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RESEARCH PAPER

Improving Reaction to Fire Properties of Thermoplastic Polyurethane with Intumescent Flame Retardants and MoS_2

Leila Taghi-Akbari[1], Mohammad Reza Naimi-Jamal[1,*], Shervin Ahmadi[2]

* *naimi@iust.ac.ir*

[1] Research Laboratory of Green Organic Synthesis and Polymers, Department of Chemistry, Iran University of Science and Technology, 16846-13114, Tehran, Iran
[2] Iran Polymer and Petrochemical Institute (IPPI), 14965-115, Tehran, Iran

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Abstract: *Two-dimensional molybdenum disulfide (MoS_2) is used as a promising flame retardant and smoke suppressant nano additive in polymer composites due to its high thermal stability and layered structure. In this study, thermoplastic polyurethane (TPU) was melt-blended with MoS_2 (1 wt. %) and a halogen-free intumescent flame retardant (IFR) system. The IFR system consisted of ammonium polyphosphate (APP), Melamine polyphosphate (MPP), and pentaerythritol (PER), with a total amount of 25 wt.%. The TPU/IFR/MoS_2 composite exhibited outstanding flame-retardant properties, achieving a UL-94 V-0 rating and a limiting oxygen index (LOI) value of 34%. Reaction-to-fire performance of the TPU/IFR/MoS_2 composite was evaluated by cone calorimeter test (CCT). The CCT results indicated high flame-retardant efficiency and considerable smoke suppression performance, along with a significant decrease in the peak heat release rate (PHRR: 65.9%), peak smoke production rate (PSPR: 65.6%), and peak CO production (PCOP: 60.7%) compared to the neat TPU. The significant improvement in fire performance of TPU composite was mainly attributed to the effects of the physical barrier of MoS_2 and catalytic carbonization of the IFR system. These formed an intumescent compact carbonized layer during the combustion, effectively restricting dripping. FESEM revealed the continuous structure of the residual char. Thermogravimetric analysis (TGA) indicated improved thermal behavior of the TPU composite in high temperatures. This work provides an effective method to improve the reaction to fire of TPU composites by incorporating traditional IFRs and MoS_2, resulting in enhanced fire safety.*

Keywords: *Reaction to fire, Intumescent flame retardant, MoS_2, Thermoplastic polyurethane, Heat release rate.*

1. INTRODUCTION

Flame retardancy, smoke suppression, and anti-dripping performances are principal considerations in the fire safety of flammable polymeric materials such as thermoplastic polyurethane (TPU). TPU, as a high-performance engineering plastic, is widely used in many industrial branches like cable and electric wiring, automotive, building, and medical devices due to its excellent properties such as outstanding abrasion resistance, high elastic properties, good processability, high chemical stability and mechanical performance [1-2]. These applications are limited due to the high flammability of TPU. Therefore, it is required to improve its fire reaction performance. TPU, like most polymeric materials, burns and generates high amounts of heat, smoke, and toxic gases with lots of dripping [3]. Hence, improving the fire behavior of TPU, while preserving its thermal and mechanical properties, is crucial. Nowadays, widespread research on developing effective flame retardants is performed to reduce fire hazards [4-5]. Among them, intumescent flame retardant additives (IFRs), especially those containing both nitrogen (N) and phosphorus (P), are considered effective environmentally friendly halogen-free flame retardants (FRs) for improving the flame retardant properties of TPU. IFRs exhibit good flame retarded efficiency and low smoke and toxicity [6-8]. The IFR system is comprised of three components: an acid source, such as ammonium polyphosphate (APP), a charring agent, and a blowing agent, like pentaerythritol (PER) and melamine compounds that facilitate the formation of a protective char layer during combustion. According to the previously reported studies [9], a high loading amount of intumescent flame retardants is needed to achieve the desired flame retardant effect, which can deteriorate the physical properties. Hence, introducing synergistic agents can be responsible [10].

