



# Facile preparation of poly(methyl methacrylate)/MoS<sub>2</sub> nanocomposites via in situ emulsion polymerization



Keqing Zhou, Jiajia Liu, Biao Wang, Qiangjun Zhang, Yongqian Shi, Saihua Jiang, Yuan Hu<sup>\*</sup>, Zhou Gui<sup>\*</sup>

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

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## ABSTRACT

In this work, poly(methyl methacrylate)/MoS<sub>2</sub> nanocomposites were prepared by a facile emulsion polymerization method. X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Transmission electron microscopy (TEM) results demonstrated that MoS<sub>2</sub> is homogeneously dispersed and partially exfoliated in a PMMA matrix. The improvement in thermal stability of the nanocomposites is remarkable with only 1% MoS<sub>2</sub> content which is attributed to the physical barrier effect and the charring effect of the MoS<sub>2</sub> nanosheets.

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## 1. Introduction

Since the discovery of graphene, great attention has been paid to other layered materials, inorganic analogs of graphene, such as transition metal dichalcogenides and hexagonal boron nitride. Among these 2D layered materials, molybdenum disulfide (MoS<sub>2</sub>) is one of the most attractive and has a similar structure to graphite. The basic unit of MoS<sub>2</sub> is composed of a molybdenum atom coordinated with six sulfur atoms. It is organized in two layers of sulfur atoms forming a sandwich structure, with a layer of molybdenum atoms in the middle. MoS<sub>2</sub> has many comprehensive applications due to their unmatched properties such as solid lubricant, lithium ion batteries, photocatalysts, sensors and conductive fillers in polymer composites [1–7].

It is well known that pristine unmodified MoS<sub>2</sub> cannot be easily dispersed in a polymer matrix. This is because there are no reactive groups on the bulk MoS<sub>2</sub> layers, which make it difficult for organic molecules or monomers to be loaded on its surface. In addition, MoS<sub>2</sub> layers lack the affinity and space for hydrophilic or hydrophobic molecules and polymers to intercalate into its galleries. Hence, pristine MoS<sub>2</sub> is usually exfoliated in order to be used for the synthesis of polymer nanocomposites. As is known to all, the bulk MoS<sub>2</sub> is formed of 2D layers held together by weak van der Waals forces which make the cleavage of bonds between

these layers very easy. Therefore, MoS<sub>2</sub> can be converted into high aspect ratio reinforcement platelets with nanometer-scale thickness through a process of intercalation and exfoliation.

In the past few decades, by exploiting the exfoliation and restacking properties of Li<sub>x</sub>MoS<sub>2</sub> in water which was prepared with n-butyllithium as an intercalating agent, different types of polymers have been included into MoS<sub>2</sub> such as polyaniline, polythiophene, polypyrrol, poly[oxyethylene-(oxyethylene)], poly(vinyl alcohol), polystyrene and poly(methyl methacrylate) [6,8–12]. To date, most of polymer/MoS<sub>2</sub> layered nanocomposites have been achieved through the direct insertion approach, where the polymers are first dispersed in water and then inserted into the MoS<sub>2</sub> layered structure [6,8,11]. Another synthetic approach involves insertion of monomer firstly, followed by polymerization with an initiator [9,10]. Unfortunately, aqueous dispersions are of limited interest in many of the applications proposed for MoS<sub>2</sub>. This is especially true regarding the preparation of MoS<sub>2</sub> based polymer nanocomposites, since most of engineering polymers are merely soluble in organic solvents rather than in water and some monomer such as methyl methacrylate and styrene cannot be compatible with water system. Moreover, MoS<sub>2</sub> nanosheets are usually apt to re-aggregate and stack after separating from the alkaline suspension which is obtained from the hydrolysis of Li-intercalated MoS<sub>2</sub>. Consequently, it is necessary to explore a new approach to prepare polymer/MoS<sub>2</sub> nanocomposites. In a recent study, Lee et al. reported the use of graphene for the synthesis of PMMA nanocomposites by in situ emulsion polymerization. The authors showed that this could be a promising route for the production of composite materials based on graphene with excellent performances [13].

<sup>\*</sup> Corresponding authors. Tel.: +86 551 3601288; fax: +86 551 3601669;

Tel.: +86 551 3601664; fax: +86 551 3601664.

