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Molybdenum disulfide nanosheets as barrier enhancing nanofillers in thermal decomposition of polypropylene composites

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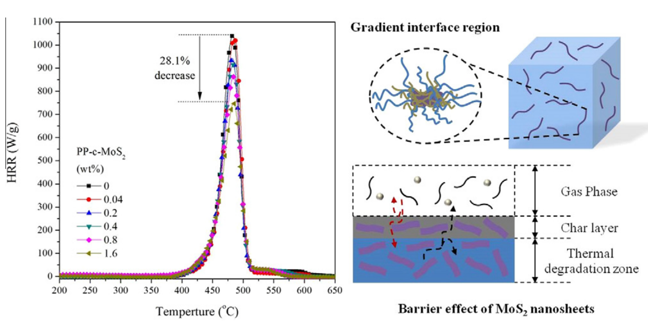
HIGHLIGHTS

- PP composites were fabricated by combing latex technology with melt-blending method.
- MA-g-PP coated MoS_2 is well dispersed in PP matrix with strong interfacial adhesion.
- The addition of MoS_2 obviously improves the thermal stability of PP composites.
- The barrier effect of MoS_2 nanosheets suppresses emission of flammable pyrolysis gas.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method of preparing the molybdenum disulfide (MoS_2) nanosheets coated by polypropylene (PP) latex enables the fabrication of PP/MoS_2 nanocomposites in scalable quantities. PP nanocomposites with various contents of MoS_2 nanosheets were prepared by simply melt-blending the coated MoS_2 and PP materials. The barrier effect of MoS_2 nanosheets in the thermal decomposition process of PP materials was investigated under different atmosphere by thermogravimetric analysis (TGA), microscale combustion colorimeter (MCC) and thermogravimetric analysis–infrared spectrometry (TG–IR). Importantly, the peak heat release rate (PHRR) of PP/MoS_2 nanocomposites with MoS_2 loadings of 1.6 wt% is decreased by 28.1% compared to that of neat PP. Moreover, the thermal oxidative stability of PP is dramatically reinforced with the incorporation of MoS_2 nanosheets. A 41.3 °C increase in the temperature of the onset of degradation ($T_{-10\%}$) and a 40.1 °C increase in the temperature of maximum weight loss (T_{max}) were observed by inclusion of as low as 1.6 wt% MoS_2 nanosheets. The excellent barrier performance together with the favorable compatibility of MoS_2 nanosheets is regarded as the key point for the reinforcement of thermal oxidative stability and reduction of flammable pyrolysis gas, which can provide promising applications in the development of fire safety polymer materials.

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1. Introduction

As a typical layered structure materials, bulk molybdenum disulfide (MoS_2) has been used as a solid lubricant for many years [1,2]. With the rise of graphene, MoS_2 nanosheets with the same two-dimensional (2D) structure have attracted considerable attentions due to their unique semiconductor characters and superior catalytic performance [3–5]. Some of these excellent properties mainly depend on atomic-layer thickness and 2D morphology of MoS_2 nanosheets. Similarly with graphene, several advanced techniques for MoS_2 have been developed to grow single layered MoS_2 sheets [6] or exfoliate 2D nanosheets from bulk materials [7,8]. Typically, chemical exfoliation method using lithium intercalation is often used to produce 2D MoS_2 nanosheets in scalable quantities [9,10]. Because MoS_2 nanosheets are finally suspended in the aqueous phase after the hydrolysis of lithium intercalated MoS_2, it is troublesome to directly employ this suspension of MoS_2 nanosheets for some applications. After further filtration of MoS_2 suspensions, MoS_2 nanosheets tend to re-stack into considerable layered structure, of which 2D geometrical features are always lost. Therefore, it is necessary to pointedly process MoS_2 nanosheets dispersed in the aqueous for specific purpose.

