Hydrothermal Synthesis of Lanthanum-Doped MgAl-Layered Double Hydroxide/Graphene Oxide Hybrid and Its Application as Flame Retardant for Thermoplastic Polyurethane

1. Introduction

As a type of burgeoning and widely used material, the terminal products of polymer-based materials have covered many fields such as electronic, electrical appliance, textile, furniture, transportation, and building material [1]. Thermoplastic polyurethane (TPU), an engineering thermoplastic, has been increasingly applied owing to its good flexibility, high compressive strength, and good abrasion resistance. However, like most polymers, TPU is highly flammable, which significantly increases the potential fire hazard in the place where it is used [2]. At present, in order to reduce fire damage and improve the safe level of mankind existence environment, flame retardancy has become one of the important factors that people often consider when choosing TPU for different purposes [3]. Hence, numerous flame retardants as additives have been added into TPU to enhance flame retardancy. With the enhancing awareness of environmental protection, halogen-based flame retardants are gradually being reduced or even banned due to their ecological damage during combustion [4]. Some new type of halogen-free flame retardants, for instance, organic phosphorus compounds [5], carbon nanotubes (CNTs) [6], and polyhedral oligomeric silsesquioxane (POSS) [7], have become more and more attractive in recent decades.

Layered double hydroxide (LDH), also known as hydrotalcite compounds (HT) or anionic clay, is a kind of layered compounds composed of positively charged metal hydroxide layers with interlayer spaces containing exchangeable anions. Thus, LDH has superior flame retardancy and smoke suppression properties because it has crystal-waters and hydroxyl groups (-OH) among layered structure [1, 8]. In recent years, there have been many studies of LDH in flame retardant polymers. Han
et al. [9] synthesized sodium dodecyl benzene sulfonate (SDBS) intercalated CoAl, MgAl, NiAl, and ZnAl LDH as flame retardant for polystyrene (PS). The results showed that peak heat release rate (PHRR) of nanocomposites were reduced by 7% and 12% with 5 wt% MgAl-SDBS LDH and ZnAl-SDBS LDH loading, respectively. Zhang et al. [10] prepared phosphotungstic acid (PWA-) intercalated MgAl LDH and investigated the effect of it on the intumescent flame retardant (IFR) poly(lactic acid) (PLA) composites. When the MgAl-PWA LDH loading was 2 wt%, the PHRR of PLA composites significantly decreased from 306.3 kW/m² of neat PLA to 40.1 kW/m². The limiting oxygen index (LOI) value reached 48 and passed the UL-94 V-0 rating.

The controllability of the composition and structure of LDH makes it possible to intercalate different cations. And, the flame retardancy of LDH within polymers can be further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8]. Lanthanum (La), a representative element of rare earths (REs), could be served as rare earth further improved [8].

2 Advances in Polymer Technology

2.1. Materials. Sulfuric acid (98%), hydrogen peroxide (30%), nitric acid (68%), aqueous ammonia (25%), graphite powder, Al(NO₃)₃·9H₂O, Mg(NO₃)₂·6H₂O, KMnO₄, and NaNO₃ were all purchased from Sinopharm Chemical Reagent Co., Ltd. (China). La₂O₃ was bought from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). La(NO₃)₃ solution was prepared through dissolving La₂O₃ in dilute nitric acid. Commercial TPU (9380A) was obtained from Bayer, German.

2.2. Synthesis of La LDH. The as-prepared La LDH samples were synthesized by using precipitation and hydrothermal methods. 0.03 mol Mg(NO₃)₂·6H₂O and 0.012 mol Al(NO₃)₃·9H₂O were dissolved in 60 ml deionized water, and then La(NO₃)₃ solution was added into the above mixture and the La³⁺/Al³⁺ molar ratio was varied at 0.02, 0.05, and 0.1 for comparison. Concurrently, the total mole amount of La³⁺ and Al³⁺ was maintained at 0.012 mol. After that, pH of the mixture was adjusted to 10 by adding dilute ammonia aqueous solution (5%) dropwise. The mixture was heated at 65°C for 30 min with rapid stirring. Then, the resulting suspension was transferred to a 100 mL Teflon-lined autoclave, and it was kept under 130°C for 12 h. After autoclave was cooled to room temperature, the resulting precipitates were filtered, washed several times with deionized water, and dried at 60°C for 24 h.

