

Supporting Information for

Covalent Modification of Graphene as 2D Nanofiller for Enhanced Mechanical Performance of Poly(glutamate) Hybrid Gels

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Experimental

Materials

Graphite powder (98%, J&K Scientific Co.), triphosgene (Aladdin Industrial Inc.), hydrogen peroxide (A.R., Bodi Chemical Co., China), and γ -benzyl-L-glutamate (A.R., Tongsheng amino acids Ltd., China) were used as received. Thionyl chloride (SOCl_2 , A.R., Bodi Chemical Co.), N,N-dimethylformamide (DMF, A.R., Kelong Chemical Co., China), and propylamine (A.R., Bodi Chemical Co.) were used after distilled.

Synthetic procedures

Preparation of PBLG. The γ -benzyl-L-glutamate-N-carboxyanhydride (BLG-NCA) monomer was synthesized from the reaction of γ -benzyl-L-glutamate using the method as reported.⁴⁰ (Yield: 57.6%) The product was characterized by ^1H NMR (400 MHz, CDCl_3): δ = 7.28–7.38 (5H, m, Ar), 6.35 (1H, s, NH), 5.14 (2H, s, Ar- CH_2), 4.35 (1H, t, α -CH), 2.50 (2H, t, γ - CH_2), 2.28 (1H, m, β -CH), 2.14 (1H, m, β -CH) ppm, respectively. In a typical experiment of PBLG, the BLG-NCA monomer (0.7899 g, 3.0 mmol) and propylamine (5.9 mg, 0.1 mmol) was dissolved in dry DMF (5 mL) in a Schlenk flask under a nitrogen atmosphere. After stirred and degassed by three freeze-pump-thaw cycles, the tube was sealed under vacuum and the mixture was stirred at room temperature for 3 days. Then the solution was concentrated and dissolved in dichloromethane. Finally, the solid PBLG was precipitated in a large volume of methanol and dried in vacuum overnight. (Yield: 60.8%) And the PBLG samples were characterized by ^1H NMR (600MHz, $\text{CDCl}_3/\text{CF}_3\text{COOH}$ (v:v=85%: 15%)): δ =7.81-7.93 (H, NH), 7.19-7.31 (5H, Ar), 5.02-5.18 (2H, Ar- CH_2), 4.41-4.65(H, α -CH), 2.30–2.42(2H, γ - CH_2), 1.80-2.12 (2H, β - CH_2), 1.25-1.48 (2H, - CH_2 -), 0.71-0.92 (3H, - CH_3) ppm, respectively.

Preparation of GO. Graphene oxide was synthesized by a modified Hummers method.¹⁰ In a typical experiment, graphite (3 g), NaNO₃ (1.5 g) were added to H₂SO₄ (69 mL, conc. 98%) in a 500 mL three-neck flask with stirring in an ice bath. Then KMnO₄ (9 g) was slowly added to the mixture and the temperature was controlled to be lower than 10 °C for 1 h. Then flask with solution was put into a 35 °C oil bath and stirred for 3 h. Then the deionized water (140 mL) was slowly added to the solution, and the temperature of oil bath increased to 98 °C and maintained at this temperature for 30 min. The reaction was terminated by addition of a large amount of 10 wt % HCl solution, followed by treatment of 30 wt % H₂O₂ solution. After the color of the mixture changed to brilliant yellow, the mixture was dialyzed for one week. Then, the yellow brownish suspension was centrifuged at 8000 rpm after sonication for 2 h to eliminate unexfoliated graphitic plates. Finally, the centrifugally sedimentated GO powder was dried under vacuum.

Preparation of GO-COCl. GO (10 mg) was dispersed in anhydrous DMF (5 mL) with the aid of sonification for 3 h. Afterwards, SOCl₂ (20 mL) was slowly added and the mixture was refluxed at 70 °C for 24 h. The chlorinated GO (GO-COCl) was obtained by centrifugation and was purified with anhydrous DMF for three times.

Preparation of GO-g-PBLG via amidation reaction. The GO-COCl (10 mg) dispersed in anhydrous DMF (10 mL) was added to the PBLG solution in anhydrous DMF (60 mL). Then the mixture was cooled to 0 °C and anhydrous triethylamine (2 mL) was added dropwise to the mixture. Afterwards, the reaction mixture was maintained at 50 °C for 24 h followed by filtration and washed with abundant dry DMF for three times. Finally, the obtained GO-g-PBLG was redispersed in toluene for further use.

Preparation of PBLG organogel and GO-g-PBLG/PBLG hybrid organogel. The gel of PBLG homopolymer in toluene was prepared as follows. Briefly, certain amount of PBLG

was added into certain amount of toluene in a sample vial. Afterward, the sealed vial was heated in a water bath at about 70 °C until the mixture became homogeneous, followed by taking out to the ambient condition. Gelation concentration was determined by preparing a series of different concentrated solutions and the gelation was monitored by tube inversion technique. And the sol-gel transition temperature was monitored by tube inversion technique during heating process of the gel.

For the preparation of the GO-g-PBLG/PBLG hybrid organogel in toluene, certain amount of GO-g-PBLG was first dispersed in toluene and then the PBLG was added to the solution. Afterward, the sealed vial was heated in a water bath until the hybrid complex became homogeneous, followed by taking out to the ambient condition. The gelation concentration and the gelation temperature were determined by the same method used in PBLG gel. The sol-gel transition temperatures and concentrations were determined by tube inversion technology (A. R. Hirst, D. K. Smith, M. C. Feiters, H. P. M. Geurts and A. C. Wright, *J. Am. Chem. Soc.* 2003, 125, 9010).

