Supporting information

Mechanical Reinforcement Fibers Produced by Gel-Spinning of Poly-acrylic acid (PAA) and Graphene Oxide (GO) Composites

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1. Experimental details

All the materials used in this work were of analytical grade, which were commercially obtained and used as received. Graphite oxide was synthesized from expanded graphite (KP9935-300, Qingdao, P.R. China) by a modified Hummers method. As-synthesized graphite oxide was suspended in water to give a golden dispersion, which was subjected to dialysis to completely remove residual salts and acids through a series of purge and centrifugation procedure. Then, the purified graphite oxide suspensions were centrifuged and freeze dried. After that, the graphite oxide powders were dispersed in ultrapure water to create dispersion of 1.000wt%, 0.500wt%, 0.250wt%, 0.125wt%, respectively. Exfoliation of graphite oxide to GO was achieved by ultrasonic treatment using a ZhongChuan Digital Sonifier (ZC-1, Shanghai, P.R. China) for 30 min. In order to prepare GO/PAA gel, 40.00g acrylic acid and 0.30g potassium persulfate were added into the obtained GO aqueous solutions. Under a nitrogen atmosphere, the free radical polymerization reaction of acrylic acid occurred. The reaction temperature was about 60℃, and the reaction time was about 4h. In the end, the GO/PAA gel was obtained.

PGO fibers were spun by homemade spinning equipments. In the spinning process, the GO/PAA gels were extruded through spinneret under pressure. Due to the dry spinning method chose, fibers had to go through the heating tube after generation. In the end, the fibers were collected by the spinning roller. The heating tube length used was higher than 3000.0mm. There are a temperature gradient of the heating tube, which is about 200-500℃ from top to bottom. The rotation speed of spinning roller was about 100mm/s. Furthermore, in order to complete the esterification reaction, the obtained fibers were treated under 150□ for 2h in an oven. After the volatilization of water, the GO content in obtained fiber become 2.42wt.%, 1.21wt.%, 0.61wt.%, 0.30wt.%.

Ultra-depth three-dimensional microscopy (VHX-100, KEYENCE, Japan) and SEM (JEOL 6300FXV operated at 5 kV and Hitachi FE-SEM S-4800 operated at 1 kV) were used for characterization of PGO fibers. SEM samples were coated with a thin layer of gold (about 5 nm) before observation. The XPS analyses (Theta probe, Thermal VG, US) were carried out with a monochromatic Al K-source (15 mA, 14 kV). The spectra were recorded with a vacuum, which was better than 10^{-9} Torr and the energy scale was referenced to the spurious carbon C 1s signal at 284.6 eV. XRD experiments (D/max-Ultima IV, Rigaku Corporation, Japan) were recorded using an optical cross-CBO using a Cu-Kα radiation. Data were recorded in the range of 5-35° 2θ with step of 0.02° 2θ and a counting time of 80 sec/step. Static mechanical uniaxial in-plane sing fiber tensile tests were conducted with a mechanical analyzer according to ASTM-D3379 (CMT8102, MTS, US). The samples were gripped using adhesive. All tensile tests were conducted in a force ramp rate of 10.0mm/min and measurement length of 20.0mm.