2.3. Synthesis of La LDH/GO Hybrid. GO was synthesized from graphite powder by using the Hummers method [17]. In addition, La LDH/GO hybrid was prepared at the similar experimental conditions, except that GO solution was added to above mixture containing Mg²⁺, La³⁺, and Al³⁺ with a La³⁺/Al³⁺ molar ratio of 0.5.

2.4. Synthesis of TPU Composites. TPU composites were prepared by the melt blending method. For example, a certain amount of TPU was put in the internal mixer under 180°C for 3 min, and the rate of agitation was 30 rpm. Then, La LDH/GO was added to the mixer, and stirred constantly at the same temperature for 10 min. Finally, the TPU composite contains La LDH/GO was hot-pressed for 10 min at 180°C and 10 MPa to form sheet with the size of 100 × 100 × 3 mm³. Moreover, the TPU composites containing MgAl LDH and La LDH were prepared under the same conditions, respectively. The formulas of all TPU composites are displayed in Table 1.

2.5. Characterization. X-ray diffraction (XRD) measurements were taken by using a Rigaku X-ray diffractometer (Japan) with Cu-Kα tube and Ni filter (λ = 0.1542 nm). Fourier transform infrared spectroscopy (FTIR) studies were recorded on a Nicolet 6700 FTIR spectrophotometer (USA) with KBr pellet technique. Scanning electron microscopy (SEM) measurements were performed by using a JSM-6700F instrument (Japan). Transmission electron microscope-
energy dispersive spectrometer (TEM-EDS) measurements were taken by a JEM-2100Plus instrument (Japan) with an acceleration voltage of 200 kV. Cone calorimeter test (CCT) was undertaken with a JCZ-2 cone calorimeter (China) according to ISO5660 standard procedures. Specimens with the size of 100×100×3 mm³ were irradiated under a heat flux of 50 kW/m². Limiting oxygen index (LOI) measurements were carried out with an HC-2 oxygen index meter (China) according to ASTM D2863. M&he size of the specimens used for the test was 100×6.5×3 mm³. M&hermal-gravimetric analysis (TGA) was carried out on a DT-50 instrument (France). M&hehe heating rates were set as 20°C/min (nitrogen atmosphere, flow rate of 20 mL/min).

3. Results and Discussion

3.1. Characterization of As-Prepared Samples. XRD can be used to determine the crystal structure of materials. The XRD spectra of La LDH with different La³⁺/Al³⁺ molar ratio are shown in Figure 1. As can be seen from the figure, the diffraction peaks of MgAl LDH at 2θ = 9.9°, 20.0°, 34.6°, 37.6°, 42.7°, 60.8°, 61.8°, and 64.7° indicate the (003), (006), (012), (015), (018), (110), (113), and (116) planes of the hydrotalcite structure, respectively [18]. The interlayer spacing of MgAl LDH is 0.89 nm from the (003) plane, showing the intercalation of NO₃⁻ into the interlayer gallery [19]. In addition, the interlayer spacing of all La LDH remains unchanged after doping La³⁺ to MgAl LDH. With the increase of La³⁺ content on MgAl LDH laminates, the intensities of three peaks between 30° and 50° are weakened. It is mainly because the ionic radius of La³⁺ is too large, which destroys the hexagonal structure of MgAl LDH. It is noteworthy that when the molar ratio of La³⁺/Al³⁺ is 0.1, the impurity phase appears. Simultaneously, the peaks for (100), (110), (101), (201), and (211) planes of La(OH)₃ can be obtained at 2θ = 15.7°, 27.4°, 28.0°, 39.5°, and 48.8° (JCPDS card no.83-2034) [12].

Based on the above research on La LDH with diverse La³⁺/ Al³⁺ molar ratio, 0.05 La LDH without new phase and GO were selected to synthesis La LDH/GO hybrid. Figure 2 displays the XRD spectra of GO, 0.05 La LDH and La LDH/GO. The spectrum of GO has a strong diffraction peak at 2θ = 11.48°, corresponding to the (002) plane and the interlayer spacing is 0.77 nm according to Bragg’s equation [20]. Furthermore, La LDH/GO and 0.05 La LDH have the same diffraction peaks, but the peak intensities of La LDH/GO become weaker. Furthermore, the diffraction peak of GO disappears, indicating that 0.05 La LDH is well dispersed on GO layer.

