



# Anisotropic thermal conductive properties of hot-pressed polystyrene/graphene composites in the through-plane and in-plane directions



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## ABSTRACT

The interactions between polystyrene (PS) and graphene as well as the factors leading to anisotropic thermal conductive properties in the in-plane and through-plane directions of the hot-pressed samples were studied. In this procedure, the PS/graphene composites (PG) were prepared via solution mixing followed by hot-pressing method, the graphene oxide (GO) was simultaneously modified and reduced to graphene nanosheets by p-phenylene diamine. And the polydispersity index of PS matrix was controlled at as narrow as 1.14 by reversible addition-fragmentation chain transfer (RAFT) polymerization. The characterization showed that the thermal conductivity of PG composites with 10 wt% graphene loading was enhanced by 66% to  $0.244 \text{ W m}^{-1} \text{ K}^{-1}$  compared with  $0.147 \text{ W m}^{-1} \text{ K}^{-1}$  of pure PS. The thermal diffusivity ( $\alpha$ ) of hot-pressed PG samples showed anisotropic behavior according to the heat transfer directions. The  $\alpha$  of in-plane direction was almost ten times higher than that of in through-plane direction. And both of them changed slowly in function of graphene loadings. This anisotropic property may be caused by the ordered arrangement of graphene sheets and PS chains after PG composites were hot-pressed.

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## 1. Introduction

Thermal conductive properties of polymer materials are becoming increasingly important because of the need for efficient heat removal in numerous systems such as light emitting diodes (LED), and automotive and aerospace products. Several polymer materials with different inorganic filler systems have been well studied and used to address heat removal/dissipation problems, in which graphene- and/or graphene oxide (GO)-based composites are considered as promising candidates and evoked much attention on the fields of thermal management applications [1,2]. Several factors have great influence on the thermal conductive properties of polymer materials. For example, it has been well demonstrated that surface functionalization of GO is generally necessary to prevent the aggregation of reduced graphene nanosheets and to improve their dispersion in polymer matrix [3]. As a result, the thermal conductivity of the reduced graphene obtained by chemical reduction of graphene oxide could be restored at a certain level due to the formation of unsaturated and conjugated carbon atoms on the graphene layers [4]. Song et al. [1] reported the enhanced thermal conductivity of  $1.53 \text{ W m}^{-1} \text{ K}^{-1}$  when incorpo-

rated in epoxy matrix with 10 wt% non-oxidized graphene flakes with non-covalent functionalization. Moreover, Choi et al. [5] prepared graphene encapsulated poly(methyl methacrylate) composites and improved the thermal conductivity as 200% with low graphene loadings. They found that the improvement in thermal conductivity was achieved by effective adhesion of graphene to the surface of microparticles and thus promoted the homogenous dispersion of graphene layers in the polymer matrix.

On the other hand, some factors, besides the surface modification, can influence the thermal conductive properties of polymer/carbon-filler composites. For example, Cao et al. [6] reported that the thermal conductivity of the poly(vinylidene fluoride)/polystyrene (PS) composites with both multi-walled carbon nanotubes (MWCNTs) and silicon carbide (SiC) is higher than that with only SiC. They found the following factors were responsible for this phenomenon. The MWCNTs acted as heat conductive bridges among the SiC nanoparticles, thus contributing considerably to the formation of a more efficient percolating network for thermal conduction. At the same time, MWCNTs and SiC showed an obvious synergistic effect on the thermal conductivity of composites. Such hybrid filler system constructed three-dimensional networks that can facilitate the heat transport in the composites. Mario et al. [7] found phonon coupling of the vibrational modes of the graphene and of the polymeric matrix plays a dominant role on the ther-

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mal conductivities of the liquid and solid states. And Bohayra et al. [8] revealed that the ultrafine-grained graphene had thermal conductivity one order of magnitude lower than that for pristine graphene and all grain boundaries exhibited an effective thermal contact conductance. Then the grain size distribution had a negligible effect on the thermal conductivity of polycrystalline graphene sheets for the grain sizes larger than 200 nm. Guo and Chen [9] prepared graphene/epoxy resin composites with high thermal conductivity via ball milling technique compared to another methods. It could mainly attribute to homogenous dispersion of graphene in matrix. Our recent work [10,11] found that the polymer molecular length had some influence on the thermal conductive properties of polyamide-6(PA6)/graphene composites. The experimental work showed that the thermal conductivity of the nanocomposites decreases with the increasing length of the PA6 chains. This study was in good agreement with previous simulation work [12] and demonstrated that shorter PA6 chains were more effective in reducing the interface thermal resistance and improving the thermal conductivity of the nanocomposites. The above researches clearly indicated that the composition and structural factors should be well studied and controlled to obtain polymer composites with excellent thermal conductivity.

In the present work, we reported anisotropic thermal conductive properties of the PS/graphene composites (PG) according to the heat transfer directions. The interactions between PS and graphene as well as the factors leading to the anisotropic behavior in the in-plane and through-plane directions of the hot-pressed PG samples were studied. Here, the PG composites were prepared via solution mixing followed by hot-pressing method (see Fig. 1). The *p*-phenylene diamine (PPD) was utilized by simple refluxing with GO sheets and expected to efficiently reduce and functionalize the GO sheets as it bore two terminal amine groups. Also, the benzene group of PPD benefited the compatibility of functionalized GO nanosheets with PS matrix. Moreover, the PS was prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization to control the molecular weight and polydispersity index, and thus to avoid the uncertainty of influence parameters on thermal conductivity and thermal diffusivity of PG composite. As PS is one of the widely used and most inexpensive polymers in many industry fields, we believe the developed thermal conductive PG composite by cost-efficient way could be applied in thermal interface materials, connectors, and other high-performance thermal management systems.

