Enhancement of Thermal Stability, Conductivity and Smoke Suppression of Polyethylene Composites with Exfoliated MoS₂ Functionalized with Magnetite

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This work reports a facile fabrication method to modify exfoliated molybdenum disulfide (e-MoS₂) nanosheets with magnetite nanoparticles with various size distribution. The obtained materials have been utilized as nanofillers of polyethylene to enhance its thermal properties and flame retardance. The incorporation of magnetite modified MoS_2 nanosheets leads to the reduction of the peak heat release rate. The best thermal conductivity has been noticed for composites with e-MoS₂/Fe₃O₄ with 2 wt. % of nanofillers. The lowest CO emission was observed for the PE/e-MoS₂ composite containing also 2 wt. % of Fe₃O₄. All composites with exfoliated MoS₂ exhibited greater thermal properties in respect to the pristine polyethylene.

Keywords: flammability; polyethylene; molybdenum disulfide nanocomposites; flame retardants.

INTRODUCTION

Polyolefins are the group of materials that are widely used across the globe for various applications such as transport, building and electrical industries. The current tendency to favor polymers over other materials is the result of the combination of properties like good processability, structural and chemical stability and availability. Among them, polyethylene (PE) polymers are the largest tonnage plastics materials. They offer good flexibility at low temperatures, corrosion resistance, ease of processing and molding and excellent electric insulation at reasonable price¹⁻². These features allow to apply them in many fields, such as housing, transportation, and electrical engineering. However, because of their chemical constitution based on hydrocarbon backbone, these materials show high flammability and produce smoke and dangerous gases during burning. These drawbacks limit the range of their applications³. Therefore, it is of great importance to understand their fire behavior, improve the flame retardancy and reduce the emissions of smoke, poisonous gases, and so on⁴. To achieve these goals, various kinds of the additives can be incorporated into polymer matrix. Since the 1970s, the safety regulations have caused the increase in production of brominated and chlorinated flame retardants. Tetra--bromobisphenol A (TBBPA), hexabromocyclo-dodecane (HBCD), and three commercial mixtures of polybrominated diphenyl ethers (PBDEs)-decabromodiphenyl ether (decaBDE), octabromo-diphenyl ether (octaBDE), and pentabromo-diphenyl ether (pentaBDE) were used most extensively. However, due to the wide range of side effects observed after the exposure to halogenated fire retardants in animals and humans, including endocrine disruption, immunotoxicity, diabetes, effects on fetal/ child development, thyroid and neurologic function, and cancer⁵⁻⁷, the scientists are facing the challenge of production of safe (in terms of health and environment) and effective fire retardants.

Basic unit of molybdenum disulfide (MoS_2) consists of a molybdenum atom coordinated with six sulfur atoms. It is organized into two layers of sulfur atoms forming a sandwich structure, with a layer of molybdenum atoms in the middle. Owing to its unique properties, MoS₂ is being widely explored in terms of the usage⁸ as a solid lubricant in rigorous environments⁹, as lithium ion batteries^{10, 11}, as photocatalysts¹², as sensors and as conductive fillers in polymer composites.

Since the efforts to eliminate polybrominated biphenyls became a major issue in the field, layered nanomaterials such as graphene and MoS₂ have gained a lot of attention from research community as a good candidate to meet new requirements. As a semiconductor, MoS₂ is generally considered as better flame retardant than graphene as its low conductivity prevents from heat transportation within polymer matrix resulting in the delay in thermal degradation¹³. Moreover, the presence of transition metal element Mo promotes the formation of charred layer which acts as a barrier to slow down heat and mass transfer between burning zone and polymer matrix beneath¹⁴. This phenomenon can inhibit the diffusion of heat and volatile products. Additionally, the presence of MoS₂ in polymer matrix constitutes physical barrier for heat and mass transport.