FTIR is used to obtain information about chemical bonds or functional groups contained in materials. The FTIR spectra of GO, MgAl LDH, 0.05 La LDH, and La LDH/GO are presented in Figure 3. From the figure, we could see that characteristic peaks of GO at 3395, 1721, 1402, and 1054 cm⁻¹ are attributed to the stretching vibrations of the O-H, C=O, epoxy C-O, and alkoxy C-O, respectively. In addition, the absorption peak of GO at 1617 cm⁻¹ is corresponded to the deformation vibration of adsorbed water
The FTIR spectra of GO, MgAl LDH, 0.05 La LDH and La LDH/GO show differences in peak positions and intensities, which are indicative of the unique chemical compositions of each material. For instance, MgAl LDH peaks at 1377 and 826 cm$^{-1}$ are attributed to the vibration of Al–O and Mg–O in the LDH [9, 23]. For 0.05 La LDH, the bands at 3446 and 1637 cm$^{-1}$ correspond to characteristic bands below 700 cm$^{-1}$ are attributed to the lattice vibrations of Al–O and Mg–O in the LDH [9, 23]. More significantly, compared with MgAl LDH, the absorption peak of Al–O bond blue-shifts 11 wavenumbers (from 666 cm$^{-1}$ to 655 cm$^{-1}$) in the FTIR spectra of 0.05 La LDH and La LDH/GO. And, the Al–O peaks of 0.05 La LDH and La LDH/GO at 555 cm$^{-1}$ disappear. It is mainly because the La$^{3+}$ partially replaces Al$^{3+}$ and destroys the lattice structure of LDH [12, 13].

The morphology and internal structure of GO and La LDH/GO can be observed by TEM. It can be seen from the Figure 4(a), GO has a two-dimensional layered structure with the size of several hundred nanometers. Meanwhile, in some areas, GO layers fold each other, thus showing different degrees of restacking. This is largely due to the existence of Van Der Waals forces between GO layers. As shown in Figure 4(b), the lateral size of 0.05 La LDH platelets is around 50–100 nm and many 0.05 La LDH sheets appear on the GO layers, thus the folded areas are significantly reduced [22]. Owing to the successful loading of LDH on GO layers, the restacking of GO sheets is effectively inhibited. Furthermore, the elements of C, O, N, Mg, Al and La can be observed from the EDS spectrum of La LDH/GO (Figure 4(c)). The molar ratio of Mg/Al/La is 2.4/1/0.05 agrees with the theoretical values, indicating that La LDH/GO hybrid is successfully synthesized.

3.2. Flame Retardancy of TPU Composites. The numerous parameters related to the potential fire hazard of the materials can be obtained by cone calorimeter, which is the most ideal test instrument for investigating the combustion performance of the materials during a fire. The heat release rate (HRR) is the most important fire characteristic parameter of the materials [24, 25]. Figure 5 gives the HRR curves of neat TPU and TPU composites. It can be seen that neat TPU has high peak heat release rate (PHRR) with a value of 1103 kW/m$^2$, which indicates that it is highly flammable and belongs to intermediate thickness non-charring samples. As for TPU containing MgAl LDH, compared with neat TPU, the PHRR value decreased by 23.3% to 846 kW/m$^2$. This can be explained by the fact that MgAl LDH absorbs heat during thermal decomposition, reducing the temperature on the surface of TPU, and decreasing the thermal decomposition and combustion rate of the polymer. Meanwhile, MgAl LDH can form a protective carbon layer on the degradation products, which prevents heat and gas transfer [26]. Furthermore, the PHRR value of TPU2 decreased by 30.3% in comparison with neat TPU. The decline in PHRR is mainly due to the further improvement of flame retardancy of MgAl LDH by the introduction of rare earth lanthanum. Among all the samples, TPU3 has the lowest PHRR value, which is 33.1% lower than that of neat TPU, indicating the physical barrier effect of the GO sheets [27]. It is worth noting that the time taken to reach the peak of all TPU composites are less than that of neat TPU, which is attributed to the decomposition of LDH at low temperature.