## 2. Experimental

### 2.1. Materials

4-Cyano-4-[(dodecylsulfanylthiocarbonyl) sulfanyl] pentanoic acid (RAFT agent, 97%, HPLC) was purchased from Sigma–Aldrich Co. LLC. (Shanghai, China). Natural graphite flakes, concentrated sulphuric acid ( $H_2SO_4$ , 98%), potassium permanganate, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), methanol, ethanol, *p*-phenylene diamine (PPD), ammonia solution, sodium hydroxide (NaOH), styrene, and azobisisobutyronitrile (AIBN) were purchased from Sinopharm Chemical Reagent Co., Ltd. Before use, styrene was purified by dealing with NaOH and then spun steaming to remove the inhibitor. AIBN was purified by recrystallization from methanol. The other agents were used as received without further treatment.

### 2.2. Reduction and functionalization of GO with PPD

GO sheets were synthesized by a modified Hummers' method [13]. In a typical procedure, graphite flakes (0.18 g) was dissolved and exfoliated in 360 ml deionized water via ultrasonication. Subsequently, PPD (1.8 g) and ammonia solution were added slowly until the solution was alkaline. The mixture was refluxed with mechanical stirring at 95 °C for 3 h and filtrated. The filtrate cake was rinsed in ethanol with the aid of ultrasonication for 3 min and then filtrated. The rinsing–filtration process was repeated for a few times to remove the physically adsorbed PPD. Finally, the GO-PPD was obtained after dried in an oven at 80 °C for 24 h.

### 2.3. Preparation of PS/GO-PPD composites

As illustrated in Fig. 1, PS was obtained by RAFT polymerization using AIBN as the primary radical source and RAFT agent as the chain transfer agent. In a typical procedure, styrene (20 g), RAFT agent (40.3 mg) and AIBN (32.8 mg) were put into a three-neck round-bottom flask (25 ml) with a steady stirring for several minutes to disperse RAFT agent and AIBN in styrene. The flask was subjected to three cycles of freeze–pump–thaw to remove oxygen. Then the bulk PS was obtained after RAFT polymerization at 75 °C for 48 h.

PG composites were prepared by solution blending. The typical procedure to prepare PG composite with 0.1 wt% GO-PPD loading

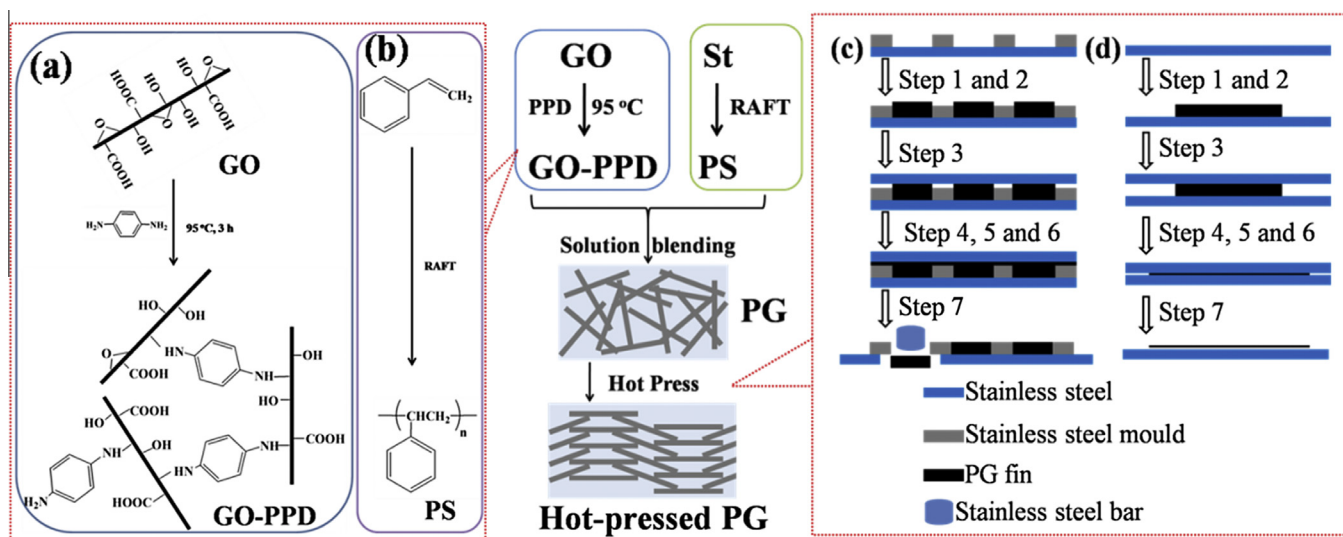


Fig. 1. Synthesis routes of hot-pressed PG composites: (a) the preparation of GO-PPD; (b) the preparation of PS; (c) the preparation of hot-pressed PG thermal conductive fins; and (d) the preparation of hot-pressed PG thermal conductive films.

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