The flame retardancy efficiency of MoS₂ strongly depends on its dispersion in polymer matrix. Bulk MoS₂ is usually poorly distributed in polymers and tends to oxidize, generating heat¹⁵. On the other hand, each of the exfoliated MoS₂ nanosheet can serve as a nano-barrier to prevent the permeation of external heat as well as oxygen and delay the emission of pyrolytic products such as hydrocarbons, CO and aromatic compounds. The nano-barrier effects of MoS₂ nanosheets also promote the aggregation of hydrocarbons and aromatic compounds to produce smoke particles and then accumulate into char residues, limiting total heat release.

Therefore, it is expected that exfoliated MoS_2 may improve the thermal stability and fire resistance of polymer-based composites. For example, the thermal stability and fire resistance properties of poly(vinyl alcohol) were strongly improved after the incorporation of MoS_2 into its structure¹⁶. Zhu et al.¹⁷ also published the results of the studies on using MoS_2 and graphene nanosheets (GNS) as nanofillers in polystyrene (PS) composites. The cone test results indicated that the PS/GNS and PS/MoS₂ composites exhibit superior flame retardance in comparison to virgin PS. Moreover, the thermal stability and smoke suppression properties of the PS/MoS₂ composites are much higher than PS/GNS composites. Similar observations were noticed in the work of Cai¹⁸ who used MoS_2 as a nanofiller for polyurethane. Several recent reports have focused on organic modification of exfoliated MoS₂. Zhou et al.¹⁹ investigated acetyl-trimethyl-ammoniumbromide-modified exfoliated MoS₂ to improve the miscibility with polystyrene. Rajamathi et al.²⁰ published paper on amine intercalated MS₂ (M 1/4 Mo or W) in organic solvents. The amine-modified MoS₂ nanosheets are well dispersed in organic solvents. Interestingly, exfoliated MoS₂ modified with an amine (octadecylamine, C18H37-NH2, ODA) having a long al interfacial adhesion with the polymer matrix was also reported although long alkyl chain groups normally exhibit strong interfacial adhesion with the polyolefin matrix. Group of Zhang et al.²¹ reported co-agglomeration method where an ODA-MoS₂/MgCl₂/TiCl₄ catalyst could be easily prepared. After in situ polymerization, the obtained PE/ODA-MoS₂ nanocomposites exhibited better physical properties. However, some problematic issues must be addressed to further enhance the flame retardant efficiency of MoS₂. Due to the large specific surface area and van der Waals interactions, exfoliated MoS₂ can agglomerate in polymer matrix¹⁹. To avoid this phenomenon, different compounds such as e.g. LDH has been used preventing the agglomeration of MoS₂ nanosheets²².

Magnetite (Fe₃O₄) has spinel structure and exhibits unique electric and magnetic properties based on the electron transfer between Fe^{2+} and Fe^{3+} in the octahedral sites. Ghanbari et al.²³ noticed that Fe₃O₄ nanoparticles can improve thermal stability and flame retardancy of the PVA matrix. Magnetite probably plays the role of a magnetic barrier layer which prevents heat or flame from reaching the sample, slowing down product volatilization and thermal transport during decomposition of the polymer²⁴. Additionally, studies carried out by Liu et al.²⁵ show the char layer of epoxy composites with the addition of Fe3O4 and sepiolite was more compact and thick in comparison with addition of sepiolite alone. The doping of epoxy with magnetite catalyzed EP to form more amount of char residue, preventing matrix from mass/heat transfer, hence improving its flame retardancy.

However, little is known about the synergistic effect of exfoliated MoS_2 functionalized with iron oxide particles used as nanofillers of the polymer nanocomposites. Therefore, in this work we present systematic study on the incorporation of these fillers in PE polymer and their influence on the thermal properties of the composite. Few aspects have been revealed: (i) how the synthesized e-MoS₂ nanocomposites with various mean size of magnetite nanoparticles improves the thermal properties and flame retardancy, (2) is CO emission of these nanocomposites reduced during heating, (3) what is the optimal weight ratio of the filler in PE composites to get their best performance, (4) is there any size effect of magnetite nanoparticles in the composites on the studied properties.