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

Inspired by this, this work reports the preparation of PMMA/MoS<sub>2</sub> nanocomposites through the emulsion polymerization of methyl methacrylate monomer in MoS<sub>2</sub> dispersions which is obtained from the hydrolysis of Li<sub>x</sub>MoS<sub>2</sub>. The as-prepared PMMA/MoS<sub>2</sub> nanocomposites were characterized by FTIR, XRD, TEM and TG analysis measurements. It provides a facile path to prepare MoS<sub>2</sub>-based PMMA nanocomposites. Moreover, the emulsion polymerization method opens a new avenue to fabricate MoS<sub>2</sub>-based nanocomposites of water-insoluble polymers on a large scale and effectively for more extensive applications.

## 2. Materials and methods

**Preparation of the MoS<sub>2</sub> dispersion:** All reagents are analytical reagents and used as received without further purification. MoS<sub>2</sub> dispersion is obtained by the hydrolysis of Li-intercalated MoS<sub>2</sub> (Li<sub>x</sub>MoS<sub>2</sub>) which was fabricated by a solvothermal approach as reported in our previous work [11].

**Synthesis of PMMA/MoS<sub>2</sub> nanocomposites:** In a typical experiment, 0.3 g Li<sub>x</sub>MoS<sub>2</sub> was ultrasonically dispersed in 100 mL distilled water for 2 h to obtain MoS<sub>2</sub> dispersion. In a 250 mL glass reactor equipped with a stainless-steel stirrer, reflux condenser, and thermometer, 1.8 g SDS was dissolved in 50 mL distilled water, to which the MoS<sub>2</sub> dispersion was added and stirred for 1 h at 80 °C. 30.0 g MMA monomer was then added into the mixture over 30 min. Next, 0.1 g KPS was added and stirred for an additional 4 h. The products were allowed to cool to room temperature, precipitated by the addition of dilute NaCl aqueous solution and then washed several times with deionized water to remove excess SDS. The powders obtained were dried under vacuum for 24 h at 60 °C. The pure PMMA and PMMA nanocomposites with a different content of MoS<sub>2</sub> were prepared in a similar procedure.

XRD patterns were performed with a Japan Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu-K $\alpha$  tube and Ni filter ( $\lambda = 0.1542$  nm). FTIR spectra were recorded with a Nicolet 6700 spectrometer (Nicolet Instrument Company, USA). TEM images were obtained on a JEOL JEM-2100 F transmission electron microscope at an accelerating voltage of 200 keV. Thermogravimetric analysis (TGA) was conducted using a Q5000 thermo-analyzer instrument (TA Instruments Inc., USA) from room temperature to 600 °C at a linear heating rate of 20 °C/min under an air flow (25 mL/min).

## 3. Results and discussion

FTIR spectra of the MoS<sub>2</sub>, PMMA and PMMA/MoS<sub>2</sub> nanocomposites are shown in Fig. 1. A broad band occurred at 1630 and 3430 cm<sup>-1</sup> in the FTIR spectrum of MoS<sub>2</sub> which are attributed to bending and stretching vibration of H–O–H. Moreover, it is clear that the FTIR spectrum of the PMMA/MoS<sub>2</sub> nanocomposites shows the same characteristic signals with pure PMMA. The characteristic absorption bands of PMMA are clearly visible in the region of 2998, 2950, 2850, and 1383 cm<sup>-1</sup> for stretching vibration of C–H in methylene and methyl groups [13]. The peak at 1450 cm<sup>-1</sup> is attributed to the alkane vibration mode in PMMA. Additionally, a stronger band at 1730 cm<sup>-1</sup> and a relatively strong band at 1243 and 1148 cm<sup>-1</sup> due to the C=O and C–O stretches can be observed [14]. The FTIR results indicate that PMMA/MoS<sub>2</sub> nanocomposites have been prepared successfully.

The morphology and structure of polymer/layered inorganic nanocomposites are generally characterized by XRD and TEM analysis. The XRD technique was used to characterize the crystallographic structure of the MoS<sub>2</sub> nanosheets and their dispersed

