



Preparing conductive poly(lactic acid) (PLA) with poly(methyl methacrylate) (PMMA) functionalized graphene (PFG) by admicellar polymerization

Lin Lei^a, Jianhui Qiu^{a,b,*}, Eiichi Sakai^a

^a Department of Machine Intelligence and Systems Engineering, Akita Prefectural University, Yurihonjo 015-0055, Japan

^b College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, PR China

HIGHLIGHTS

- ▶ Poly(methyl methacrylate) (PMMA)-functionalized graphene (PFG) nanoparticles were synthesized by admicellar polymerization.
- ▶ The PMMA films were coated on the surface of graphene nanosheets by this method.
- ▶ The mechanical and electrical properties of PFG/PLA composites were enhanced.
- ▶ It is owing to the improvement of interfacial adhesion between PFG and PLA matrix.

ARTICLE INFO

Article history:

Received 11 April 2012

Received in revised form 2 July 2012

Accepted 16 July 2012

Available online 3 August 2012

Keywords:

Graphene nanosheets
Admicellar polymerization
Biodegradable
Conductive PLA
Functionalized graphene

ABSTRACT

We synthesized conductive poly(lactic acid) (PLA) polymer by spiking PLA matrices with poly(methyl methacrylate) (PMMA)-functionalized graphene (PFG) by virtue of admicellar polymerization. The PFG was prepared by admicellar polymerization of methyl methacrylate monomers adsorbed onto the graphene oxide. The electrical conductivity of the prepared PFG/PLA considerably increases up to 2.58×10^{-4} S/cm with the percentage of PFG under experimented conditions, ~ 12 orders of magnitude greater than the PLA. Aside from electrical conductivity, the tensile strength and Young's modulus of the PFG/PLA also exhibit increases of ~ 5 MPa ($\sim 10\%$) and ~ 0.7 GPa ($>80\%$) after the 5 wt.% addition of the PFG, respectively. Moreover, with the aid of transmission electron microscopy (TEM), it is clear that the graphene surface is covered by the PMMA films rather than usual discrete nanospheres. Our method may offer an alternative green procedure to synthesize conductive PLA polymer since the materials used in the experiments are bio-degradable and environment-begin.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

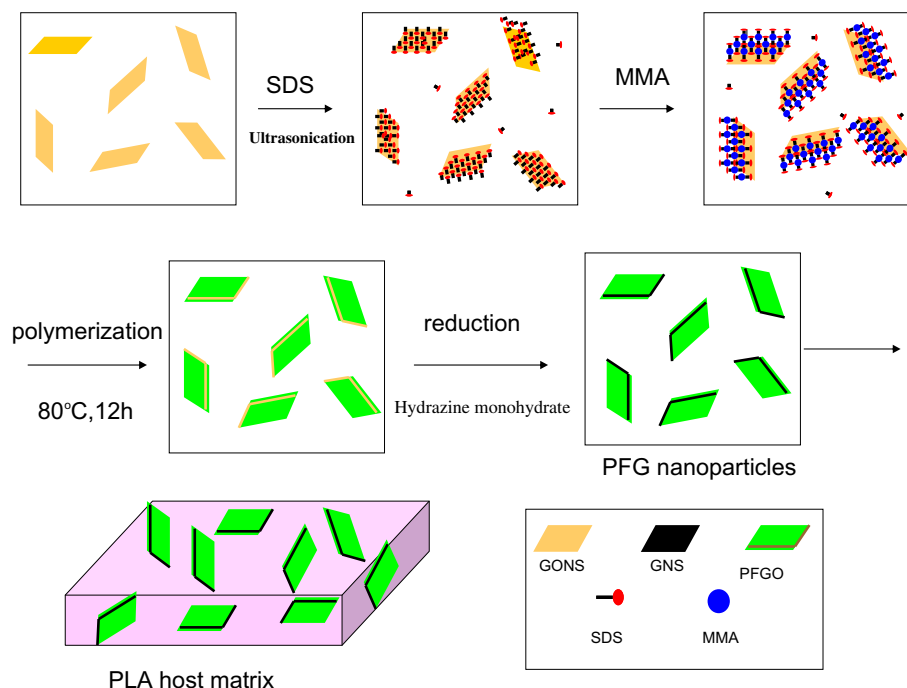
Conductive plastics with excellent electrical and mechanical properties have been the heart of many investigations owing to wide applications in energy storage devices [1,2], supercapacitors [3], construction and electronics industries [4]. The conductive plastics generally consist of nanofillers, such as carbon black [5], expanded graphite (EG) [6], carbon nanotubes (CNTs) [7], carbon nanofiber (CNF) [8] and reduced graphene oxides (RGOs) [9,10] which substantially improve electrical conductivity as well as mechanical strength of the plastics. Among the potential nanofillers, graphene is probably suitable nanofiller in polymer matrices due to its extraordinary electrical, thermal, mechanical, optical properties [11–13].