In recent years, nanoscale fillers, as a promising generation of flame retardant and smoke suppressant synergist agents, have attracted wide attention in the field of fire safety. In Particular,

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the use of two-dimensional (2D) nanomaterials, such as black phosphorus [11], molybdenum disulfide [12-14], graphene [15-16], Nano silica [17], and their derivatives, is increasing due to their ability to enhance thermal stability, flame retardant properties, and smoke suppression. It is achieved by forming a dense carbon structure as an effective thermal/physical barrier on the surface of the polymer. The most significant advantage of the synergistic agents is their low loading amounts due to their high aspect ratio [18-19]. One of the effective two-dimensional (2D) flame retardants is molybdenum disulfide (MoS_2) which has high thermal stability and good smoke suppression performance. MoS_2, like graphene, has a hexagonal structure and falls into the category of layered nanomaterials [20]. The thermal conductivity of MoS_2 is lower than that of graphene, which can delay thermal degradation by hindering the heat transfer within the polymer matrix [21].

According to the literature, incorporating MoS_2 into the polymer composite promotes char-forming, thereby enhancing flame retardancy and smoke suppression characteristics in the polymer. According to Wang's study, MoS_2 added to the waterborne polyurethane (WPU) improves the thermal and mechanical properties [22]. The effects of carbon microspheres (CMS) and MoS_2 core-shell structure to enhance flame retardant properties of fireproof coating based on APP/MPP/PER in epoxy were studied by Chen et al. [23]. The findings showed excellent flame retardancy and smoke suppression performance. It has been reported that the combination of MoS_2 with other flame retardants prevents the aggregation of MoS_2 (due to van der Waals forces in the MoS_2 alone) and enhances its flame retardant efficiency [24]. Qian et al. studied the incorporation of MoS_2 into TPU and observed significant reductions in heat and smoke released and a decrease in toxic volatiles emitted during combustion. Recently, Feng et al. reported a synergistic effect of nickel phosphide (Ni_2P) nanoparticles and molybdenum disulfide (MoS_2) nanosheets on enhancing flame retardancy and smoke suppression of thermoplastic polyurethane (TPU) [25].

Nevertheless, our current knowledge indicates a lack of extensive research on the flame retardant application of MoS_2 in improving the fire performance of TPU. The present study aims to investigate the effects of the MoS_2 and a traditional IFR system, consisting of APP, PER, and MPP with a mass ratio of 3:1:1, on flame retardancy and smoke suppression of TPU composite. This study is considered a novel addition to the existing literature since there has been no previous report on this topic.

2. EXPERIMENTAL PROCEDURES

2.1. Materials

A polyester-based thermoplastic polyurethane (TPU) (Estane® 58277) was obtained from Lubrizol. APP (Exolit® AP 422) was purchased from Clariant. Melamine polyphosphate (Melapur200) was obtained from BASF, and Pentaerythritol (PER) was provided by the MERCK group. Molybdenum disulfide (MoS_2) powder was supplied by Sigma Aldrich with a density of 5.06 g/cm^3.

2.2. Sample Preparation

Before mixing, TPU was dried at 80°C for 12 h, and the IFR components (APP/MPP/PER) were dried at 100°C for 10 h in a vacuum oven. TPU composite was prepared by adding 15 wt.% APP, 5 wt.% PER, 5 wt.% MPP, and 1 wt.% MoS_2 by melt mixing at 170°C for 5 min. The TPU sheets were prepared by a hot press machine. The thicknesses of the TPU samples were 3 mm.

2.3. Characterization

The limiting oxygen index (LOI) was performed according to ASTM D2863 on the samples with dimensions of (130 × 6.5 × 3.2) mm^3 by HC-2 oxygen index meter (China).

The UL 94 vertical burning test was performed according to the ASTM D3801 test method on the samples with dimensions of 130 mm × 13 mm × 3.2 mm.

Thermal stability was characterized by TGA analysis under a nitrogen/O_2 atmosphere using a TGA-Mettler (Mettler Toledo, Switzerland) instrument. TPU samples were heated from room temperature to 600°C with a heating rate of 20°C/min under N_2 atmosphere and up to 800°C in airflow.