MATERIALS AND METHODS

Exfoliation of MoS₂

Exfoliation procedure can be briefly described briefly: to 220 mg of MoS_2 a mixture of N-methylpyrrolidone (NMP) and H_2O_2 (1:19 v/v) has been poured and stirred for 5 h at 35 °C. Then it was centrifuged and the supernatant has been replaced with fresh mixture of NMP and H_2O_2 . The obtained product has been centrifuged, washed with ethanol few times and dried in vacuum.

Preparation of e-MoS₂-Fe₃O₄ nanocomposites

In the first method, 40 mg of exfoliated MoS_2 was mixed with 40 ml of H_2O and 20 ml of ethylene glycol (EG) and as-prepared mixture was sonicated for 2h. Similar procedure was applied to $Fe(NO_3)_3 \cdot 9H_2O$. 30 mg of $Fe(NO_3)_3 \cdot 9H_2O$ was mixed with 30 ml H_2O and 15 ml EG. Prepared dispersions were mixed together and placed in the autoclave where the reaction took place at 250 °C over 140 minutes. In the second method, the amount of EG was reduced to 10 ml and 7,5 ml, respectively. The reaction has been stopped after 115 minutes. As-prepared dispersions of nanocomposites have been centrifuged and washed few times with ethanol.

Preparation of MoS₂-Fe₃O₄-PE composites

Prepared e-MoS₂-Fe₃O₄ nanocomposites served as nanofillers for PE in amounts equal to 0.5, 1 and 2 wt %. To incorporate it into polymer matrix, the mixtures of PE and appropriate amounts of nanocomposites were put together into a laboratory twin-screw extruder (Zamak Mercator EHP 2x12, L/D = 48). The extruder barrel's temperature profile for production of MoS₂-Fe₃O₄-PE and MoS₂ – PE composites was set as follows: zones 1 to 4: 85 °C, 85 °C, 85 °C and 82 °C at the annular die. The determined rate of screw rotation was altered within the range of 50–100 rot./min. The pipes of extruded materials were cooled in the room temperature and were cut in the appropriate shape and dimensions suitable for following measurements.

Characterization

High-resolution transmission electron microscopy (HRTEM) (FEI Tecnai F30, Frequency Electronics Inc.) was employed to examine the morphology of the nanomaterials and the size and distribution of the magnetite nanoparticles. X-ray diffraction technique (Xray diffractometer Philips X'Pert PRO, PANalytical B.V., Ka 1 = 1.54056 Å) was used to investigate the structure of the nanomaterials. Thermogravimetric analysis (TGA) was carried out using a SDT Q6000 thermoanalyzer instrument (TA Instruments Inc.) under argon flow of 100 mL/min. In each case, the samples placed in alumina crucibles were heated from room temperature to 700 °C at a linear heating rate of 10 °C per minute. TGA was coupled with a Quadrupole Mass Spectrometer QMS 422 to analyze gaseous products evolved during the heating process. The thermal diffusivity of the composites was determined using a Linseis XFA 300 laser flash apparatus. Prior to measurement, samples with a diameter of 12.7 mm were prepared and spray-coated with a thin graphite layer. All the measurements were carried out at room temperature. The measurement of the flame

retardancy was carried out via a Micro Calorimeter (FAA MICRO Calorimeter). This technique is used to estimate parameters such as peak heat release rate (W/g) and total heat release (kJ/g) from very small (2 mg) specimens.