The cone calorimeter data of neat TPU and TPU composites are displayed in Table 2. From TPU1 to TPU3, total heat release (THR) values are basically unchanged, indicating that heat is kept constant before and after combustion. But average mass loss rate (AVMLR) values decreased, showing that 0.05 La LDH and GO play the role of flame retardancy by the mechanism of charring in the TPU composites. In the meantime, the average heat release rate (AVHRR) values of TPU1, TPU2, and TPU3 decreased; in turn, the respective HRR curves also became more and more flat after reaching the peak value. Combining the results of Figure 5, it is shown that all TPU composites belong to thermally thick charring (residue forming) samples [4]. In addition, the average effective heat combustion (AVEHHC), THR, AVHRR, and AVMLR values of TPU1 are all slightly higher than those of neat TPU as listed in Table 2, which indicates that the flame retardant effect of low MgAl LDH content on TPU is not significant.

In order to further comprehensively analyze the effect of La LDH/GO hybrid on the flame retardancy of TPU, an oxygen index meter was used to obtain the LOI value. Figure 6 presents LOI values of neat TPU and TPU composites. As can be seen from the figure, the LOI value of neat TPU is 21.4%, while the LOI values of TPU composites are 21.8%, 22%, and 23.2%, respectively. The LOI increased only by 1.8 from neat TPU to TPU3 (with 2 wt% La LDH/GO loading), showing that La LDH/GO fails to significantly increase the LOI value of TPU composites. Therefore, the above results show that if La LDH/GO is used as a synergistic flame retardant, it will have a better effect on TPU matrix [28].

3.3. Smoke Suppression of TPU Composites. The fire hazard of polymer materials is not only related to heat, but also to smoke. The smoke parameters obtained by cone calorimeter can also be used to evaluate the smoke suppression

![Figure 3: FTIR spectra of GO, MgAl LDH, 0.05 La LDH and La LDH/GO.](image-url)
Figure 4: TEM images of (a) GO, (b) La LDH/GO, and (c) EDS analysis of La LDH/GO.

Figure 5: HRR curves of TPU and TPU composites.
The smoke suppression performance of materials [29]. Figure 7 shows the smoke production rate (SPR) curves of neat TPU and TPU composites. As can be seen from Figure 7, neat TPU has the highest peak smoke production rate (PSPR) value of 0.1 m²/s in all samples, which proves that TPU produces heavy smoke during combustion process. However, compared with neat TPU, the PSPR reductions of TPU1, TPU2, and TPU3 are 39%, 45%, and 51%, respectively. The smoke suppression performance of TPU1 is attributed to the presence of MgAl LDH. On the one hand, the water vapor produced by thermal decomposition of LDH can dilute and absorb part of the smoke; on the other hand, the MgAl LDH lamellae also contains basic metal ions (such as Mg²⁺) besides large specific surface area, so it has a good adsorption effect on acidic gases [30]. For TPU2 containing 0.05 La LDH, the catalytic effect of rare earth lanthanum could promote the charring of TPU and form protective carbon layer, thus protecting the polymer matrix. When GO and 0.05 La LDH are incorporated into TPU, the char formation is further promoted by combining the physical barrier effect of GO [31].

Table 2 also illustrates certain smoke parameters of neat TPU and TPU composites. It can be observed that total smoke production (TSP) values of all TPU composites decreased in comparison with neat TPU. Nevertheless, the TSP values of TPU2 and TPU3 are mildly higher than those of TPU1, which is mainly attributed to the prolongation of burnout time by 0.05 La LDH and GO. Through the SPR curves of TPU composites after 250 s, this phenomenon could also be explained. The peak CO yield (PCOY) and peak CO₂ yield (PCO₂Y) are also important parameters to characterize the smoke emission behavior of materials [31]. As shown in Table 2, from neat TPU to TPU3, the values of PCOY and PCO₂Y are reduced in turn. Compared with neat TPU, the reduction for PCOY and PCO₂Y of TPU3 are 93% and 98%, respectively, which ascribed to the adsorption of La LDH and GO on CO and CO₂. The specific extinction area (SEA) is used to characterize the relationship between volatile products and smoke release during combustion process of materials, and it has a fine correlation with smoke parameters in large-scale experiments. As revealed in Table 2, compared with neat TPU, the average specific extinction area (AvSEA) values of all TPU composites decreased by varying degrees. Moreover, TPU3 has the lowest AvSEA value of 106.0 m²/kg in all samples, with a decrease of 33.6%. Therefore, these results show that La LDH/GO has a better smoke suppression effect.