Graphene based conductive plastics can be composed via melt intercalation in which the graphene and polymer matrix are mixed

when polymer is heated to molten state. However, because it has a pronounced tendency to agglomerate in polymer matrix, pristine graphene is unsuitable for intercalation by polymer chains with the aforementioned method [14,15]. It appears that the agglomeration can be mitigated and the dispersibility can be ameliorated by functionalizing graphene. In addition, graphene functionalization is able to improve the affinity of graphene in various solvents and to increasing the loading ability of graphene onto nanomaterials and polymers [16,17]. To functionalize the graphene, covalent attachment and functional group adsorption can be utilized [18,19]. Several methods inclusive of bi-functional organosilanes, grafting, carbon materials act as initiator [20–22] and admicellar polymerization are at present available for the purpose of the graphene functionalization. The prevailing admicellar polymerization refers to coating the graphene with nanofilms of polymers that is formed by polymerization of monomers inside the admicelles [23,24]. In case of the admicellar polymerization, the concentration of surfactant was always well below the critical micelle concentration (CMC) to obviate emulsion polymerization. As a result, a thin

* Corresponding author. Fax: +81 184 27 2134.

E-mail address: qiu@akita-pu.ac.jp (J. Qiu).



Scheme 1. The admicellar polymerization procedure for preparing the PFG/PLA.

film of polymer should be deposited on a graphene surface. The main objective of the coating was redispersing graphene in water without any visible aggregation by forming a polymer layer around the graphene and preventing van der Waals induced aggregation [25]. The polymer-coating composites should exhibit good compatibility with the polymer matrix when blended with polymers. The admicellar polymerization is also environmentally benign since the process of polymerization can be fulfilled in aqueous solutions and can consume minimal use of chemical agents because the films coated onto the graphene are ultra-thin.

Poly(lactic acid) (PLA) is a biodegradable thermoplastic polymer which can be readily processed into molded parts, although it is difficult to be *in situ* polymerized. As a consequence, a common-use resin poly(methyl methacrylate) (PMMA) is employed in the paper as an intermediate material to improve the compatibility of PLA with graphene due to the fact that the PMMA can be simply polymerized and possesses excellent compatibility with both graphene and PLA which is attributed to the interaction of the ester groups contained in both PMMA and PLA matrix and the hydrophobicity of PMMA conducive to adsorption and coating of PMMA onto graphene. The modification of graphene surface by admicellar polymerization, to the best of our knowledge, has seldom been reported. The main motivation behind the admicellar reaction is to use a higher surface area of graphene flakes to anchor PMMA polymeric chains. Therefore, ultra thin PMMA films can be expected to coat on the surface of graphene nanosheets.

The objective of the present research is to prepare conductive PLA with polymer-functionalized graphene nanoparticles (PFG) which is produced by admicellar polymerization of methyl methacrylate monomers adsorbed onto the graphene. The prepared PFG/PLA polymers were evaluated in terms of mechanical strength and electrical performance. It is found that both the mechanical and electrical properties of the PFG/PLA were enhanced. The tensile strength is increased by >5 MPa (~10%) while the Young's modulus almost doubles and reaches ~1.6 GPa. In the meantime, the electrical conductivity soars to 2.58×10^{-4} S/cm with the increase in the concentration of PFG, a dozen or so orders of magnitude greater than pure PLA.

Table 1

The list of main chemicals and agents in the experiments.

Poly(lactic acid) (PLA TE-4000)	Unitika Co. (Japan)
Methyl methacrylate (MMA)	Ciba Specialty Chemicals Ltd. (Japan)
Ammonium persulfate (APS, purity 98.0%)	Tianjin Baishi Chemical Industry Co. Ltd. (Tianjin, China)
Graphite powder	Zhongdong Graphite Company (Qingdao, China)
Fuming nitric acid (63%)	Ciba Specialty Chemicals Ltd. (Japan)
Sulfuric acid (98%)	Ciba Specialty Chemicals Ltd. (Japan)
Potassium chlorate (98%)	Ciba Specialty Chemicals Ltd. (Japan)
Hydrochloric acid (37%)	Ciba Specialty Chemicals Ltd. (Japan)
Dodecyl sulfate	Ciba Specialty Chemicals Ltd. (Japan)

Table 2

The electrical conductivity of PMMA and PFG.

	Pure PMMA	PFG
Electrical conductivity	1×10^{-16} S/cm	4.83 S/cm

2. Experimental

2.1. Materials

2.1.1. Preparation of the PFG/PLA

2.1.1.1. Preparation of the GO and GNS. Graphite oxide (GO) were prepared by Hummers method [26]. Graphene nanosheets (GNSs) were then obtained by reduction of GO by hydrazine hydrate as a reducing agent at 100 °C for 6 h.

2.1.1.2. Preparation of PFG by admicellar polymerization. 100 mg GO was dispersed in 40 mL DI water and homogenized 30 min via ultrasonic vibration in a 100 mL round-bottom flask that was water-bathed. 0.0345 g dodecyl sulfate (SDS) were added in the flask and then dispersed evenly with ultrasonics for 10 min nitrogen. The concentration of SDS was 3 mmol which is well below

Download English Version:

<https://daneshyari.com/en/article/149247>

Download Persian Version:

<https://daneshyari.com/article/149247>

[Daneshyari.com](https://daneshyari.com)