D) composites.



**Figure 4.** AFM height image of GO (A) and PCL-G composites (C) on mica deposited from CHCl<sub>3</sub> solution. 3D-view images of GO (B) and PCL-G composites (D) on mica.

ment of surface topography and properties on the molecular scale [24]. The samples for AFM were deposited by spin-casting from its chloroform solution. Figure 4A and C shows the tapping mode AFM images of GO and PCL-G sheets, respectively. The grafted chains on two sides of graphene sheets increase its thickness to about 15 nm, compared to the thickness of GO about 1 nm. In the case of



Figure 5. TEM images of GO (A) and PCL-G composites (B).

PCL-G, the grafted polymers cover the whole plane of graphene with a bumped surface (Fig. 4D), compared to the even height of GO (Fig. 4B), suggesting the high density of grafting PCL with a fabulous efficiency. Interestingly, the irregularities of the PCL-G's surface represent the different size PCL molecules non-uniformly anchored on the substrate surface for the functional initiator sites' non-uniform distribution.

In order to further investigate the morphologies of the prepared hybrids, TEM images were recorded. Figure 5A and B shows the TEM images of GO and PCL-G. From the TEM image of GO, it can be seen the presence of graphene layer with smooth surface. After grafting of PCL onto the surface of GO, a significant change was observed. Figure 5B shows the morphology of PCL-G, in which the dark regions are related to the grafted PCL onto the GO surface. It is interesting to note that the intensity of the dark color on the basal plane of GO is relatively higher than on the edges, indicating the higher density of grafted PCL on these regions. It can be explained by higher density of hydroxyl functional groups on the basal plane of GO [21, 25].

Given the excellent elastic modulus and intrinsic strength of graphene sheets [26–29], we examined the effect of functionalized graphene sheets on the mechanical properties of PCL-G composites. Figure 6A presents the representative stress–strain curves of pristine PCL and PCL-G composites. Pure PCL performs a tensile strength of 3.0 MPa and an elongation-at-break of 140%. In the case of PCL-G composites, tensile strength increased to 7 MPa (2.3-times that of PCL), accompanied by a further decrease of elongation-at-break to 80%. Undoubtedly, the excellent reinforcement of graphene could be attributed to the good dispersion of graphene sheets in composites and the strong interaction between the PCL-grafted graphene and PCL matrix. Figure 6B shows the photos of the as-made composites after being removed from the filter membrane. The as-made composite is very flexible and shows certain mechanical robustness when subjected to bending.

## 4. Conclusion

In summary, an efficient strategy for the preparation of an organic–inorganic hybrid material containing graphene oxide and PCL by an *in situ* grafting approach is



Figure 6. Stress–strain curves of neat PCL and PCL-G composites (A) and the as-prepared composites showing the mechanical robustness when subjected to bending (B).

demonstrated. The resultant nanocomposites show good solubility in the solvents of polymers. The efficient PCL grafting makes the graphene homogeneously dispersed in polymer matrix and increased the mechanical properties of resultant composites. The *in situ* grafting polymerization approach paves the way to prepare graphene-based nanocomposites with high performances and novel functionalities.

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## References

- Y. Zhu, S. Murali, W. Cai, X. Li, J. W. Suk, J. R. Potts and R. S. Ruoff, *Adv. Mater.* 22, 3906 (2010).
- 2. A. K. Geim and K. S. Novoselov, Nature Mater. 6, 183 (2007).
- 3. O. C. Compton and S. B. T. Nguyen, Small 6, 711 (2010).
- 4. J. R. Potts, D. R. Dreyer, C. W. Bielawski and R. S. Ruoff, Polymer 52, 5 (2010).
- S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, R. D. Piner, S. T. Nguyen and R. S. Ruoff, *Nature* 442, 282 (2006).

- 6. T. Ramanathan, A. A. Abdala, S. Stankovich, D. A. Dikin, M. Herrera-Alonso, R. D. Piner, D. H. Adamson, H. C. Schniepp, X. Chen, R. S. Ruoff, S. T. Nguyen, I. A. Aksay, R. K. Prud'Homme and L. C. Brinson, *Nature Nanotechnol.* 3, 327 (2008).
- P. Blake, P. D. Brimicombe, R. R. Nair, T. J. Booth, D. Jiang, F. Schedin, L. A. Ponomarenko, S. V. Morozov, H. F. Gleeson, E. W. Hill, A. K. Geim and K. S. Novoselov, *Nano Lett.* 8, 1704 (2008).
- 8. G. Eda and M. Chhowalla, Nano Lett. 9, 814 (2009).
- 9. R. Pasricha, S. Gupta and A. K. Srivastava, Small 5, 2253 (2009).
- S. H. Lee, D. R. Dreyer, J. An, A. Velamakanni, R. D. Piner, S. Park, Y. Zhu, S. O. Kim, C. W. Bielawski and R. S. Ruoff, *Macromol. Rapid Commun.* 31, 281 (2010).
- M.-C. Hsiao, S.-H. Liao, M.-Y. Yen, P.-I. Liu, N.-W. Pu, C.-A. Wang and C.-C. Ma, ACS Appl. Mater. Interfaces 2, 3092 (2010).
- 12. Q. Su, S. Pang, V. Alijani, C. Li, X. Feng and K. Müllen, Adv. Mater. 21, 3191 (2009).
- 13. Q. Yang, X. Pan, F. Huang and K. Li, J. Phys. Chem. C 114, 3811 (2010).
- 14. H. J. Salavagione, M. A. Gómez and G. Martińez, Macromolecules 42, 6331 (2009).
- 15. K. P. Loh, Q. Bao, P. K. Ang and J. Yang, J. Mater. Chem. 20, 2277 (2010).
- 16. W. Hummers and R. Offerman, J. Am. Chem. Soc. 80, 1339 (1958).
- 17. G. Jiang and H. Xu, J. Appl. Polym. Sci. 118, 1372 (2010).
- 18. S. Yurteri, I. Cianga and Y. Yagci, Designed Monomers Polymers 8, 61 (2005).
- 19. A. Harrane, R. Meghabar and M. Belbachir, Designed Monomers Polymers 9, 181 (2006).
- 20. T. A. Pham, N. A. Kumar and Y. T. Jeong, Synth. Met. 160, 2028 (2010).
- 21. X.-Z. Tang, Z. Cao, H.-B. Zhang, J. Liu and Z.-Z. Yu, Chem. Commun., 3084 (2011).
- 22. G. Jiang, W. Chen and Z. Wang, Macromol. Indian J. 3, 8 (2007).
- S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhamma, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon* 45, 1558 (2007).
- 24. Z. Xu and C. Gao, Macromolecules 43, 6716 (2010).
- 25. M. Jahan, Q. Bao, J.-X. Yang and K. P. Loh, J. Am. Chem. Soc. 132, 14487 (2010).
- 26. S. Park and R. S. Ruoff, Nature Nanotechnol. 4, 217 (2009).
- 27. D. Li and R. B. Kaner, Science 320, 1170 (2008).
- 28. C. G. Lee, X. D. Wei, J. W. Kysar and J. Hone, Science 321, 385 (2008).
- 29. A. K. Geim, Science 324, 1530 (2009).