3.4. Char Residues Analysis of TPU Composites. The structure and morphology of carbon layer also affect the flame retardancy of polymers [32]. In order to further explore the flame retardancy mechanism in condensed phase, the morphology and structure of the char residues left after CCT were investigated by SEM and XRD. The SEM images of char residues of TPU and TPU composites after CCT are presented in Figure 8. As Figure 8(a) shows, when neat TPU is burned out, the char residue is loose, porous, and fragile, which shows that TPU is a porous material and prone to smoldering. As for TPU1 containing MgAl LDH shown in Figure 8(b), the number of holes on the surface of char

Table 2: Cone calorimeter data of TPU and TPU composites.

| Sample | PHRR (kW/m²) | THR (MJ/m²) | AvHRR (kW/m²) | AvEHC (MJ/kg) | AvMLR (g/s) | PSPR (m²/s) | TSP (m²) | AvSEA (m²/kg) | PCOY (kg/kg) | PCO₂Y (kg/kg) |
|--------|--------------|-------------|---------------|---------------|--------------|-------------|---------|---------------|--------------|---------------|
| TPU    | 1103         | 139.1       | 261.2         | 15.6          | 0.089        | 0.100       | 13.22   | 159.6         | 0.090        | 8.802         |
| TPU1   | 846          | 139.6       | 283.8         | 16.3          | 0.092        | 0.061       | 10.62   | 142.5         | 0.063        | 8.537         |
| TPU2   | 769          | 140.3       | 237.2         | 15.8          | 0.078        | 0.055       | 11.06   | 129.2         | 0.043        | 8.502         |
| TPU3   | 738          | 140.0       | 209.8         | 13.3          | 0.068        | 0.049       | 10.76   | 106.0         | 0.006        | 0.172         |
residue are reduced, but the char residue is still loose. Compared with neat TPU, the holes on the surface of char residue from TPU2 (with 0.05 La LDH added) become hollows and the cracks basically do not exist. The main reason for this phenomenon is that 0.05 La LDH plays a catalytic role in the pyrolysis of TPU, thus promoting the cross-linking of TPU. Noticeably, after the incorporation of 0.05 La LDH and GO into TPU, it can be seen that the surface of char residue of TPU3 is compact and there are no holes and cracks, showing that GO can enhance the barrier effect of carbon layer. Figure 9 shows the XRD patterns of char residues of TPU2 and TPU3 composites. It can be seen that (002) diffraction peak representing the symmetric vibration of graphite crystallite appears near 25° for both TPU2 and TPU3, which further indicates the existence of graphitized structure in the carbon layer. However, the intensity of the (002) diffraction peak of TPU3 is stronger than that of TPU2, which means that the carbon layers formed by GO and 0.05 La LDH after combustion constitute an enhanced double-carbon layer structure, thus playing a more effective barrier role [33].

**3.5. Thermal Behavior of TPU Composites.**

Thermogravimetric analysis (TGA) is a thermal analysis technique for measuring the relationship between the quality and temperature change of the samples under programmed temperature control, which is used to investigate the thermal stability and composition of the materials [34]. The TGA and derivative thermogravimetry (DTG) curves of neat TPU and TPU composites in nitrogen atmosphere are shown in Figure 10, and the detailed data are summarized in Table 3. As shown in Figure 10(a) and 10(b), $T_{\text{onset}}$ (defined as the temperature at which the mass loss of sample is 5 wt%) and $T_{\text{max}}$ (defined as the maximum temperature at which the mass loss rate of sample is the fastest) decreased in different levels in

![Figure 8: SEM images of char residues of (a) TPU, (b) TPU1, (c) TPU2, and (d) TPU3 after CCT.](image)

