Materials Research Bulletin 56 (2014) 107–112

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Poly(methyl methacrylate)/layered zinc sulfide nanocomposites: Preparation, characterization and the improvements in thermal stability, flame retardant and optical properties

Biao Wang [a], Keqing Zhou [a], Saihua Jiang [a], Yongqian Shi [a,b], Bibo Wang [a], Zhou Gui [a,*], Yuan Hu [a,b,**]

[a] State Key Laboratory of Fire Science, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, PR China
[b] Suzhou Key Laboratory of Urban Public Safety, Suzhou Institute for Advanced Study, University of Science and Technology of China, 166 Ren'ai Road, Suzhou, Jiangsu 215123, PR China

ARTICLE INFO

Article history:
Received 17 December 2013
Received in revised form 23 April 2014
Accepted 25 April 2014
Available online 28 April 2014

Keywords:
Layered
Hydrothermal method
Thermal stability
Flame retardant
Optical properties

ABSTRACT

Layered zinc sulfide (LZnS) was synthesized successfully via hydrothermal method and poly(methyl methacrylate) (PMMA)/layered zinc sulfide nanocomposites were obtained by in situ bulk polymerization of methyl methacrylate (MMA). X-ray diffraction (XRD) and transmission electron microscopy (TEM) were used to characterize the as-synthesized layered zinc sulfide and PMMA/layered zinc sulfide nanocomposites. Microscale combustion calorimeter (MCC), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA) were used to test the thermal properties of the composites. Ultraviolet visible (UV–vis) transmittance spectra and photoluminence (PL) spectra were obtained to investigate the optical properties of the composites. From the results, the thermal degradation temperature is increased by 20–50 °C, the peak of heat release rate (pHRR) and total heat release (THR) are both decreased by above 30%, and the photoluminescence intensity is enhanced with the increasing loading of layered zinc sulfide.

1. Introduction

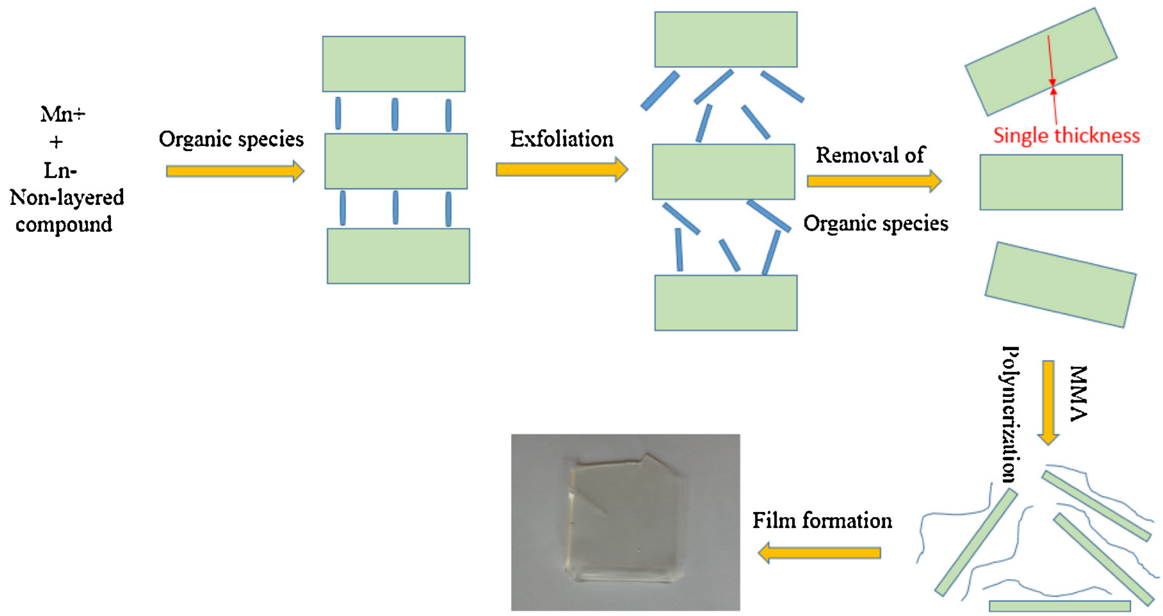
Recently, two-dimensional (2D) nanomaterials such as graphene and molybdenum disulfide are a conceptually new class of materials that offer new opportunities for high-quality and large-area nanodevices [1,2]. Beyond graphene itself, inorganic graphene analogues (IGAs) with high percentage of surface atoms have recently sparked worldwide interests owing to their novel properties and great potential for applications in transistors [2], energy storage [3,4], thermal conductors [5] and topological insulators [6]. Although the IGAs often bring on a wealth of innovative applications, their species are still only limited to layered compounds. In other words, controllable exfoliation of layered compounds is regarded as the exclusive way to obtain single-layered IGAs with few atomic thickness [7–9] whereas the hard bond-cleavage of non-layered compounds enables the fabrication of their single layers with few atomic thickness [10,11] making it a great challenge. Xie et al. have reported the fabrication of large-area freestanding single layers of non-layered ZnSe with four-atomic thickness, using a strategy involving a lamellar hybrid intermediate [12].

