



# Strong and ductile poly(lactic acid) nanocomposite films reinforced with alkylated graphene nanosheets



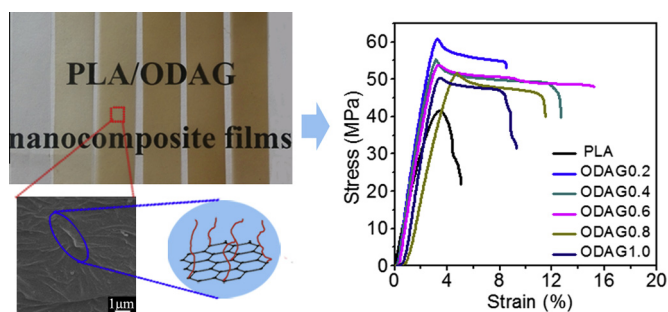
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## HIGHLIGHTS

- Alkylated graphene sheets (ODAG) can strengthen and toughen the PLA nanocomposites.
- PLA/ODAG nanocomposites were prepared by simple solution blending and casting method.
- PLA/ODAG nanocomposites show improved crystallization behavior and thermal stability.
- It is owing to the unique interphase and homogeneous dispersion of ODAG in PLA.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 26 September 2014

Received in revised form 10 November 2014

Accepted 11 November 2014

Available online 18 November 2014

### Keywords:

Poly(lactic acid)  
Graphene  
Nanocomposites  
Mechanical properties  
Thermal properties  
Crystallization behavior

## ABSTRACT

Balanced strength and toughness is always the goal of high-performance polymer materials for practical applications. In this work, a series of transparent poly(lactic acid) (PLA) nanocomposite films incorporated with fully exfoliated octadecylamine-functionalized graphene (ODAG) as effective nanofiller were prepared by solution blending and casting method. Because of the good hydrophobic compatibility between ODAG and PLA, a homogeneous dispersion of ODAG into PLA matrix and improved interfacial adhesion between them can be achieved. The obtained PLA/ODAG nanocomposite films present markedly improved crystallization behavior, mechanical properties and thermal stability. Compared to neat PLA, the nanocomposite films show a 34% increase in tensile strength, 44% increase in Young's modulus, and 300% improvement in tensile toughness by the addition of only 0.4 wt% of ODAG. The simultaneous improvement in both strength and toughness could be attributed to homogeneous dispersion of ODAG in PLA matrix, improved interfacial interaction due to unique interphase structure, as well as enhanced crystallization.

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## 1. Introduction

As a potential substituent for petroleum-based polymers, poly(lactic acid) (PLA) has received much attention in the field of environmental protection and biomedical applications, due to its

biodegradability, biocompatibility, balanced mechanical properties and versatile fabrication processes [1,2]. However, some disadvantages such as the inherent brittleness, low heat resistance, slow crystallization rate and slow degradation rate have limited its development and wide practical application. Therefore, several techniques have been developed to improve the physical properties of PLA, including copolymerization [3], plasticization [4,5], polymer blending [6] and reinforced composites [7]. Among which, composite formation with nanoscale particles, such as layered

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silicate [8,9], carbon nanotubes [10,11], nanodiamond [12] and nanofiber [13], is the most effective and promising method to extend the application of PLA because the combination of PLA with a small proportion of nanofillers is expected to produce new biodegradable and biocompatible composites with high performance or even unexpected properties.

Graphene, a single-atom thick graphite sheet, structurally analogous to silicate layers and chemically similar to carbon nanotubes, is considered as an ideal reinforcing nanofiller in fabrication of multifunctional polymer nanocomposites owing to its huge specific surface area, superior mechanical strength, remarkable electronic and thermal properties [14,15]. To achieve its maximal reinforcing efficiency, graphene sheets must be homogeneously dispersed in the polymer matrix and their effective interfacial interaction with the polymer matrix must be realized [16,17]. However, because of the poor compatibility of pristine graphene with most polymers as well as strong van der Waals interactions among graphene sheets, the dispersion of pristine graphene sheets in a polymer matrix is not individual and homogeneous [18]. To address this problem, covalent and non-covalent surface functionalization methods have been proposed, which can not only improve the compatibility and dispersion of graphene nanosheets in polymer host but also prompt the interfacial stress transfer between graphene and polymer matrix [19–21].

Recently, effective mechanical reinforcement of PLA using graphene oxide (GO) and functionalized graphene nanosheets has been reported by several authors [22–25]. For instance, Song et al. utilized non-covalent functionalized graphene with PLA chain containing a pyrene fragment as compatibilizer to enhance the tensile strength and storage modulus of PLA matrix in some degree [22]. Hu et al. prepared PLA/graphene nanocomposite by masterbatch-based melt blending and found the increases of 35% and 58% in tensile strength and storage modulus of PLA with the incorporation of 0.08 wt% graphene. The graphene nanosheets were in the form of chemically reduced GO which were prepared by pressurized oxidation and multiplex reduction [23]. In these reports, however, it is noted that the enhancement of mechanical strength by the addition of graphene nearly always accompanies a reduced ductility or breaking elongation, which is probably because of that the stronger interfacial adhesion between graphene sheets and PLA restricts the movement of the polymer chains, leading to the brittleness of the composites. Besides, with the strategy of chemical modification of graphene to control the interfacial interaction between graphene sheets and PLA, Xu et al. [26,27] increased fracture toughness of PLA significantly, but tensile strength and modulus were diminished. Strength and toughness are two important properties for practical application of the PLA-based materials. To realize simultaneous strength and toughness enhancement remains a great challenge so far, and some fundamental issues related to the dispersion, alignment, and interfacial adhesion in the construction of high-quality composite materials are still the topics for study.