2. Supplementary Figure(s):

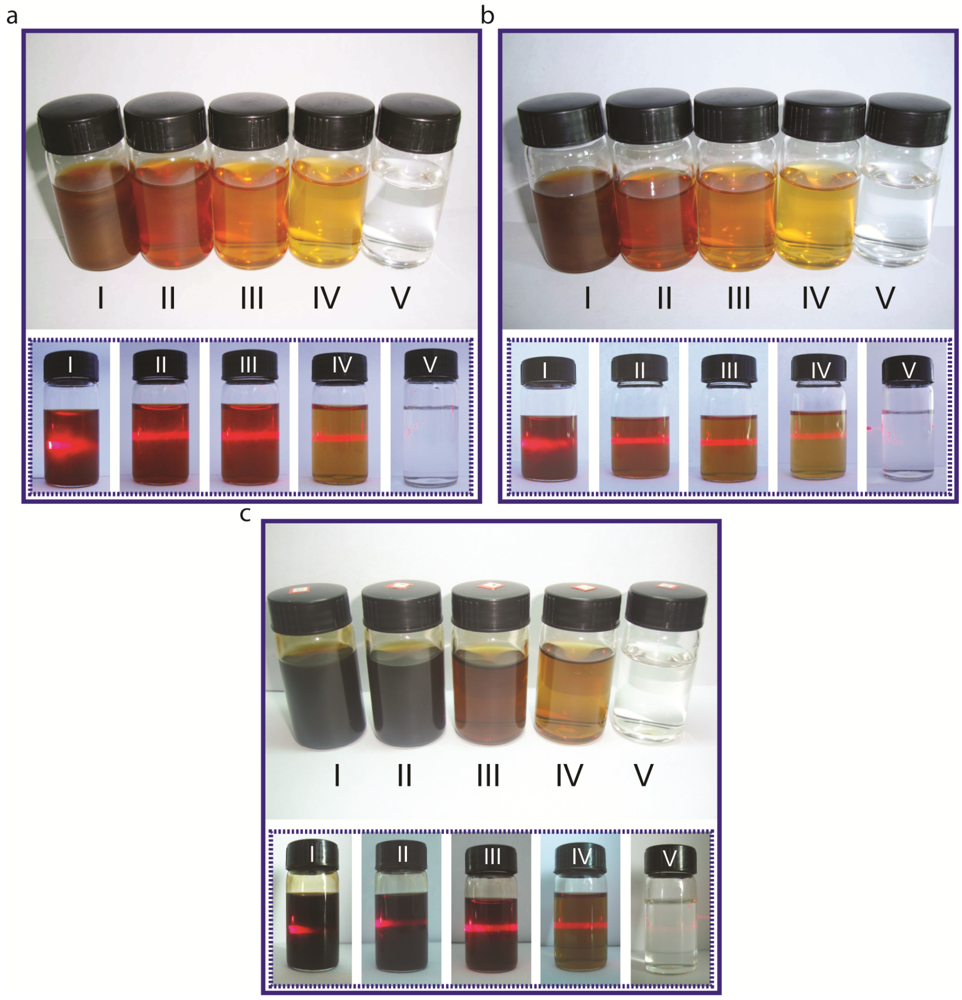

Figure S1. a. Images of the GO aqueous solutions. The GO used are Ⅰ, 1.000 wt.%; Ⅱ,0.500 wt.%; Ⅲ,0.250 wt.%; Ⅳ,0.125 wt.%; Ⅴ.0.000 wt.%. The dyndall effects of corresponding solutions are shown below. All of the GO aqueous solutions give rise to the tyndall effect, in which a laser beam passing through a colloidal solution leaves a discernible track as a result of light scattering. While it also can be found that the tyndall effect for GO aqueous solutions become indistinct after the GO content reached 0.500 wt.%. b. Images of the GO/AA aqueous solutions (acrylic acid and potassium persulfate are all added). The GO used are same as above. The acrylic acid used is 40.000g. The potassium persulfate used is 0.300g. The homogenous solutions show that the additions of acrylic acid do not lead to coagulation of GO. The dyndall effect of the corresponding solutions are also shown below. All of the GO/AA aqueous solutions exhibit the tyndall effect. c. Digital camera images of the GO/PAA gels. The GO concentrations, acrylic acid and potassium persulfate are all same as above. Compared with images in a and b, the colors of the GO/PAA gels are somewhat darken. The homogenous gels indicate the uniformly distribution of GO. And it also indicates that the polymerization of AA will not affect the uniform distributions of GO. All of the GO/PAA gels give rise to dyndall effect.

