Composites Science and Technology 107 (2015) 120–128

Contents lists available at ScienceDirect

Composites Science and Technology

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

In situ synthesis, morphology, and fundamental properties of polymer/MoS_2 nanocomposites

Keqing Zhou, Jiajia Liu, Wenru Zeng, Yuan Hu *, Zhou Gui *

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China

ARTICLE INFO

Article history:
Received 30 September 2014
Received in revised form 27 November 2014
Accepted 28 November 2014
Available online 4 December 2014

Keywords:
A. Polymer-matrix composites (PMCs)
A. Layered structures
B. Thermal properties
D. Thermogravimetric analysis (TGA)

ABSTRACT

As a graphene-like layered nanomaterial, molybdenum disulfide (MoS_2) had gained enormous attention from the materials fields. In this work, MoS_2 nanosheets were firstly modified by cation surfactant with long alkyl chain (CTAB) and then the modified MoS_2 nanosheets (CTAB-MoS_2) were incorporated into polystyrene (PS) and poly(methyl methacrylate) (PMMA) matrices via in situ polymerization method. The structure, thermal stability and fire resistance properties of the PS and PMMA/CTAB-MoS_2 nanocomposites were studied by X-ray diffraction (XRD), Transmission electron microscopy (TEM), Thermogravimetric analysis (TGA), Microscale combustion colorimeter (MCC) and Cone test, respectively. The modified MoS_2 nanosheets were dispersed well in the PS matrix with intercalated structure as indicated by XRD pattern and TEM techniques. The introduction of MoS_2 into the polymer matrix such as PS and PMMA can markedly improve its thermal properties and reduce the fire hazards. With the addition of 3 wt% CTAB-MoS_2, $T_{-50\%}$ and $T_{-\max}$ of the PS nanocomposites were increased by 48 and 46 °C, respectively. The peak of heat release rate (PHRR) and total heat release (THR) values of the PS/5% CTAB-MoS_2 nanocomposites decreased by 40% and 27% respectively compared with that of the pure PS. For the PMMA nanocomposites with 1% CTAB-MoS_2, the $T_{-5\%}$ and $T_{-10\%}$ increased by 35 and 53 °C compared to that of neat PMMA. Meanwhile, the PHRR and THR were decreased by 25% and 20%, respectively. The method used in this research work provided a novel route to other MoS_2-based polymer nanocomposites with excellent performances.

1. Introduction

In the past few years, two dimensional (2D) nanosheets such as graphene, transition metal dichalcogenides (TMDs), hexagonal boron nitride (h-BN) and carbon nitride (C_3N_4) have been attracting plentiful attention due to the unique performances associated with their ultrathin structure. Layered transition metal dichalcogenides, such as MoS_2 and WS_2, have been successfully established as a new paradigm as well as the graphene analogs [1–3]. From the structural point of view, MoS_2 is a typical family member of TMDs, in that MoS_2 crystals are characterized as hexagonal layered configurations in which the atoms in the layer are bonded with strong covalent bonding, while the layers are packed together to form a sandwich structure with weak Van der Waals forces like graphite and h-BN [1].

MoS_2 has attracted considerable interest over the last few years on account of its extraordinary optical, thermal, and mechanical properties arising from its unique structure [3]. The unique sandwich structure has potential applications in many technological fields, such as super lubricant, sensors, batteries, photocatalyst, hydrogen storage and nanocomposites [4–15], where MoS_2-based polymer composites are a novel class of materials that combine the attractive functional properties of MoS_2 (electrical, optical, thermal, mechanical properties, etc) with the advantages of polymers, such as low cost and good processability.

Polymer/layered inorganic nanocomposites have attracted tremendous attention for their potential in improving polymer properties such as mechanical, thermal, and physical properties. MoS_2 nanosheets are expected to become one kind of useful fillers for improving the properties of polymers. Firstly, it has been reported that a monolayer of MoS_2 have an extraordinarily high breaking strength (~23 GPa) and Young modulus (~300 GPa), which can be compared to those of chemically reduced graphene. Thus MoS_2 can be used to improve the mechanical properties of polymers [15]. In addition, as a typical layered inorganic material, MoS_2 is expected to disperse and exfoliate in polymers and results in the physical barrier effects which inhibit the diffusion of heat and the decomposition products of the polymer and also the tran-

---

* Corresponding authors. Tel.: +86 551 3601288; fax: +86 551 3601669 (Z. Gui). Tel./fax: +86 551 3601664; (Y. Hu).

E-mail addresses: yuanhu@ustc.edu.cn (Y. Hu), zgui@ustc.edu.cn (Z. Gui).

http://dx.doi.org/10.1016/j.compscitech.2014.11.017

sition metal element Mo promotes the formation of the charred layer acting as a physical barrier which could slow down heat and mass transfer during the burning. So it is reasonable that MoS_2 may improve the thermal stability and fire resistance of polymer-based composites just like MMT, LDHs and graphene [10].

However, the preparation of such polymer composites requires not only that MoS_2 nanosheets can be produced on a sufficient scale but that they also are incorporated, and dispersed into various polymer matrices with homogeneous structure. To achieve high-performance of MoS_2/polymer nanocomposites, homogeneous dispersion of MoS_2 nanosheets in the polymer hosts and proper interfacial interactions between the nanosheets and the surrounding matrix must be considered. In fact, the preparation of polymer/MoS_2 nanocomposites based on parent MoS_2 is difficult to achieve. The amphiphobic nature of the MoS_2 nanosheets causes poor dispersion in a variety of organic solvents and not compatible with the organic polymer matrix [15]. Most monomers and polymers cannot be easily intercalated between MoS_2 nanosheets in its pristine state which are mainly due to no reactive groups on the surface of MoS_2 and parent MoS_2 lacks both the space and affinity for polymer molecules (or monomers) to be intercalated into its galleries. Furthermore, the individual sheets tend to restack owing to their large specific surface area and Van der Waals interactions between the interlayers of MoS_2 nanosheets, which make the interlayer distance between MoS_2 nanoplatelets very narrow. An effective way to overcome the agglomeration and enhance the compatibility between MoS_2 nanosheets and polymer matrix is the surface modification of MoS_2 via noncovalent and covalent interaction. Therefore, it is very urgent to explore a facile and efficient method to make MoS_2 nanosheets homogeneously dispersed in the matrix and to improve the compatibility with polymers.

