

# Chemical functionalization of graphene oxide for improving mechanical and thermal properties of polyurethane composites



Qifei Jing<sup>a,b,c</sup>, Wanshuang Liu<sup>a</sup>, Yongzheng Pan<sup>d</sup>, Vadim V. Silberschmidt<sup>c</sup>, Lin Li<sup>e,\*</sup>, ZhiLi Dong<sup>a,b,\*\*</sup>

<sup>a</sup> School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

<sup>b</sup> Institute for Sports Research, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

<sup>c</sup> Wolfson School of Mechanical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

<sup>d</sup> Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602, Singapore

<sup>e</sup> School of Mechanical and Aerospace Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore

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## ABSTRACT

Graphene oxide (GO) was chemically functionalized to prepare polyurethane (PU) composites with improved mechanical and thermal properties. In order to achieve a well exfoliated and stable GO suspension in an organic solvent (dimethylformamide, DMF), 4, 4'-methylenebis(phenyl isocyanate) and polycaprolactone diol, which were the two monomers for synthesizing PU, were selectively used to functionalize GO. The obtained functionalized GO (FGO) could form homogeneous dispersions in DMF solvent and the PU matrix, as well as provide a good compatibility with the PU matrix. The most efficient improvement of mechanical properties was achieved when 0.4 wt.% FGO was added into the PU matrix, showing increases in the tensile stress, elongation at break and toughness by 34.2%, 27.6%, and 64.5%, respectively, compared with those of PU. Regarding the thermal stability, PU filled with 1 wt.% FGO showed the largest extent of improvement with  $T_{2\%}$  and  $T_{50\%}$  (the temperatures at which 2% and 50% weight-loss happened) 16 °C and 21 °C higher than those of PU, respectively. The significant improvement in both mechanical properties and thermal stability of FGO/PU composites should be attributed to the homogeneous dispersion of FGO in the PU matrix and strong interfacial interaction between them.

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## 1. Introduction

Graphene, a one-atom-thick hexagonal lattice of  $sp^2$  carbon atoms, exhibits a two-dimensional sheet-like structure. Research into graphene has been one of the fastest growing areas due to its many fascinating properties such as ultrahigh thermal and electrical conductivity, excellent thermal stability, high specific surface area, and remarkable mechanical strength [1,2]. Graphene was proven experimentally [3] to be the strongest material developed so far. Significant efforts have been put in developing multi-functional polymer composite materials using graphene as nanofiller for various applications, such as electromagnetic interference shielding materials, shape memory devices, drug release, actuators, and infrared-triggered sensors [4–13]. To obtain defect-free, high-quality graphene sheets, the most widely used approaches are chemical vapor deposition [14,15] and micromechanical cleavage of graphite [16]. Nevertheless, these approaches show a low production yield and are time consuming. In this situation, graphene oxide (GO), originated from the exfoliation of graphite oxide, has been extensively studied as an alternative to graphene. The established advantages of

GO in production yield and cost [17] make it an attractive candidate as a nanofiller used in polymer composites.

GO, having the same framework as graphene, contains massive oxygen functional groups such as epoxide, hydroxyl, carboxyl and carbonyl groups located at its edges and basal planes [18]. Hence, GO can be readily dispersed in water and form a stable colloidal suspension due to its strong hydrophilicity [19,20]. However, the strong hydrophilicity of GO could only benefit the fabrication of GO-based aqueous polymer composites. The exfoliation of GO in organic solvents is not favored, presumably due to strong interlayer hydrogen bonds originated from those attached oxygen functional groups. The strong interactions between adjacent GO layers could prevent the penetration of organic solvent molecules into the interlayer spaces, thus preventing full exfoliation of GO in organic solvents. Ruoff et al. [21] consider the hydrophilicity of GO as an obstacle to prepare high-performance GO-reinforced polymer composites in organic solvents. In their work, reactions between organic isocyanates and hydroxyl, carboxyl groups were taken advantage of to reduce the amount of hydrogen bond donor groups on GO sheets, thus weakening the strength of interlayer hydrogen bonding and hydrophilicity of GO. As a result, the isocyanate-treated GO can be fully exfoliated in some organic solvents, e.g., dimethylformamide (DMF), after a mild ultrasonication.