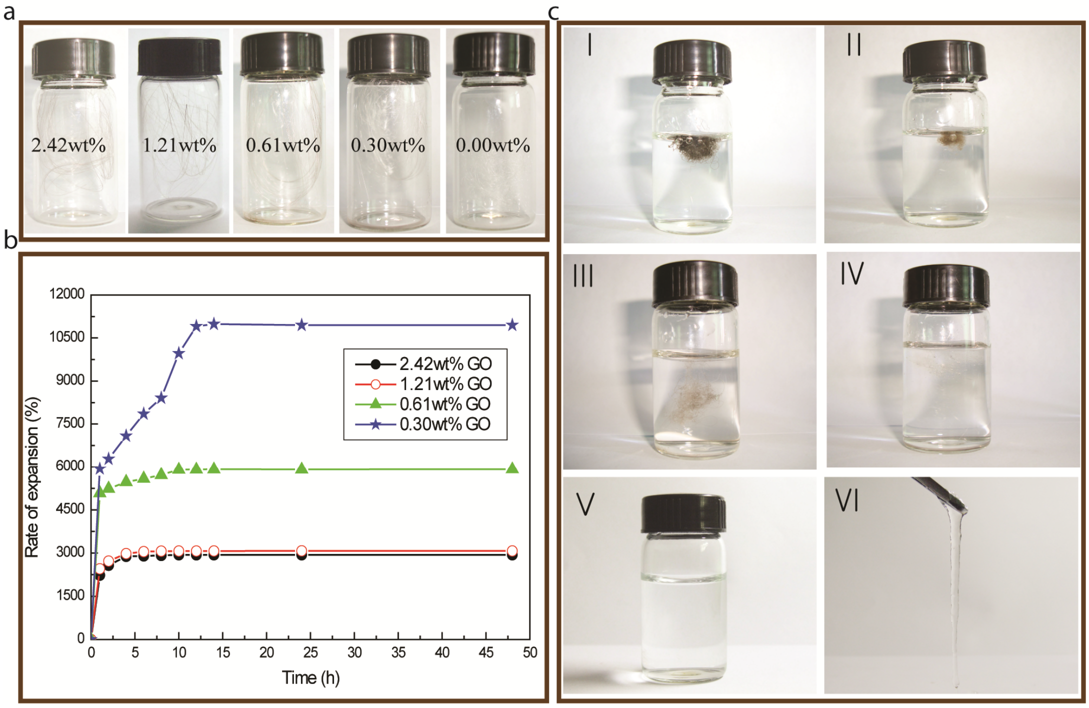

Figure S2. Expansion experiments of PGO fibers and PAA fibers. a. digital images of PGO fibers and PAA fibers. b. Expansion results of the PGO fibers. After 10h, all of the fibers achieve the saturated water absorption. It is found that the crosslinking degrees of PGO fibers have inverse relationship with their absorptions. These results indicate the occurrences of esterification reactions between GO and PAA in PGO fibers. c. digital images of PGO fibers and PAA fibers after water expansion. The weight of GO in fiber used are Ⅰ, 2.42 wt.%; Ⅱ,1.21 wt.%; Ⅲ,0.61 wt.%; Ⅳ,0.30 wt.%; Ⅴ.0.00 wt.%. The image Ⅵ is the status of PGO fiber after water swelling (GO concentration is 0.30 wt.%).