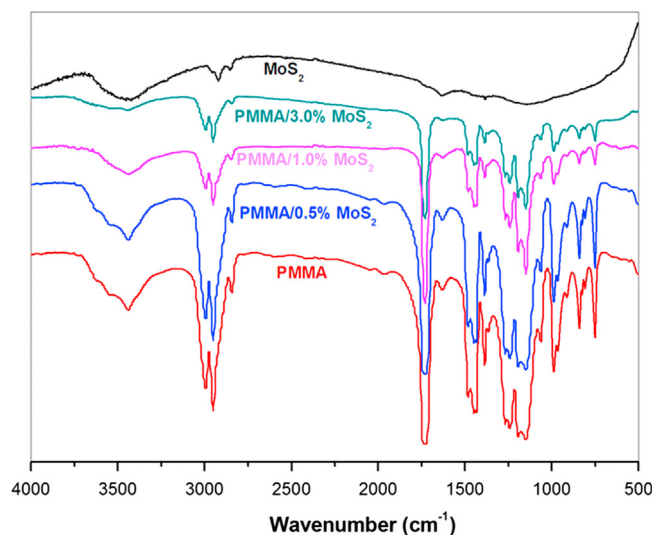


Fig. 1. FTIR spectra of MoS<sub>2</sub>, PMMA and PMMA/MoS<sub>2</sub> nanocomposites.

homogeneity in the PMMA (Fig. 2a). The virgin PMMA exhibits a wide crystalline peak around  $2\theta = 14.0^\circ$  which is corresponding to amorphous PMMA. For the PMMA/1% MoS<sub>2</sub> nanocomposites, almost all the peaks of the MoS<sub>2</sub> in the PMMA matrix disappeared comparing with the original inorganic sample except for the (0 0 2) peak. The intensity of the (0 0 2) peak is still seen in the PMMA nanocomposites, and the peak position does not change. However, the intensity is obviously decreased. It indicates that some of the MoS<sub>2</sub> in the PMMA matrix are few-layer platelets which are not completely exfoliated. It can be concluded that a good dispersion of MoS<sub>2</sub> in the PMMA matrix has been obtained in PMMA/1% MoS<sub>2</sub> nanocomposites, but the MoS<sub>2</sub> layers are partial exfoliated [11]. However, these conjectures still need to be supported by TEM analysis. Fig. 2b presents the TEM image of PMMA/1% MoS<sub>2</sub> nanocomposites, it is clearly visible that the MoS<sub>2</sub> sheets are homogeneously dispersed in the PMMA matrix, providing direct evidence of crystal layer exfoliation. TEM images also show some large ordered parts, which looks like a MoS<sub>2</sub> layer aggregate together, it may be the reason for the small (0 0 2) peak appeared in the XRD pattern of the PMMA nanocomposites. These demonstrate that MoS<sub>2</sub> is well dispersed in the PMMA matrix with a partial exfoliation structure. The TEM observations are in good agreement with the XRD results.

It is well known that layered nanofillers usually increase the thermal stability of a polymer matrix due to the physical barrier effect which retards the diffusion of degradation products, gases and heat. In the temperature range of 250–420 °C where PMMA is mainly degraded, MoS<sub>2</sub> (99% residue) is only slightly decomposed [11], so MoS<sub>2</sub> nanosheets can present better physical barrier effects, which may increase the thermal stability of PMMA in theory. TG profiles of pure PMMA and PMMA nanocomposites under air atmosphere are presented in Fig. 3 and the corresponding data are listed in Table 1. The PMMA/MoS<sub>2</sub> nanocomposites exhibit a similar thermal decomposition process to the pure PMMA, which is mainly ascribed to the decomposition of the polymer molecular chains. However, the thermal stability of the PMMA/MoS<sub>2</sub> nanocomposites is enhanced compared with that of the neat PMMA, which can be ascribed to the barrier effect of MoS<sub>2</sub> on the diffusion of volatile products throughout the composite materials. The temperatures corresponding to 10 wt% weight loss ( $T_{0.1}$ ) which are used to evaluate the decomposition of PMMA on the onset stage and 50 wt% weight loss ( $T_{0.5}$ ) are summarized in Table 1. From Table 1, it can be observed that  $T_{0.1}$  and  $T_{0.5}$  of all the composites are higher than that of pure PMMA. When adding 1 wt

