



# Fabrication of fullerene-decorated graphene oxide and its influence on flame retardancy of high density polyethylene



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## ABSTRACT

Fullerene (C<sub>60</sub>) decorated graphene oxide (GO), denoted as GO-*d*-C<sub>60</sub>, was synthesized through a three-step chemical process, including acylating chlorination of GO, amino-functionalization of GO and addition reaction of C<sub>60</sub> molecules with amino groups, with the purpose of promoting the dispersion of GO in high density polyethylene (HDPE) and further improving thermal stability and flame retardancy of HDPE/GO composite. Infrared spectroscopy (IR), transmission electron micrographs (TEM) and X-ray photoelectron spectroscopy (XPS) proved that about 2.3 wt.% of C<sub>60</sub> molecules, with the size of about 40–70 nm, were bonded onto the surface of GO and mainly located on the edge of GO sheets. The chemical decoration made GO-*d*-C<sub>60</sub> to have better dispersion in HDPE than GO, favoring the formation of compact and integrated char barriers when heated or ignited. Consequently, GO-*d*-C<sub>60</sub> improved the thermal stability and flame retardancy of HDPE more effectively than pristine GO, due to the assembly of the barrier effect of GO and the radical-trapping effect of C<sub>60</sub>.

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## 1. Introduction

Abundant miraculous materials constituting of carbons are found in nano-world, such as fullerene (C<sub>60</sub>), carbon nanotubes (CNTs), graphene and so on. There is a high level of interest, all the time, in using these nano-carbon materials in polymers to prepare polymeric nanocomposites with magical physical properties and chemical structures. Among these researches, excellent performances of nano-carbon materials in improving flame retardancy of polymers have been received extensive attention. During heating and ignition, CNTs will move to the surface of matrix to form a crosslinked network, which can be seen as the physical protective barrier to block the transfer of mass and heat between the gas and condensed phase, resulting in the increase in thermal stability and the reduction in the flammability of the polymers [1–6]. Graphene also has the char barrier effect to retard the permeation of flame and the escape of volatile degradation products via a tortuous

pathway, which is benefit to slowing down the thermo-oxidative degradation and favoring the condensed-phase flame retardancy of polymers [7–12]. C<sub>60</sub>, a strong electron acceptor, has been found to have high reactivity to free radicals. Since most polymers thermally degrade by free-radical-chain reaction, C<sub>60</sub> can delay the thermal degradation and combustion by trapping free radicals produced during the degradation of those polymers [13–17].

We are more interested in the combination of various nano-carbon materials, considering their similar chemical composition but different geometric structure, which may emerge the synergistic effects in flame retarded polymers. As an example, our team prepared C<sub>60</sub> decorated multi-walled carbon nanotubes [15], which improved the dispersity of nanotubes in polypropylene (PP) and further reduced the flammability of PP because of the combination of the radical-trapping effect of C<sub>60</sub> and the barrier effect of nanotubes network.

In this paper, in order to combining the unique physical and chemical characteristics of GO and C<sub>60</sub>, C<sub>60</sub>-decorated GO (GO-*d*-C<sub>60</sub>) was fabricated through a three-step chemical process, including acylating chlorination of GO, amino-functionalization of GO and addition reaction of C<sub>60</sub> molecules with amino groups. The produced GO-*d*-C<sub>60</sub> was characterized by infrared spectroscopy

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(IR), X-ray photoelectron spectroscopy (XPS), thermogravimetric analyses (TG), transmission electron micrographs (TEM) and Raman spectroscopy. Moreover, GO-*d*-C<sub>60</sub> was introduced to HDPE to investigate whether GO-*d*-C<sub>60</sub> had the positive influence on the thermo-oxidative stability and flame retardancy of HDPE.