There is a general agreement that 2D nanomaterials can be employ to reinforce polymers, which always results in obvious enhancement effect on properties of polymer materials at an extremely low content of nanofillers [11,12]. For example, robust graphene has been proved to be a kind of promising nanofillers for properties reinforcement of polymer composites [13,14]. Owing to its high aspect ratio, high specific surface area, superb thermal stability as well as semiconductor characteristic, MoS_2 nanosheet may be an excellent alternative to graphene used in these applications that require effective properties reinforcement while also maintain electrical insulation property and high dielectric constant of polymer composites. Eksik et al. demonstrated that MoS_2 nanoplatelets are highly effective at enhancing the mechanical properties of the epoxy resin at very low nanofiller loading fractions (below 0.2% by weight) [15]. Wang and his co-authors developed an in situ polymerization approach to covalently functionalize MoS_2 nanosheets, the incorporation of which induced significant thermal stabilization and mechanical reinforcement in the nylon-6 matrix [16]. In our previous reports, MoS_2 nanosheets prepared by liquid ultrasonic techniques have been used to reinforce thermal and mechanical properties of polymer matrix, which is benefited from the proper surface modification, inherent thermal stability and mechanical characters [17,18]. Therefore, preparation of dispersible 2D MoS_2 nanosheets is a committed step to obtain significantly reinforced polymer nanocomposites. To disperse the nanofillers homogeneously in polymer matrix, solution-mixing is considered to be a simple strategy [19,20]. When it comes to MoS_2 nanosheets based polymer nanocomposites, solution-mixing technique becomes impossible since the large-scale and high-quality MoS_2 nanosheets are only obtained in the aqueous phase by chemical exfoliation process, nevertheless, most of polymer materials are water-insoluble. Additionally, solution-mixing method also has limited applicability and scalability. The latex premixing method combined with subsequent melt-blending is regarded as an effective and convenient technique to incorporate these water-dispersed nanofillers into polymer matrix [21,22].

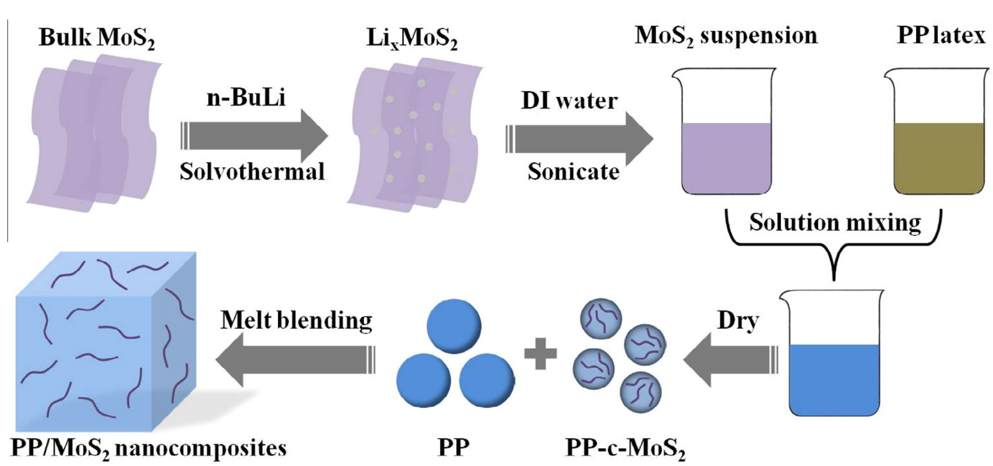
Polypropylene (PP) as a classic non-polar polymer material has been extensively applied in various kinds of engineer fields [23,24]. In recent years, there are many kinds of nanofillers has been performed to reinforce the properties of PP materials, such as carbon nanotube [25], graphene [26], layered double hydroxide [27], etc., [28,29]. For the improvement of thermal stability and fire retardancy, physical barrier effect of 2D nanofillers in polymer matrix is proved to be an ingenious pathway [30,31]. Song and his co-authors have proved that the 2D graphene can lead to superior gas permeability, flame retardancy and melt viscosity of PP matrix relative to CNTs [32]. All of these properties enhancements benefit from the physical barrier effect of specific 2D lamellar structure. As far as we know, there is no report yet about the physical barrier effect of MoS_2 nanosheets as well as the properties enhancements of PP/MoS_2 nanocomposites.

In this work, we incorporated MoS_2 nanosheets into PP matrix by a convenient latex premixing combined with subsequent melt-blending method, which effectively overcomes the dispersibility barrier of MoS_2 nanosheets obtained by chemical exfoliation in aqueous phase and provides sufficient interface adhesion between the MoS_2 nanosheets and PP matrix. Thermal decomposition behavior under different conditions was monitored to investigate the physical barrier effect of MoS_2 nanosheets in PP matrix. It is anticipated that this work will enable MoS_2 nanosheets to achieve their whole potential in polymer nanocomposites.

2. Experiment section

2.1. Materials

Molybdenum disulfide (MoS_2, AP) and n-hexane (AP) were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). n-Butyl



Scheme 1. Schematic illustration for preparation of PP-c-MoS_2 and corresponding production of PP nanocomposites.