![Figure 9: XRD patterns of char residues of TPU2 and TPU3 composites.](image)
comparison with neat TPU. In the meantime, the flame retardancy of polymers is closely related to their char yield during pyrolysis or combustion. It can be seen from Table 3 that the char residues of TPU1, TPU2, and TPU3 are 8.4%, 8.8%, and 9.7% at 800°C, which are higher than those of neat TPU, especially the TPU3 with La LDH/GO is added. The thermal stability of TPU matrix improved by La LDH/GO can be attributed not only to the catalytic effect of 0.05 La LDH on the formation of protective carbon layer, but also to the high thermal conductivity and physical barrier effect of GO [35]. The heat conduction and coke blockage produce the so-called labyrinth effect, resulting in heat and combustion gas must follow the tortuous path to fuel, which effectively prevents the spread of flame [31, 36].

**4. Conclusions**

To sum up, a La LDH/GO hybrid was synthesized by the hydrothermal method and characterized using XRD, FTIR, and TEM. The results showed that La$^{3+}$ has been doped into MgAl LDH, and La LDH/GO hybrid was successfully prepared. Afterwards, TPU composites containing MgAl LDH, 0.05 La LDH, and La LDH/GO were prepared through melt blending, respectively. Of all TPU composites, the TPU3 filled with 2 wt% La LDH/GO had better flame retardancy and smoke suppression performance. Compared with neat TPU, the PHRR and PSPR values of TPU3 decreased by 33.1% and 51%, respectively. Meanwhile, the char residue quality and char yield of TPU3 were also further improved. The reduced fire hazard of TPU3 could attribute to the interaction of 0.05 La LDH and GO. For one thing, the flame retardancy of 0.05 La LDH is due to the combination of heat absorption, gas dilution, and char formation. On the other hand, the carbon layers formed by GO and 0.05 La LDH after combustion constitute an enhanced double-carbon layer structure, thus playing a more effective barrier role.

**Data Availability**

All data used to support the findings of this study may be released upon application to the Qingdao University of Science and Technology, who can be contacted at qdkjdx@qust.edu.cn.

**Conflicts of Interest**

The authors declare that there are no conflicts of interest regarding the publication of this paper.

**Acknowledgments**

The authors gratefully acknowledge the National Natural Science Foundation of China (No. 51572138), the Key R&D Project of Shandong Province (No. 2019GSF109001, 2019CSF109080 and 2017GSF217013), the Shandong Provincial Natural Science Foundation, China (No. ZR2018BB072), the Original Innovation Project of Qingdao City (No. 19-6-2-23-cg), the Foundation of State Key Laboratory of High-Efficiency Utilization of Coal and Green Chemical Engineering (Nos. 2018-K09 and 2018-K43), Key Laboratory of Coastal Environmental Processes and Ecological Remediation, YICCAS (No. 2018KFJ102), and
References

[1] Y. Gao, J. Wu, Q. Wang, C. A. Wilkie, and D. O’Hare, “Flame retardant polymer/layered double hydroxide nanocomposites,” Journal of Materials Chemistry A, vol. 2, no. 29, pp. 10996–11016, 2014.

[2] K. Zhao, W. Xu, L. Song, B. Wang, H. Feng, and Y. Hu, “Synergistic effects between boron phosphate and micro-encapsulated ammonium polyphosphate in flame retardant thermoplastic polyurethane composites,” Polymers for Advanced Technologies, vol. 23, no. 5, pp. 894–900, 2012.

[3] A. Toldy, G. Harakaly, B. Szolnoki, E. Zimonyi, and G. Marosi, “Flame retardancy of thermoplastics polyurethanes,” Polymer Degradation and Stability, vol. 97, no. 12, pp. 2524–2530, 2012.

[4] A. B. Morgan and J. W. Gilman, “An overview of flame retardancy of polymeric materials: application, technology, and future directions,” Fire and Materials, vol. 37, no. 4, pp. 259–279, 2013.

[5] X. Chen, Y. Jiang, J. Liu, C. Jiao, Y. Qian, and S. Li, “Smoke suppression properties of fumed silica on flame retardant thermoplastic polyurethane based on ammonium polyphosphate,” Journal of Thermal Analysis and Calorimetry, vol. 120, no. 3, pp. 1493–1501, 2015.