Thermoplastic polyurethane (PU) is an important class of polymers, which has been widely used in various applications such as foams,

\* Corresponding author.

\*\* Correspondence to: Z. Dong, N4.1-01-04, School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.

E-mail address: [zldong@ntu.edu.sg](mailto:zldong@ntu.edu.sg) (Z. Dong).

coatings, elastomers, and adhesives. PU has a block copolymer structure, with polyol as soft segment and isocyanate and chain extender as hard segment. The molecular structure of PU could be easily adjusted to fulfill different property requirements [22]. It is commonly acknowledged that two factors should be mainly concerned in order to prepare high-performance nanofiller/polymer composites: (1) dispersion of nanofillers in the polymer matrix; (2) interfacial interactions between nanofillers and the matrix. The nanofillers tend to aggregate due to strong van der Waals forces among them, hindering their homogeneous dispersion in a polymer matrix. Besides, a lack of strong interfacial interactions between the nanofillers and matrix would greatly compromise the reinforcement effect of the nanofillers. One feasible and effective strategy to promote the reinforcement of composites is through chemical functionalization of nanofillers [23–26]. Among chemical functionalization methods, grafting molecules and/or polymer chains onto the surface of graphene sheets were studied for many polymers. [27–29] The grafted molecules and/or polymer chains can usually enhance the dispersion of graphene sheets in the polymer matrix and interfacial interactions between them.

In this work, GO/PU composites were prepared via a solution mixing method. In order to obtain a homogeneous dispersion of GO in DMF, as well as a strong interfacial interaction between GO and PU, 4,4'-methylenebis(phenyl isocyanate) (MDI) and polycaprolactone diol (PCL) were selectively used to functionalize GO. On one hand, MDI and PCL functionalization of GO was expected to improve the dispersion of GO in DMF, which could consequently improve the dispersion of GO in the PU matrix. On the other hand, since MDI and PCL were the monomers for synthesizing PU, a good compatibility between the functionalized GO (FGO) and the PU matrix was also expected, considering their structural similarity. Detailed characterizations of FGO were conducted and presented to confirm the successful functionalization of MDI and PCL on the GO surface. In addition, mechanical properties and thermal stability were tested to demonstrate the reinforcement effect of FGO on the composite materials.

## 2. Experimental

### 2.1. Materials

Graphene oxide (purity > 99%) was provided by XFNANO Materials Tech Co., Ltd. (Nanjing, China) which was synthesized from graphite powders using a common Hummers' method. PCL (average Mn

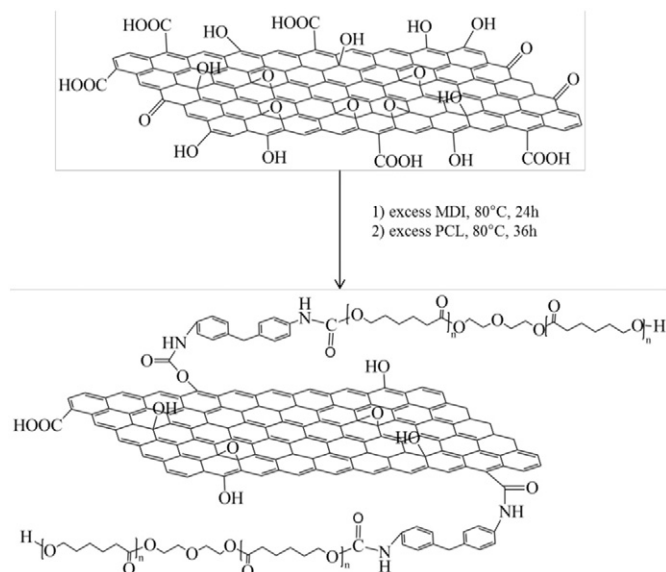


Fig. 1. Schematic of FGO preparation.