RESULTS AND DISCUSSION

Morphology and structure of the nanomaterials

The Transmission electron microscopy (TEM) was used for characterization of starting materials and final products. Representative TEM images of exfoliated MoS₂, MoS₂-Fe₃O₄_1, and MoS₂-Fe₃O₄_2 are shown in Figure 1. Images of magnetite indicate a spherical shape of magnetite nanoparticles. The histograms presenting diameter distribution of the Fe_3O_4 nanoparticles are placed as an insets. The reduction of the amount of EG and time of the reaction resulted in the change in nanoparticles size. The diameter of the nanoparticles in e-MoS₂-Fe₃O₄_1 is in the range of 10 to 48 nm with strong peak at 32 nm, while in e-MoS₂- Fe₃O₄_2 - 2 to 14 nm with mean size approximately 4 nm. Uniform coverage of e-MoS₂ with magnetite nanoparticles can be observed in the images of the obtained nanocomposites (Figure 1B, Figure 1C).

X-ray diffraction (XRD) patterns of $e-MoS_2$, $e-MoS_2$ -Fe₃O₄_1, $e-MoS_2$ -Fe₃O₄_2 are shown in Figure 2. XRD



Figure 1. TEM images of e-MoS₂ (A), e-MoS₂-Fe₃O₄_1 (B), e-MoS₂-Fe₃O₄_2 (C)

spectrum of e-MoS₂ is dominated by peaks at 17°, 32°, 40°, 59° ²⁶. Positions of the peaks and their relative intensities shown in XRD pattern of e-MoS₂-Fe₃O₄_1 and e-MoS₂-Fe₃O₄_2 (Figure 2B, Figure 2C) are consistent with the standard XRD data for magnetite (ICSD 65339).

Thermal stability and smoke suppression properties of PE composites

In order to investigate the thermal stability of PE and PE composites, TGA has been carried out. Figure 3 shows TGA profiles collected during heating to 700 °C in the argon atmosphere. Presented results clearly shows the enhancement in thermal stability of PE composites in comparison with pure PE. This phenomena can be attributed to the formation of a char which acted as a mass transport barrier and an isolator between the bulk polymer matrix and the surface, where combustion occurred. It could be also ascribed to the effect of MoS₂ on the diffusion of volatile products throughout the composite materials²⁸. Interestingly, we did not observe the dependency of the thermal stability on the content and type of nanofiller. When 10% and 50% mass loss point is selected as a point of comparison, the highest thermal decomposition temperatures were noticed for PE_e-MoS₂_Fe₃O₄ $_2$ _1% and PE_e-MoS₂_1%. Compared to neat PE, T10wt% for these samples was increased by ca. 18 °C, while T_{50wt.%} by ca. 6°C. Summary of TGA results is placed in Table 1.

Additionally, mass spectrometry results had been obtained after coupling with TGA and presented in Figure 4. The composition of the gases emitted during the combustion of each sample has been studied. This method is a great tool to evaluate smoke suppression properties of prepared samples as it allows to determine the amount of CO evolved during heating process. This factor is of particular importance due to the possibility of death occurrence in fire associated with CO inhalation.

Table	1.	Temperatures	corresponding	to	characteristic	mass
	losses of investigated samples					

Sample	T _{10wt.%}	T _{50wt.%}
PE	390	453
PE_e-MoS ₂ _0.5%	392	455
PE_e-MoS ₂ _1%	408	460
PE_e-MoS ₂ _2%	400	458
PE_e-MoS ₂ _Fe ₃ O ₄ _1_0.5%	398	456
PE_e-MoS ₂ _Fe ₃ O ₄ _1_1%	398	457
PE_e-MoS ₂ _Fe ₃ O ₄ _1_2%	405	459
PE_e-MoS ₂ _Fe ₃ O ₄ _2_0.5%	401	456
PE_e-MoS ₂ _Fe ₃ O ₄ _2_1%	408	459
PE_e-MoS ₂ _Fe ₃ O ₄ _2_2%	392	434