The reaction to fire performance was evaluated by an FTT Dual Cone Calorimeter apparatus (Fire Testing Technology, UK), according to ISO 5660-1 standard test method under a radiant heat flux of 50 kW.m^{-2}. The dimensions of the TPU samples were (100 × 100 × 3) mm^3. The wrapped

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specimen in aluminum foil was exposed to the heat flux horizontally.
Field emission scanning electron microscopy (FE-SEM) was used for the microstructure analysis using a FESEM TESCAN MIRA-III at 20 kV acceleration voltage.

3. RESULTS AND DISCUSSION

3.1. Flammability

The flammability results are given in Table 1. As seen in Table 1, there is no rating for TPU in the UL 94 vertical burning test, while a V-0 rating was achieved for TPU/IFR/MoS_2 composite. It shows that TPU/IFR/MoS_2 effectively inhibits melt-dripping in TPU composite; in contrast, TPU burns fast with high dripping. LOI is an important index to evaluate flame retardancy. LOI value exhibits the minimum oxygen concentration in terms of volume percentage required to burn the material. TPU, with lots of melt-dripping during burning, reached an LOI value of 21%. The LOI value increased to 34% when the IFR/MoS2 was added to TPU. It exhibited a high flame retardant efficiency in the TPU composite.

Table 1. Flame retardant properties of TPU samples

Samples	LOI	UL 94
TPU	21	No rating
TPU/IFR/MoS_2	34	V0

3.2. Reaction to Fire and Flame Retardancy

Cone calorimetry is one of the most effective methods for evaluating fire reaction performance and flame retardant properties of polymers. The heat release rate (HRR) measured By the cone calorimeter is the most critical parameter for fire hazard assessment [26-27].
The measured thermal, smoke, and toxicity parameters of reaction-to-fire, including time to ignition (TTI), peak HRR (PHRR), total heat release (THR), peak smoke production rate (PSPR), total smoke release (TSR), peak carbon monoxide production (PCOP) for the TPU samples are listed in Table 2.

3.3. Thermal Parameters

The curves of heat released during the combustion of TPU and TPU/IFR/MoS_2 were shown in Fig. 1. As seen in Fig. 1, a sharp peak appeared after ignition of TPU by PHRR value of 693 kW/m^2, while the TPU composite showed a broad peak with a significant decrease in PHRR value of 237.5 kW/m^2. Besides, ignition time (TTI) for TPU composite was shorter than TPU. It is attributed to the earlier decomposition of flame retardants in the TPU composite, promoting char formation and prohibiting the release of heat and pyrolysis gases during combustion [28]. This matter was confirmed by increased char residue after the cone calorimeter test, as shown in Fig. 1.

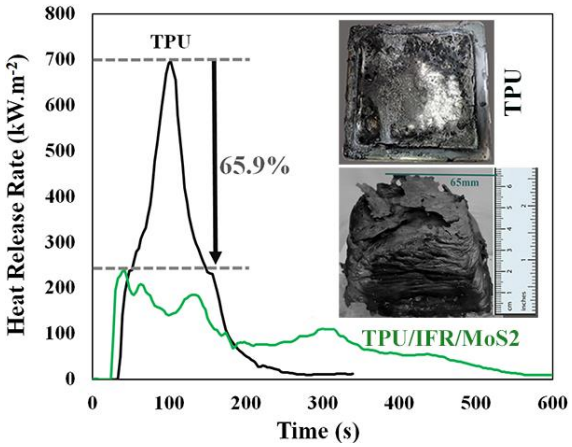

Fig. 1. HRR curves and char residues for TPU and TPU composite

The results indicated that the catalytic degradation of the IFR system and barrier effect of MoS_2 were effective in reducing heat released from the TPU composite. The other reason for the high efficiency of the IFR/MoS_2 is the increased residual mass after CCT. According to data in Table 2, the char residue that remained in the TPU composite significantly increased compared to the neat TPU. This result is supported by thermal analysis.