[6] G. Huang, S. Wang, P. a. Song, C. Wu, S. Chen, and X. Wang, “Combination effect of carbon nanotubes with graphene on intumescent flame retardant polypropylene nanocomposites,” Composites Part A: Applied Science and Manufacturing, vol. 59, no. 2, pp. 18–25, 2014.

[7] S. Bourbigot, T. Turf, S. Bellayer, and S. Duquesne, “Polyhedral oligomeric silsesquioxane as flame retardant for thermoplastic polyurethane,” Polymer Degradation and Stability, vol. 94, no. 8, pp. 1230–1237, 2009.

[8] Q. Wang and D. O’Hare, “Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets,” Chemical Reviews, vol. 112, no. 7, pp. 4124–4155, 2012.

[9] Y. Han, Y. Wu, M. Shen et al., “Preparation and flame retardance of polystyrene nanocomposites based on layered double hydroxides,” Polymer Composites, vol. 38, no. 8, pp. 1689–1688, 2015.

[10] S. Zhang, Y. Yan, W. Wang et al., “Intercalation of phosphotungstic acid into layered double hydroxides by reconstruction method and its application in intumescent flame retardant poly (lactic acid) composites,” Polymer Degradation and Stability, vol. 147, pp. 142–150, 2018.

[11] Z. B. Peng, B. Hu, Q. D. Su, and J. Z. Qu, “Study on mechanism of rear earth PVC stabilize,” Journal of Rare Earths, vol. 21, no. 3, p. 328, 2003.

[12] R. Wen, Z. Yang, H. Chen, Y. Hu, and J. A. Duan, “Zn-Al-La hydrotalcite-like compounds as heating stabilizer in PVC resin,” Journal of Rare Earths, vol. 30, no. 9, pp. 895–902, 2012.

[13] S. Yi, Z.-H. Yang, S.-W. Wang et al., “Effects of MgAlCe-Co3 layered double hydroxides on the thermal stability of PVC resin,” Journal of Applied Polymer Science, vol. 119, no. 5, pp. 2620–2626, 2011.

[14] Z. Matusinovic and C. A. Wilkie, “Fire retardancy and morphology of layered double hydroxide nanocomposites: a review,” Journal of Materials Chemistry, vol. 22, no. 36, pp. 18701–18704, 2012.

[15] B. Sang, Z.-W. Li, X.-H. Li, L.-G. Yu, and Z.-J. Zhang, “Graphene-based flame retardants: a review,” Journal of Materials Science, vol. 51, no. 18, pp. 8271–8295, 2016.

[16] W. Xu, B. Zhang, B. Xu, and A. Li, “The flame retardancy and smoke suppression effect of heptapeamolybdate modified reduced graphene oxide/layered double hydroxide hybrids on polyurethane elastomer,” Composites Part A: Applied Science and Manufacturing, vol. 91, pp. 30–40, 2016.

[17] S. Park, J. B. An, R. D. Piner et al., “Aqueous suspension and characterization of chemically modified graphene sheets,” Chemistry of Materials, vol. 20, no. 21, pp. 6592–6594, 2008.

[18] S. P. Lonkar, B. Kultu, A. Leuteritz, and G. Heinrich, “Nanohybrids of phenolic antioxidant intercalated into MgAl-layered double hydroxide clay,” Applied Clay Science, vol. 71, no. 1, pp. 8–14, 2013.

[19] J. Wang, Q. Pan, Q. Liu et al., “Synthesis and photoluminescence properties of europium doped Mg-Al layered double hydroxides intercalated with anions,” Solid State Sciences, vol. 14, no. 5, pp. 562–566, 2012.

[20] K. Zhou, Z. Gui, Y. Hu, S. Jiang, and G. Tang, “The influence of cobalt oxide-graphene hybrids on thermal degradation, fire hazards and mechanical properties of thermoplastic polyurethane composites,” Composites Part A: Applied Science and Manufacturing, vol. 88, pp. 10–18, 2016.

[21] Y. Q. Han, T. Q. Wang, X. X. Gao, T. X. Li, and Q. Zhang, “Preparation of thermally reduced graphene oxide and the influence of its reduction temperature on the thermal, mechanical, flame retardant performances of PS nanocomposites,” Composites Part A: Applied Science and Manufacturing, vol. 84, pp. 336–343, 2016.