It is commonly now believed that in order to produce homogeneous polymer/inorganic nanocomposites, inorganic particles are frequently surface-modified (by the attachment of polymerisable (organic) functionalities) or introduced into the polymer matrix in the presence of surfactants in order to improve the compatibility between the organic and inorganic segments [16]. According to previous research work, surfactant-modified graphene or clays can more easily disperse in an organic polymer matrix to form polymer nanocomposites [17,18]. For the layered MoS_2, treatment with strong reducing agents such as *n*-butyl lithium can result in Li ions being inserted into the layered structure of MoS_2 to form the lithium intercalated MoS_2 (Li_xMoS_2) by a solvothermal method. The resulting Li_xMoS_2 can be exfoliated to single or few layers MoS_2 with negatively charged via the rapid hydrolysis and ultrasonication of Li_xMoS_2 in distilled water [9,10]. In the presence of positively charged guest species such as organic cationic surfactant, the MoS_2 host layers will be restacked and result in the formation of novel intercalation compounds. Organic functionality in the modified layered nanofillers makes it more compatible with the organic polymer. With a suitable distribution of nanofillers in the polymer matrix, nanocomposites can exhibit improved mechanical, thermal, electrical, and gas barrier properties [19].

In general, the predicted potential of polymer nanocomposites is not achieved because of a poor homogeneous distribution and a weak interfacial adhesion. Layered nanofillers tend to aggregate for their high surface energy, and hence, how to get a nanometer-scale dispersion of nanofillers is still a challenge for preparation of polymer nanocomposites. Many approaches have been developed for preparing polymer/inorganic nanocomposites, such as melt blending method, solvent blending method, and in situ polymerization method. Melt blending is the most economically attractive and scalable method. However, melt blending also presents several severe problems due to the high melt viscosity of most polymers, such as impregnation, flow of resin and removal of bubbles [20]. Although solvent blending method generally leads to better particle dispersion than melt processing, slow solvent evaporation often induces particle reaggregation and commercialization is restricted by cost and the required organic solvent is poisonous and not convenient for industrial processing [21]. The in situ polymerization of monomers in the presence of nanofillers is a promising approach for improvement of nanofiller dispersion in the polymeric matrix because of the intimate contact of fillers and the polymer matrix during synthesis [22]. In previous work, it had been reported that the in situ polymerization of monomer in the presence of CNT is considered to be a good approach for a homogeneous dispersion, providing advanced polymer/CNT composites with improved mechanical properties [23]. In addition, Potts et al. reported good dispersion of CRG in PMMA using in-situ free-radical polymerization [24]. Moreover, some reports in the literature deal with the in situ polymerization of vinyl monomers in the presence of graphene nanosheets [25,26]. This procedure has shown to be more effective than melt mixing, since it allows a better distribution and dispersion of the graphene nanosheets within the polymer matrix. Recently, MoS_2 had been applied as a reinforcing material in polymers using a variety of methods including solution or melt blending [9–11,13–15] and in situ-emulsion polymerization [12]. Nonetheless, the in situ polymerization of heterogeneous systems in the presence of organic modified MoS_2 nanosheets has been scarcely studied.

Motivated by these results, in this work, we sought to explore a facile and efficient route for preparing MoS_2/polymer nanocomposites via in situ bulk-polymerization of MMA and St in the presence of CTAB-modified MoS_2 which are prepared by assembling from MoS_2 nanosheets and alkylammonium cations [27]. The long-alkyl chain attached onto the surfaces of MoS_2 nanosheets favored homogeneous dispersion of MoS_2 in the matrix and good compatibility between MoS_2 and polymer matrices. Scheme 1 presented the whole synthesis strategy. The obtained PS and PMMA/CTAB-MoS_2 nanocomposites exhibited significant enhancements in thermal stability and fire resistance properties.

2. Experimental section

2.1. Materials

Molybdenum disulfide (MoS_2, AP), Cetyl trimethyl ammonium bromide (CTAB) and *n*-hexane (AP) removing the moisture with the coronizing molecular sieve was purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The *n*-butyl lithium (2.2 M in hexane) was purchased from Alfa Aesar without further purified. Styrene (St) and Methyl methacrylate (MMA) monomers were used after further purification including retarder removal, water removal and reduced pressure distillation. Benzoyl peroxide (BPO) was further purified by recrystallization from methanol. The distilled water was produced in our laboratory. All other chemicals were used as received.

2.2. Preparation of the CTAB modified MoS_2

Firstly, Li_xMoS_2 was prepared by the solvothermal methodology, similar to the preparation procedure of our previous work [9]. And then the Li_xMoS_2 was exfoliated to single or few layers MoS_2 with negatively charged via the rapid hydrolysis and ultrasonication process. Excess amount of CTAB was dissolved in distilled water and then added into the colloidal suspension of MoS_2 nanosheets under stirring for 8 h. The CTAB-modified MoS_2 were collected after being centrifugally separated at 4500 rpm for 8 min, washed with hot water and ethanol for several times and then dried in vacuum at 60 °C for 24 h.