Table 2. Thermal parameters obtained from cone calorimeter

Samples	Thermal parameters			Smoke/Toxicity parameters			Char residue (%)
	TTI (s)	PHRR (kW.m^{-2})	THR (MJ.m^{-2})	PSPR (m^{-2}. s^{-1})	TSR (m^2.m^{-2})	PCOP (g.s^{-1})	
TPU	37	696.30	51.5	0.096	952.1	0.015	6.3
TPU/IFR/MoS_2	28	237.5	45.7	0.033	624.8	0.006	31.6

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The curves of mass loss during the combustion of TPU and TPU/IFR/MoS_2 are shown in Fig. 2. It can be seen from Fig. 2 that lower mass loss is observed due to the char formed on the surface of TPU. It shows the combustion of the TPU/IFR/MoS_2 composite results in a significantly higher residual mass compared to the neat TPU. According to the findings presented in Figure 2, the TPU composite exhibits a residue of 49.9% at 300°C, whereas the neat TPU only has a residue of 8.1%. It indicates that MoS_2 acts as a physical barrier during the combustion, protecting the under-layer TPU composite and facilitating the catalytic carbonization of the IFR. As a result, the overall mass loss is reduced.

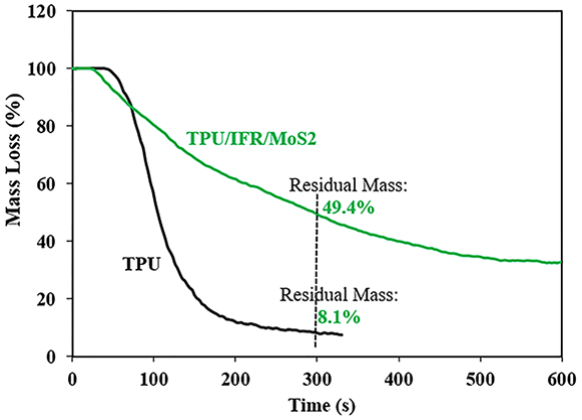

Fig. 2. Mass loss curves for TPU and TPU composite

3.4. Smoke/Toxicity Parameters

According to data in Table 2, the high value of TSR for TPU (952.1 $m^2.m^{-2}$) showed that lots of smoke is generated during the combustion of TPU. When the IFR/MoS_2 was added to the TPU, the TSR value was reduced by 34.4% (624.8 $m^2.m^{-2}$).

The decomposition of the IFR system forms the acidic components reacting with TPU to create an intumescent char. This issue was studied by Liu et al. [29], who investigated smoke suppression in TPU composite with APP/carbon black. Further, MoS_2 creates a protective shield by the physical barrier effect, which helps to strengthen the char structure with integrity and densification. By forming the integrated carbonized layer on the polymer surface, the release of heat and smoke is effectively inhibited, and dripping is highly restricted consequently. This trend was also observed for peak SPR in TPU and TPU composite, so PSPR decreased by 65.6% in TPU/IFR/MoS_2 compared to TPU. Fig. 3 shows The SPR curves for TPU samples. As seen in Fig 2, the SPR curve of TPU composite remarkably dropped compared to the SPR curve of TPU.

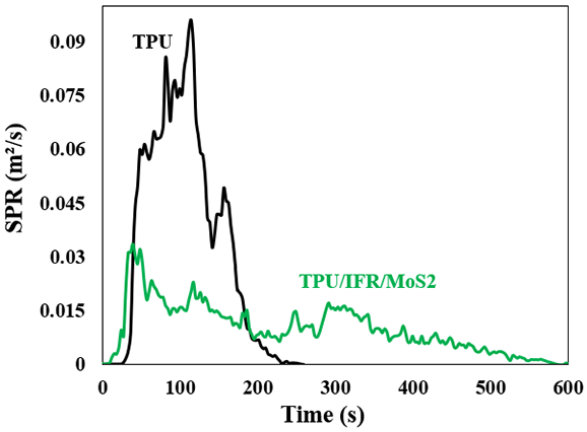

Fig. 3. SPR curves for TPU samples

The reduced smoke production is a critical factor in fire accidents because the inhalation of toxic smoke affects people's survival and the rescue performance of fire brigades. Moreover, smoke and toxic gas inhalation are two crucial factors in fire deaths [30]. CO toxic gas has been known as the most hazardous gas in fires. The COP curves for TPU samples are shown in Fig. 4. The IFR/MoS_2 exhibited high performance in toxicity suppression by the reduced PCOP of 60.7%.