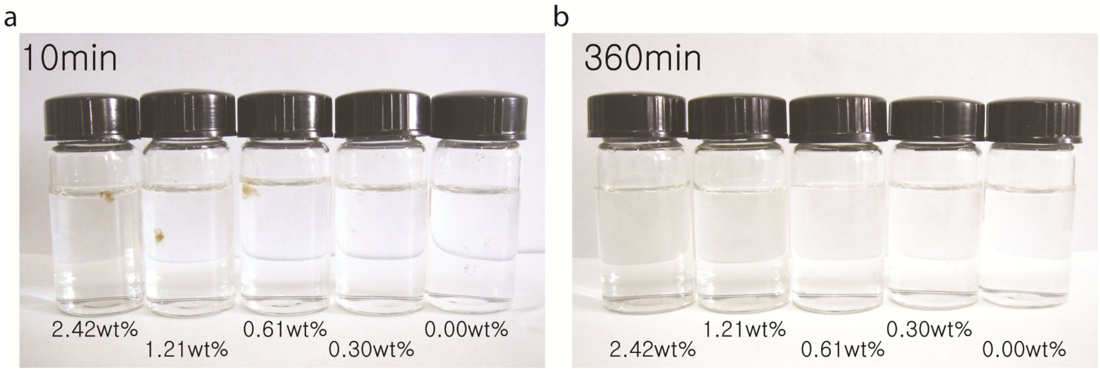

Figure S3 Digital images of expansion experiments of GO/PAA fibers and PAA fibers. a, Dissolution time is 10min. b, Dissolution time is 360min. It is clearly found that the fibers which was not heat treated are easily to be resolved in water. This result is proved from the other side of the esterification reaction after heat treated.

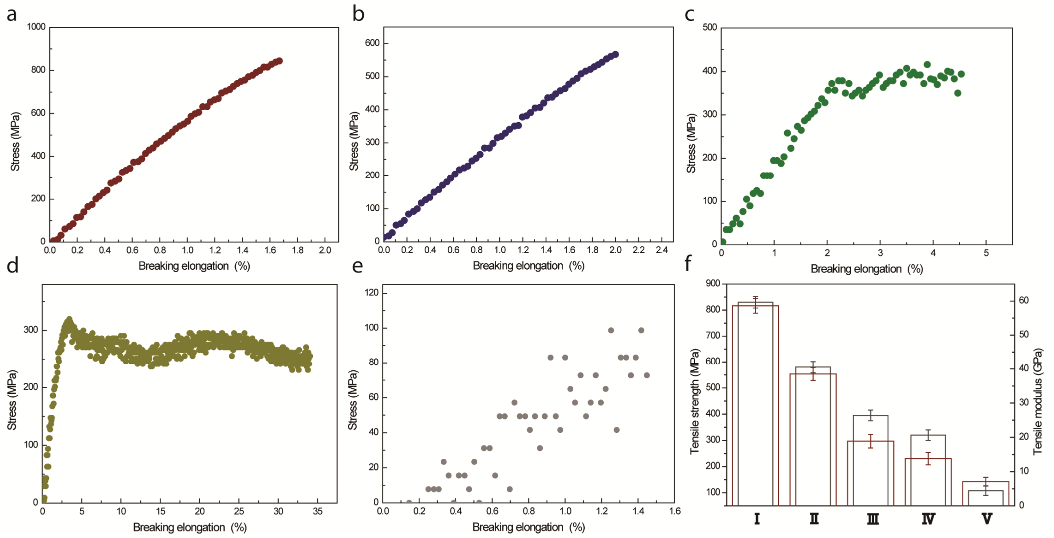

Figure S4 Typical curves of tensile strengths of PGO fibers. The weight of GO in fiber used are a, 2.42 wt.%; b,1.21 wt.%; c,0.61 wt.%; d,0.30 wt.%; e.0.00 wt.%. f, Mechanical properties of PGO fibers (black rectangle represents tensile strength, red rectangle represents tensile modulus). The weight of GO used are Ⅰ, 2.42 wt.%; Ⅱ,1.21 wt.%; Ⅲ,0.61 wt.%; Ⅳ,0.30 wt.%; Ⅴ.0.00 wt.%. As seen, the tensile strengths and modulus of the PGO fibers decrease with the GO used. These characteristics have highly relationship with the fiber crosslinking degrees. The role of GO has two-folds: it created more crosslinking points as well as decreasing the distance between two GO sheets which promoted the probability of esterification reactions.