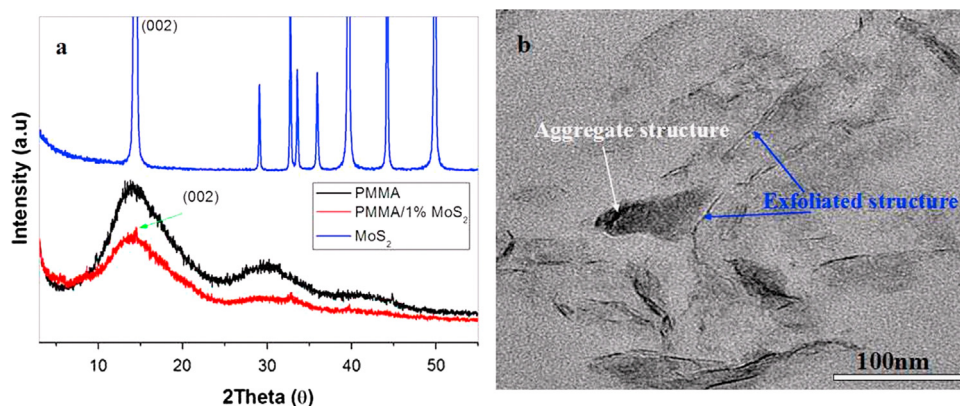


Fig. 2. X-ray diffraction patterns of the MoS<sub>2</sub>, pure PMMA and PMMA/1%MoS<sub>2</sub> nanocomposites (a), TEM observations of the ultrathin sections obtained from PMMA/1%MoS<sub>2</sub> nanocomposites (b).

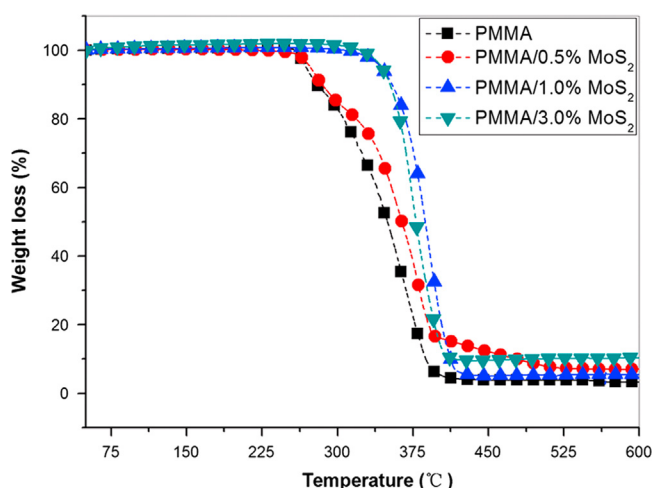


Fig. 3. TG curves of pure PMMA and PMMA/MoS<sub>2</sub> nanocomposites.

Table 1  
TGA data of PMMA and PMMA/MoS<sub>2</sub> nanocomposites.

Sample	$T_{-10\%}$ (°C)	$T_{-50\%}$ (°C)	Char residue <sup>a</sup> (%)
PMMA	280	350	3.37
PMMA/0.5% MoS <sub>2</sub>	285	364	7.04
PMMA/1.0% MoS <sub>2</sub>	354	387	5.42
PMMA/3.0% MoS <sub>2</sub>	352	378	10.31

<sup>a</sup> At 600 °C

% MoS<sub>2</sub>,  $T_{0.1}$  and  $T_{0.5}$  of the composites is increased to 354 and 387 °C, which are 74 and 37 °C higher than that of pure PMMA. It indicates that the presence of MoS<sub>2</sub> defers the thermal degradation of PMMA. Moreover, it is well known that the char formed during thermal degradation and combustion is also important for fire safety applications. The char yield of pure PMMA is 3.37% at 600 °C, and the char yield of the PMMA/MoS<sub>2</sub> nanocomposites is all higher than that of the pure PMMA. It is clear that MoS<sub>2</sub> can catalyze the char formation of PMMA during thermal degradation. All in all, these results suggest that incorporating MoS<sub>2</sub> nanosheets into PMMA via in situ emulsion polymerization would retard the thermal degradation of PMMA molecular chains, the significantly

enhanced thermal stability can be attributed to the physical barrier effect of the MoS<sub>2</sub> nanosheets and the presence of MoS<sub>2</sub> can promote char formation.

#### 4. Conclusions

In this work, MoS<sub>2</sub> was incorporated into PMMA using a facile emulsion polymerization method. The structure, morphology and thermal behavior of the PMMA/MoS<sub>2</sub> nanocomposites have been studied. FTIR, XRD and TEM results demonstrated that the MoS<sub>2</sub> were homogeneously dispersed in PMMA matrix with a partial exfoliation structure. The thermal stability of the PMMA/MoS<sub>2</sub> nanocomposites was significantly improved, which is attributed to the physical barrier effect and charring effect of MoS<sub>2</sub> nanosheets.

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