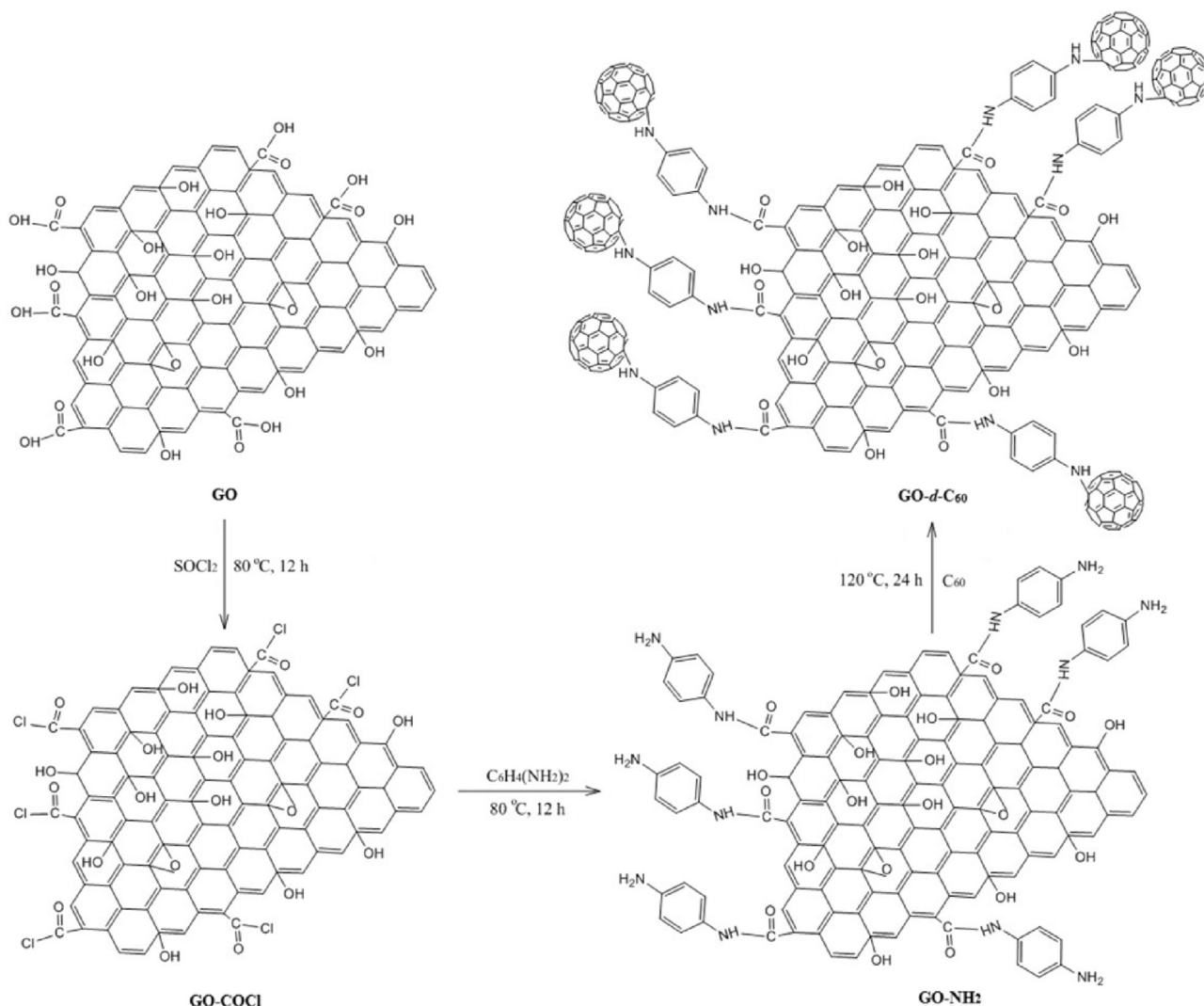
## 2. Experimental parts

### 2.1. Materials

C<sub>60</sub> (purity: >99.99%) was purchased from Henan Puyang Yongxin Science and Technology Co., Ltd., China. Graphene oxide (purity: >99.99%) was purchased from Nanjing Xianfeng Nano-materials Co., Ltd., China. *p*-phenylenediamine (analytical grade) was got from Sigma Reagent Co., Ltd., China. High density polyethylene (HDPE, 5000S) was purchased from Yangzi Petrochemical Co. Ltd., China, melt flow rate (MFR) is 0.9 g/10min (230 °C, 2.16 kg) and density is 0.954 g/cm<sup>3</sup>. Other chemical agents, including thionyl chloride (SOCl<sub>2</sub>), toluene, xylene and *N,N*-dimethyl formamide (DMF), were analytical grade and used as received.

### 2.2. Synthesis of GO-*d*-C<sub>60</sub>

The synthesis route for GO-*d*-C<sub>60</sub> comprised of three steps as shown in Scheme 1. GO was firstly acylating chlorinated by thionyl chloride, followed by the amino-functionalization with *p*-phenylenediamine, and finally the amino-functionalized GO was reacted with C<sub>60</sub> to form GO-*d*-C<sub>60</sub>. In a typical acylating chlorination procedure, 100 mg pristine GO was added into a three-necked flask with 100 mL SOCl<sub>2</sub>. After ultrasonic dispersion for 5 min, magnetic stirred for 30 min and ultrasonic dispersion for 5 min again, the solution was refluxed for 7 h. Then the temperature was increased to 120 °C to steam out most of the unreacted SOCl<sub>2</sub>. The residue was dried at 80 °C under a vacuum for 12 h and the resultant product was designated as GO-COCl. In the amino-functionalization procedure, GO-COCl was dispersed with 100 mL DMF via ultrasonication for 10 min in a three-necked flask. Then the mixture was heated to 80 °C with stirring and a few drop of pyridine was added. Afterward, 1 g *p*-phenylenediamine was added into the mixture to react at 80 °C under N<sub>2</sub> for 12 h to make reaction to go to completion. The amino-functionalized GO was filtered, washed with DMF three times, and dried at 80 °C under a vacuum for 12 h and designated as GO-NH<sub>2</sub>. In the preparation of GO-*d*-C<sub>60</sub> procedure, GO-NH<sub>2</sub> was dispersed in a three-necked flask with 100 mL



Scheme 1. Schematic chemical reaction for GO-*d*-C<sub>60</sub>.

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