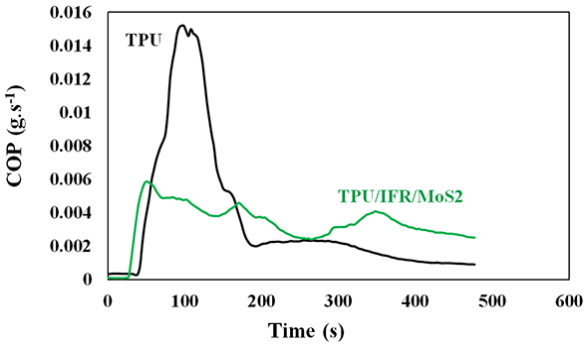

Fig. 4. COP curves for TPU samples

3.5. Char Morphology

The microstructure of the residual chars that remained in the TPU samples was investigated by the FESEM. Fig. 5 shows the FESEM images of the residual chars. It can be seen from Fig. 4 that pure TPU forms little char residue with many cracks and holes and a loose structure. Adding 25 wt.% IFR and 1 wt.% MoS_2 leading to an intumescent compact residual char with significantly reduced surface cracks and holes.

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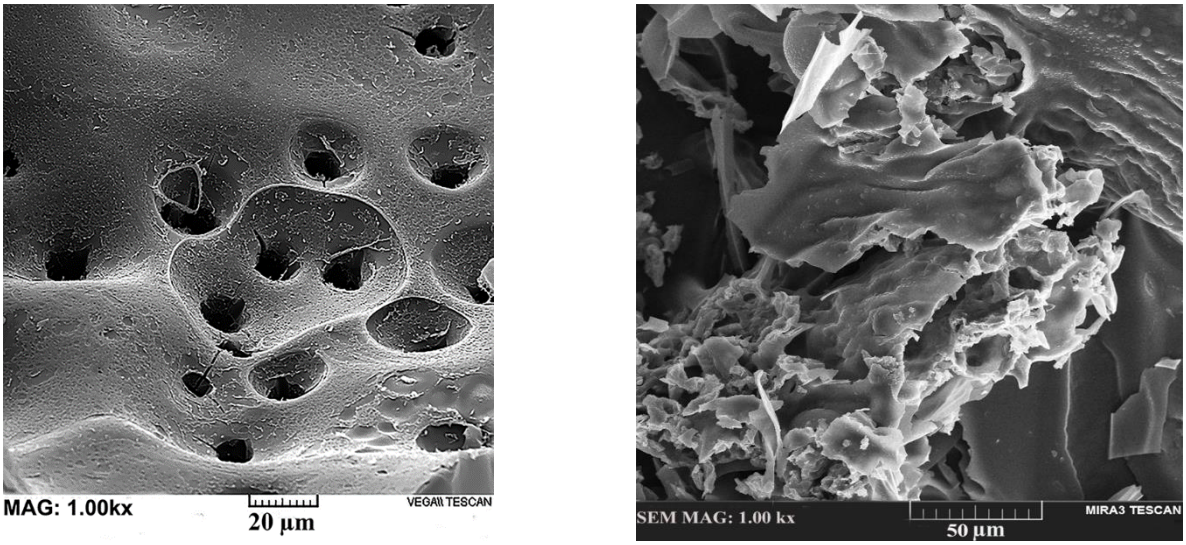

Fig. 5. The microstructure of the residual chars for the TPU samples

3.6. Thermal Stability

The thermal degradation of TPU and TPU/IFR/MoS_2 were investigated by TGA analysis. Fig. 6 and Fig. 7 show the TGA/DTG curves of the TPU samples. According to the curves, there are two degradation steps in the chain of TPU starting at 311.7°C. The first step corresponds to the breakage of the hard segment of the main chains of TPU and the elimination of the volatile compounds. The second step at 396°C is attributed to the further degradation of C-C and C-O bonds in soft segments [7].