II–VI semiconductors have attracted great deal of attention among researchers in the past two decades due to their unique properties and potential applications. The related semiconductor materials have a potential for a variety of applications such as optical coatings, electro-optic modulators, photoconductors, optical sensors, phosphors, and other light emitting materials [13,14]. Zinc sulfide (ZnS), a wide direct band gap semiconductor, is one of the most typical and important II–VI compound semiconductors with broad applications in different fields such as optoelectronics, catalysis, and so on [15–17]. In recent years, ZnS nanoparticles have been gaining extensive attention for their luminescence properties [18,19].

Organic/inorganic hybrid materials, based on interactions between organic and inorganic components, have been greatly developed in the past decades. Among them, polymer nanocomposites consisted of a polymer matrix and layered nano-fillers have gained a lot of interest in the past two decades due to their markedly enhanced properties [20–25]. When polymers are mixed

* Corresponding author. Tel.: +86 551 3601288; fax: +86 551 3601669.
** Corresponding author. Tel.: +86 551 3601664; fax: +86 551 3601664.
E-mail addresses: zgui@ustc.edu.cn (Z. Gui), yuanhu@ustc.edu.cn (Y. Hu).

http://dx.doi.org/10.1016/j.materresbull.2014.04.066
0025-5408/



Scheme 1. Illustration of the preparation process of PMMA nanocomposites.

with layered inorganic components at the molecular level, some significant improvements can be obtained, including mechanical properties, thermal stability, fire resistance, and gas permeability, etc. [26–31]. And on the other hand, development of optical materials with high refractive indices has received wide attention in the past decades. One of the common approaches is to introduce characteristic substituents such as aromatic ring and sulfur atoms of high molar refractions and low molar volumes to the polymers in order to improve their optical properties [31–33]. So far, ZnS quantum dots and metal atom doped ZnS were incorporated into polymer for enhancing the optical properties [34,35].

PMMA is a typical transparent amorphous polymer which has been widely used as an important material for plastic optical fibers as well as optical lenses. Though it has several desirable properties such as good flexibility, high strength, and excellent dimension stability, poor heat resistance of PMMA makes it unable to fulfill the current demands [36]. To fabricate PMMA nanocomposites, scientists have to face one challenge that is to enhance thermal and mechanical properties with the limiting loss in transparency [37]. A series of studies on PMMA nanocomposites had been conducted in our group, recently we first synthesized PMMA/LZnS nanocomposites with both high transparency and good thermal properties [38–40].

In this paper, layered zinc sulfide was first synthesized via hydrothermal method [41], and then incorporated into PMMA matrix by in situ bulk polymerization. These nanocomposites were endowed with the advantages of PMMA, ZnS and layered material. Transparent nanocomposites with good optical and thermal properties were obtained. The synthesized route of the PMMA/LZnS nanocomposites is shown in Scheme 1.

2. Experimental

2.1. Reagents and materials

Zinc nitrate (98%, AP), sulfur (98%, AP), *n*-propylamine (pa, 99%, AP), methyl methacrylate (AP) and benzoyl peroxide were purchased from Sinopharm Chemical Reagent Co., Ltd., and MMA was used after further purification including retarder remover, water remover and reduced pressure distillation. Absolute ethyl alcohol was purchased from Shanghai Suyi Chemical Reagent Co., Ltd. The distilled water was produced in our laboratory.

2.2. Synthesis of layered zinc sulfide

In a typical experimental, 2.97 g of $Zn(NO_3)_2 \cdot 6H_2O$, 0.16 g of sulfur, and 20 mL of pa were transferred into 50 mL reaction vessels, the vessels were then sealed in ovens at 110 °C for 5 days. The vessels were naturally cooled down to room temperature after the reactions were completed. The final products were washed by absolute ethyl alcohol and distilled water several times, the samples were further dried at 60 °C. 1 g of ZnS and 20 mL of ethanol were added into a weighing bottle with a capacity of 50 mL. The weighing bottle was then sealed and sonicated for 0.5 h, the resultant dispersions were centrifuged at 500 rpm for 0.5 h. After centrifugation, the dispersions become almost transparent. The dispersions were then laid aside for different time. We estimated the mass remaining in the supernatant by drying and weighing the sediments in the centrifugal tube.

2.3. Preparation of PMMA/LZnS nanocompsoites

20 mL of as-prepared LZnS dispersions and 50 mg of benzoyl peroxide (BPO) initiator were added into 10 g of freshly distilled MMA under ultrasonication to form a transparent solution. The subsequent bulk polymerization was carried out with the prepolymerization process at 90 °C for 10 min and the subsequent programmed heating process of 70 °C for 10 h. Neat PMMA was directly polymerized without adding LZnS. The compositions of the PMMA/LZnS nanocomposites are listed in Table 1.

Table 1
Formulation of PMMA nanocomposites.

Sample	Component
PMMA0	PMMA
PMMA1	PMMA/LZnS (0.1%)
PMMA2	PMMA/LZnS (0.5%)
PMMA3	PMMA/LZnS (1.0%)