The amount of evolved CO dropped significantly after the addition of nanofillers. Moreover, with the increasing content of e-MoS₂ or e-MoS₂ Fe₃O₄, the reduction of the amount of CO decreased. The best smoke suppression properties are exhibited by PE e-MoS₂ Fe₃O₄ 2 2% with the CO amount reduction by ca. 94 % comparing to pristine PE. Also when nanofiller content of 1% is selected as a point of comparison, nanocomposite with smaller nanoparticles exhibited better smoke suppression properties. The amount of CO evolved during heating PE_e-MoS2_Fe3O4_21% is 20% smaller than during heating PE e-MoS₂ Fe₃O₄ 1 1%. The presence of MoS₂ can promote char formation in the PE/MoS₂ composites obviously. That implies there is more compact char residue formed on the surface of the sample with e-MoS₂. The compact carbonaceous char residue and physical barrier effect of MoS₂ nanosheets can restrain combustible gases, so the released flammable gases undergo complete combustion, which leads to the little carbon monoxide production. Therefore, the strong synergistic effect, physical barrier effect of nanosheets and nanoparticles and the promoted charring effect should be the main reasons for the excellent smoke suppression properties of composites²⁸. It is also worth noting that



Figure 2. XRD pattern of e-MoS₂ (A), e-MoS₂-Fe₃O₄_1 (B), e-MoS₂-Fe₃O₄_2 (C)



Figure 4. Mass spectrometry results for pristine polyethylene (A) and polyethylene composites (B, C)

 MoS_2 can catalyse carbon monoxide carbon dioxide, lowering the CO production rate²⁹. Additionally, the presence of iron compounds promote early crosslinking of polymers during decomposition to increase char formation leading to great reduction of smoke formation during the pyrolysis or combustion of polymers³⁰. Better smoke suppression properties of e-MoS₂ combined with Fe₃O₄ compared to pristine PE or e-MoS₂ alone is the result of synergistic effect of the nanomaterials.

Flammability tests were performed using calorimeter, which is considered as one of the most effective methods for the laboratory evaluation of the fire properties of polymers. Despite the small-scale character, the results correspond to those received from a large scale fire tests and can be used to predict the combustion behavior of materials in a real fire. Several key parameters like heat release rate (HRR), total heat release (THR), peak HRR (PHRR), which could be employed to evaluate the developing, spreading, and intensity of fires can be obtained from calorimeter³¹. The higher the PHRR, the more self-propagation of flame on the sample is likely.

Figure 5 depicts heat release rates plots noted for PE and its composites with 0.5, 1 and 2 wt.% of nanofillers. The reduction in peak HRR constitutes important issue in fire safety, as PHRR represents the point in a fire where heat is likely to propagate further, or ignite adjacent objects³². The addition of MoS₂ slightly decreases HRR value, while this effect in case of the addition of magnetite nanoparticles is much more noticeable. All collected data indicate that the presence of magnetite nanoparticles and MoS₂ has significant synergistic effect in improving the flame retardancy of the PE composites. Is is known that flame retardant efficiency is closely related to the dispersion of nanofillers in polymer matrix, so the decoration of layered MoS₂ with nanoparticles can prevent it from aggregating and consequently im-



Figure 5. Heat release rates versus burning time for PE and PE composites with 0.5% (A), 1% (B), 2% (C) of particular nanofillers

prove the flame retardant efficiency¹⁶. Peak HRR has been decreased from 1216 for virgin PE to 817, 139, 134 for PE-e-MoS₂, PE_e-MoS₂_Fe₃O₄_1 and PE_e--MoS₂Fe₃O₄_2 with 2 wt. % of nanofillers, respectively (Table 2). The reduction of PHRR is strongly dependent of the content of nanofiller. Additionally, flat curves of HRR values versus burning time in case of composites with e-MoS₂ Fe₃O₄ (except for 0.5% of e-MoS₂ Fe₃O₄ 1) are associated with prolongation of burning, which can be ascribed to the degradation as well as the stabilization of the char formation³³. It is worth noting that composite with smaller magnetite nanoparticles shows better fire retardancy properties than composite with bigger sizes of nanoparticles. Zhang et al³⁴ found that the fire resistance of nano-Mg(OH)₂ was better than that of micro-Mg(OH)₂ in rubber. Moreover, the addition of nanofiller enhanced its mechanical properties. Shen et al. noticed flame retardant improvements with the usage of montmorillonite with a smaller particle size due to the formation of stronger char layer comparing to larger particle size. The effect of particle size was also studied by comparing the heat release rate of the nanocomposite with nanoscale TiO2 particles to that with micrometer size of TiO_2^{35} . PHHR reduction of 39% for PMMA-TiO₂ microcomposite was observed compared to 45% for PMMA-TiO₂ nanocomposite.