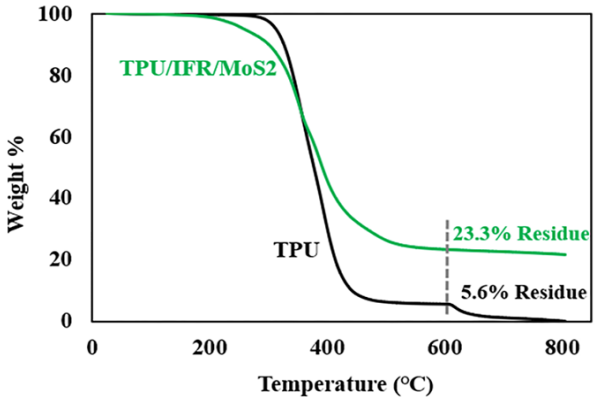

Fig. 6. TGA curves for TPU samples

In the TPU/IFR/MoS_2 composite, the first degradation step started at 257.0°C, which is lower than that of TPU due to the earlier decomposition of the IFR. Three thermal degradation peaks appeared at 354.3°C, 411.7°C, and 498.3°C, respectively. The enhanced thermal stability of the TPU composite can be attributed to the intumescent protective char layer formed by the IFR and strengthened by MoS_2. The residues at 600°C in Fig. 5 confirm the effective role of IFR/MoS_2 in promoting char formation, as seen in the CCT results (Table 2). The protective char layer inhibits the further degradation of TPU, and improved thermal behavior is achieved.

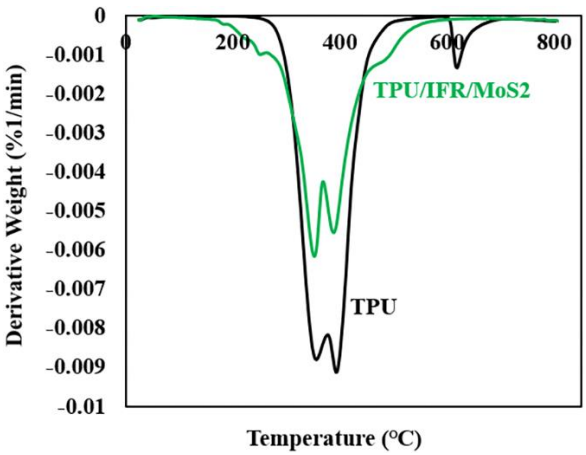

Fig. 7. DTG curves for TPU samples

4. CONCLUSIONS

The combination of MoS_2 (1 wt.%) and a halogen-free intumescent flame retardant (IFR) system consisting of APP/PER/ MPP with a ratio of 3:1:1 and a total amount of 25 wt.% was used to improve the reaction to fire performance of TPU. The TPU/IFR/MoS_2 composite showed excellent flame-retardant properties with an increased LOI of 34% and UL 94 V-0. The measured reaction-to-fire properties by cone

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calorimeter indicated high efficiencies in flame retardancy and smoke/toxic gas suppression with reduced PHRR by 65.9%, PSPR by 65.6%, and PCOP by 60.7%, respectively, compared with the neat TPU. FESEM revealed a high-quality char with an integrated structure. The catalytic degradation of the IFRs and the barrier effect of MoS_2 resulted in protecting the underlayer polymer by creating a highly intumescent continuous char residue. The TGA results confirmed the high charring ability of TPU/IFR/MoS_2 and the enhanced thermal stability in high temperatures. The results indicated that incorporating MoS_2 nano additive and traditional IFRs into TPU can significantly improve fire reaction properties, leading to enhanced fire safety.

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