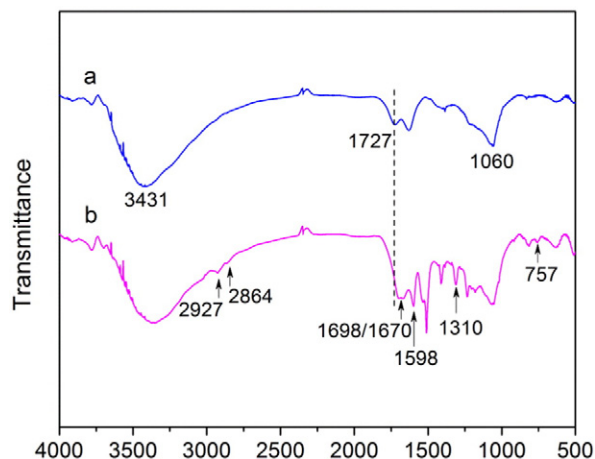


Fig. 2. FTIR spectra of GO (a) and FGO (b).

~530 g/mol and ~2000 g/mol), MDI (molecular weight 250.25 g/mol), 1,4-butanediol (BD, molecular weight 90.12 g/mol), and dibutyltin dilaurate (DBTDL) were all obtained from Sigma-Aldrich. DMF (Tritech Scientific), anhydrous DMF (Tritech Scientific) and anhydrous acetone (Tritech Scientific) were used as received.

### 2.2. Functionalization of GO

GO was vacuum freeze-dried to reduce the amount of stored water in its  $\pi$ -stacked structure [30] before using. In a typical operation,

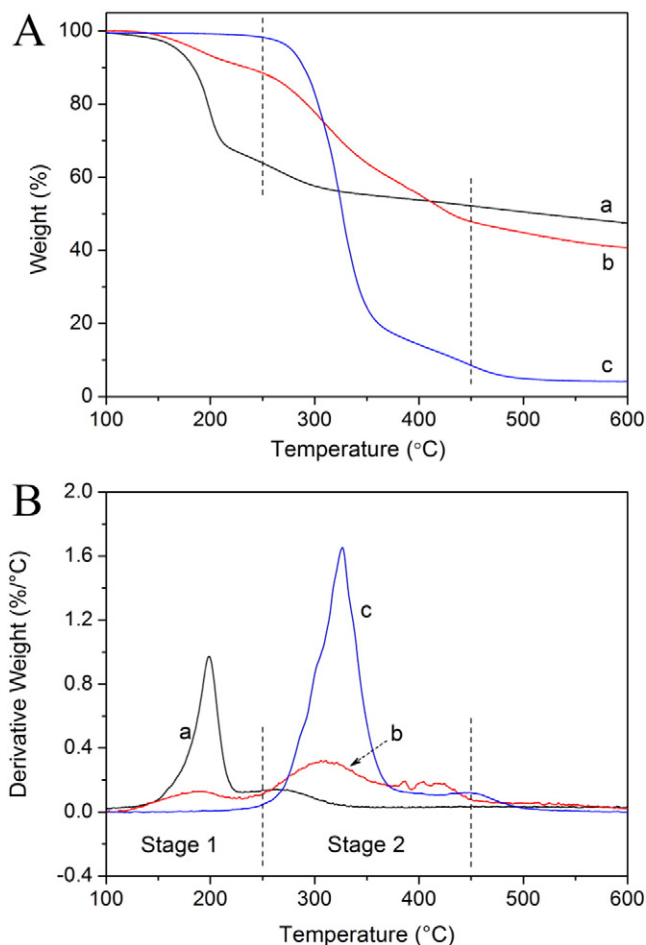


Fig. 3. TGA (A) and DTG (B) curves of GO (a), FGO (b), and PU (c).

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