Thermal conductivity

Thermal conductivity results collected for pristine PE and PE with MoS_2 -Fe₃O₄ are presented in Table 3. The addition of nanofillers significantly enhances thermal conductivity from 0.185 W/mK for pristine polymer to even 0.690 W/mK for PE_e-MoS_2_Fe₃O₄_2_2%. Thermal conductivity increases with the increasing content of nanofiller. Moreover, composites with smaller iron oxide nanoparticles exhibit better thermal properties than the composites with bigger nanoparticles within

Sample	pHRR	THR [kJ/g]
PE	1216	47
PE_e-MoS ₂ _0.5%	1187	43.4
PE_e-MoS ₂ _1%	922	43.2
PE_e-MoS ₂ _2%	817	42.4
PE_e-MoS ₂ _Fe ₃ O ₄ _1_0.5%	759	41.1
PE_e-MoS ₂ _Fe ₃ O ₄ _1_1%	170	40
PE_e-MoS ₂ _Fe ₃ O ₄ _1_2%	139	41
PE_e-MoS ₂ _Fe ₃ O ₄ _2_0.5%	175	41
PE_e-MoS ₂ _Fe ₃ O ₄ _2_1%	139	40.5
PE_e-MoS ₂ _Fe ₃ O ₄ _2_2%	134	41

 Table 2. PHHR and THR values for PE and PE composites with various amount of nanofillers

Sample	Thermal conductivity [W/m*K]		
PE	0.185		
PE_e-MoS ₂ _Fe ₃ O ₄ _1_0.5%	0.401		
PE_e-MoS ₂ _Fe ₃ O ₄ _1_1%	0.537		
PE_e-MoS ₂ _Fe ₃ O ₄ _1_2%	0.541		
PE_e-MoS ₂ _Fe ₃ O ₄ _2_0.5%	0.459		
PE_e-MoS ₂ _Fe ₃ O ₄ _2_1%	0.666		
PE_e-MoS ₂ _Fe ₃ O ₄ _2_2%	0.690		

 Table 3. Thermal conductivity of polymer composites with various content of nanofillers

the same content of nanofiller. This phenomenon can be attributed to the smaller particles tendency to create more readily conductive pathways or networks in comparison with larger particles. The formation of conductive channels from the smaller filler particles in composites is more likely³⁶.

CONCLUSIONS

In this paper, we have developed a facile approach for modifying exfoliated MoS_2 nanosheets with magnetite nanoparticles with different size distribution. The modified MoS_2 nanosheets were used as nanofillers to prepare PE composites with the usage of extruder. The calorimetry results indicated that the fire resistance properties of

the PE_e-MoS₂Fe₃O₄ composites are better than that of the PE e-MoS₂. The calorimetry test results shown that the composites with smaller magnetite nanoparticles exhibited superior flame retardance to PE e-MoS₂ and PE e-MoS₂ Fe₃O₄ with bigger nanoparticles. However, the composite with smaller nanoparticles exhibited the highest thermal conductivity and the best smoke suppression properties. MoS₂ constitutes physical nanobarrier preventing from spreading volatile products in polymer matrix. It also promotes char formation and the oxidation of CO to CO₂. Magnetite nanoparticles not only prevents exfoliated MoS₂ from restacking, but also enhances the smoke suppression properties and thermal conductivity of composites. Enhancement of both flame retardancy and mechanical properties of polyethylene after the addition of nanofillers can be ascribed to the synergistic effect of exfoliated MoS₂ and Fe₃O₄.

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