[22] Y.-T. Pan, J. Wan, X. Zhao, C. Li, and D.-Y. Wang, “Interfacial growth of MOF-derived layered double hydroxide nanosheets on graphene slab towards fabrication of multifunctional epoxy nanocomposites,” Chemical Engineering Journal, vol. 330, pp. 1222–1231, 2017.

[23] L. Zhang, X. Zhang, L. Shen et al., “Enhanced high-current capacitive behavior of graphene/CoAl-layered double hydroxide composites as electrode material for supercapacitors,” Journal of Power Sources, vol. 199, pp. 395–401, 2012.

[24] B. Scharlet and T. R. Hull, “Development of fire-retarded materials-interpretation of cone calorimeter data,” Fire Materials, vol. 31, no. 5, pp. 327–354, 2007.

[25] Z. Matusinovic, H. Lu, and C. A. Wilkie, “The role of dispersion of LDH in fire retardancy: the effect of dispersion on fire retardant properties of polystyrene/CA-Al layered double hydroxide nanocomposites,” Polymer Degradation and Stability, vol. 97, no. 9, pp. 1563–1568, 2012.

[26] W. Xu, X. Wang, Y. Liu, W. Li, and R. Chen, “Improving fire safety of epoxy filled with graphene hybrid incorporated with zeolitic imidazolate framework/layered double hydroxide,” Polymer Degradation and Stability, vol. 154, pp. 27–36, 2018.

[27] J. R. Potts, D. R. Dreyer, C. W. Bielawski, and R. S. Ruoff, “Graphene-based polymer nanocomposites,” Polymer, vol. 52, no. 1, pp. 5–25, 2011.

[28] A. Edenharter, P. Feicht, B. Diar-Bakerly, G. Beyer, and J. Breu, “Superior flame retardant by combining high aspect ratio layered double hydroxide and graphene oxide,” Polymer, vol. 91, no. 17, pp. 41–49, 2016.

[29] L. Liu, X. L. Zhao, C. Y. Ma, X. L. Chen, S. X. Li, and C. M. Jiao, “Smoke suppression properties of carbon black on flame retardant thermoplastic polyurethane based on ammonium polyphosphate,” Journal of Thermal Analysis and Calorimetry, vol. 126, no. 3, pp. 1821–1830, 2016.
S. Xu, L. Zhang, Y. Lin, R. Li, and F. Zhang, “Layered double hydroxides used as flame retardant for engineering plastic acrylonitrile-butadiene-styrene (ABS),” Journal of Physics and Chemistry of Solids, vol. 73, no. 12, pp. 1514–1517, 2012.

S. Wang, R. Gao, and K. Zhou, “The influence of cerium dioxide functionalized reduced graphene oxide on reducing fire hazards of thermoplastic polyurethane nanocomposites,” Journal of Colloid and Interface Science, vol. 536, pp. 127–134, 2019.

J. Yu, Q. Wang, D. O’Hare, and L. Sun, “Preparation of two dimensional layered double hydroxide nanosheets and their applications,” Chemical Society Reviews, vol. 46, no. 19, pp. 5950–5974, 2017.

S. Liu, H. Yan, Z. Fang, Z. Guo, and H. Wang, “Effect of graphene nanosheets and layered double hydroxides on the flame retardancy and thermal degradation of epoxy resin,” RSC Advances, vol. 4, no. 36, pp. 18652–18659, 2014.

X. Chen, C. Jiao, and J. Zhang, “Thermal and combustion behavior of ethylene-vinyl acetate/aluminum trihydroxide/Fe-montmorillonite composites,” Polymer Engineering & Science, vol. 52, no. 2, pp. 414–419, 2012.

C. Lee, X. Wei, J. W. Kysar, and J. Hone, “Measurement of the elastic properties and intrinsic strength of monolayer graphene,” Science, vol. 321, no. 5887, pp. 385–388, 2008.

D. Wang, Q. Zhang, K. Zhou, W. Yang, Y. Hu, and X. Gong, “The influence of manganese-cobalt oxide/graphene on reducing fire hazards of poly(butylene terephthalate),” Journal of Hazardous Materials, vol. 278, pp. 391–400, 2014.