Additionally, the alkylation of graphene nanosheets has been suggested to be an effective way to obtain the desired nanocomposites by providing enhanced compatibility and interfacial adhesion between graphene and nonpolar polymer matrix [28,29]. But no research report is available on the effect of alkylated graphene nanosheets on the properties of PLA matrix. In the present work, we used fully exfoliated octadecylamine-functionalized graphene (ODAG) as efficient nanofiller to prepare PLA/ODAG nanocomposite films with different ODAG loading. By means of solution blending and casting, ODAG could be uniformly dispersed in the PLA matrix, and the prepared PLA/ODAG nanocomposite films exhibit markedly enhanced mechanical strength and toughness. The improvement effect of ODAG on morphology, thermal stability and crystallization behavior of PLA was also investigated and the

mechanism was discussed. The research reported herein is expected to be of great help for understanding the relationship between structure and properties of biodegradable polymer nanocomposites.

## 2. Experimental section

### 2.1. Materials

PLA (3051D,  $M_n = 11.8 \times 10^5$  mol/g,  $M_w/M_n = 1.72$ , and a density of  $1.24$  g/cm<sup>3</sup>) was supplied by NatureWorks (Minnetonka, USA). Natural graphite powder (325 meshes) was purchased from Qingdao HuaTai Lubricant Sealing S&T Co., Ltd. (Qingdao, China). Octadecylamine was obtained from Beijing Chemical Reagent Co. All the chemicals were used as received without further purification.

### 2.2. Preparation of octadecylamine-functionalized graphene (ODAG)

Graphene oxide (GO) was prepared from natural graphite powder by oxidation with  $\text{KMnO}_4$  in concentrated  $\text{H}_2\text{SO}_4$  according to the modified Hummer's method [30,31]. It was purified by dialysis for one week to remove the remaining salt impurities, and then lyophilized. In order to introduce alkyl moieties, the carboxylic groups located on the edges of the GO nanosheets were activated by reacting with thionyl chloride ( $\text{SOCl}_2$ ). For this process, the resulting fluffy powdery GO (100 mg) was refluxed in 20 mL of  $\text{SOCl}_2$  in the presence of 0.5 mL of anhydrous *N,N*-dimethylformamide (DMF) in a three-necked flask at  $70^\circ\text{C}$  for 24 h using a  $\text{CaCl}_2$  guard tube. At the end of the reaction, excess  $\text{SOCl}_2$  was removed by distillation, and remaining acylated GO was allowed to react with 1 g of octadecylamine (ODA) at  $120^\circ\text{C}$  for 4 days, according to a similar method previously described in the literature [32]. The resulting product was dispersed in hot ethanol, filtered through a  $0.2\ \mu\text{m}$  PTFE membrane, and washed with 200 mL of hot ethanol. The dried product was dissolved in 50 mL of chloroform ( $\text{CHCl}_3$ ) and centrifuged at 4000 rpm for 30 min. The upper solution was collected and centrifuged at 10,000 rpm to obtain the deposit at the bottom. This procedure was repeated twice to get the purified ODAG with a yield of 60%.

### 2.3. Preparation of PLA/ODAG nanocomposites

PLA/ODAG nanocomposite films were prepared via solution blending and casting using chloroform as a mutual solvent. Firstly, ODAG was dispersed in chloroform at a concentration of 5 mg/mL in an ultrasonic bath (Ningbo Xinzhi Instrument Model: SB 5200DTD, 400W) for 30 min at room temperature. In this process, ODAG was fully exfoliated to individual sheets to form a stably dispersed ODAG/ $\text{CHCl}_3$  solution. Meanwhile, PLA was completely dissolved in chloroform at a concentration of 50 mg/mL at room temperature. Then, desired amount of the above ODAG/ $\text{CHCl}_3$  dispersion was gradually added to the PLA solution under sonication and further sonicated for an additional 30 min at room temperature. Finally, the resulting homogeneous PLA/ODAG solutions were poured onto a clean glass plate to evaporate the solvent under ambient condition for 1 h, and the obtained PLA/ODAG films were further dried at  $75^\circ\text{C}$  in a vacuum for 48 h to remove the solvent completely. In this way, PLA/ODAG nanocomposite films ( $\sim 30\ \mu\text{m}$  thick) with different ODAG loadings between 0.1 and 1.0 wt% relative to PLA (abbreviated as ODAG0.1, ODAG0.2, ODAG0.4, ODAG0.6, ODAG0.8, ODAG1.0 in all figures and table) were fabricated and peeled off from the glass plate for structure, morphology, thermal and mechanical performance measurements. Neat PLA film was also prepared in similar procedures for comparison.

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