Characterization

¹H NMR spectra were obtained with Bruker 400 and 600 MHz spectrometers using CDCl₃ and CDCl₃/CF₃COOH as solvents. Gel permeation chromatography (GPC) was conducted on a HLC-8380 instrument (Dong Chao Corporation, Japan) with DMF as eluent (0.6 mL/min) in presence of LiBr (1.0 g/L). The calibration curve was obtained with linear polymethyl methacrylate as standards. Fourier transform infrared (FTIR) spectra was conducted on Nicolet 6700 spectrophotometer (Thermal Scientific, USA) in attenuated total reflection mode at resolution of 0.5 cm⁻¹. Thermal gravimetric analysis (TGA) was performed on a Netzsch TG 209 F1 instrument under a nitrogen atmosphere at the heating rate of 10 °C/min from 30 to 800 °C. XPS was carried on an XSAM800 (Kratos Company,

UK) with Al K α as radiation ($h\nu=1486.6$ eV). The 1D wide-angle X-ray diffraction (1D WAXD, X'pert Pro MPD, Philips Company, Netherlands)) was conducted to determine the secondary structure of PBLG, and $q = 4\pi(\sin\theta)/\lambda$, where q is scattering vector, θ is scattering angle and λ the wavelength of X-ray. Rheological measurements were carried out on a Haake Mars III rheometer with a parallel plate (diameter 20 mm). The dynamic oscillatory stress sweep measurements were performed from 0.1 to 100 Pa at a constant frequency of 1 Hz. TEM images were acquired on Tecnai G2 F20 transmission electron microscope (SEI, USA) at 200 kV. TEM samples of GO and GO-g-PBLG were prepared by casting one drop of the corresponding dispersion solution (*ca.* 20 mg) on the carbon-coated copper grid. For the preparation of gel sample of TEM experiment, a fraction of gel was gently placed onto a carbon-coated copper grid.

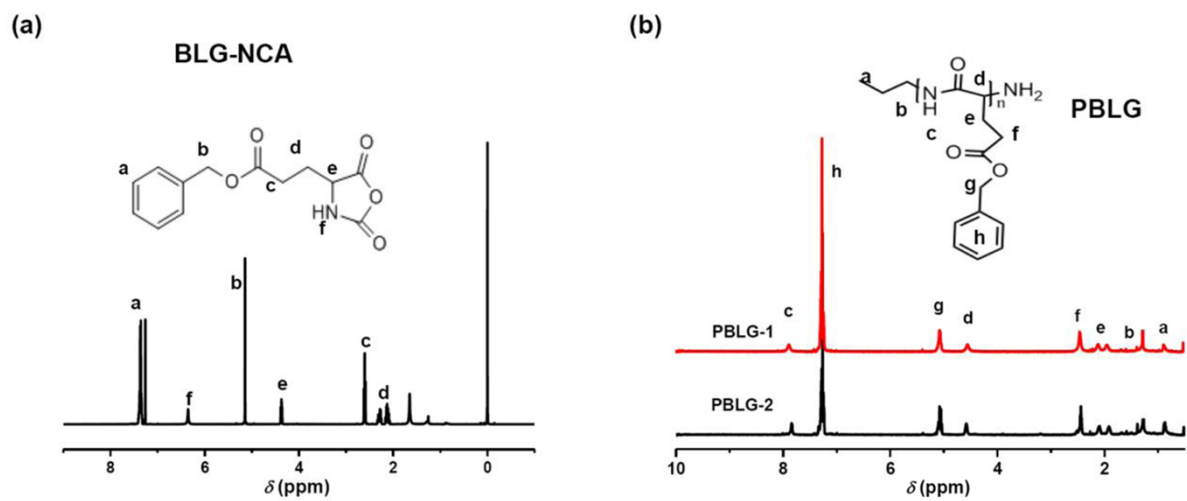


Fig. S1 ^1H NMR spectra of BLG-NCA and PBLG samples.

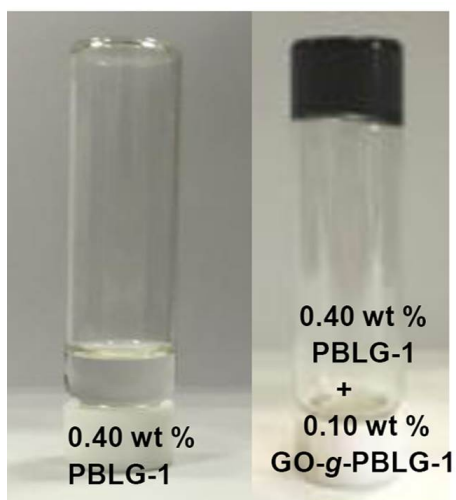


Fig. S2 Digital photographs of solutions or gels of the PBLG-1 and GO-g-PBLG-1/PBLG-1 hybrid complex in toluene with indicated compositions.

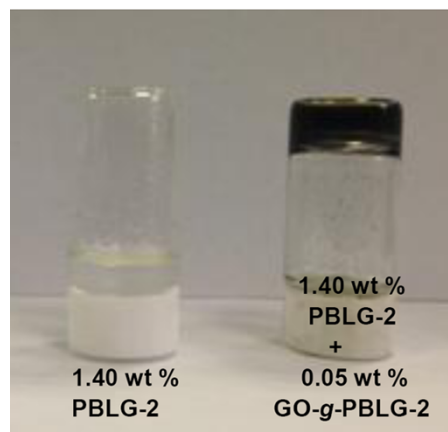


Fig. S3 Digital photographs of solutions or gels of the PBLG-2 and GO-g-PBLG-2/PBLG-2 hybrid complex in toluene with indicated compositions.