



Graphene-based flame retardants: a review

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ABSTRACT

Graphene and its derivatives are potential flame retardant materials with good flame retardant performance; in particular, graphene as an adjuvant in combination with inorganic nanomaterials may be a promising candidate of flame retardant. This review describes the flame retardant mechanism, the development trend, and the classification of graphene-based flame retardants. It points out that graphene has attracted intensive interests in the fields of electronics, energy, and information, due to its excellent properties such as high thermal conductivity, good electron transport ability, and large specific surface area. In the meantime, graphene can change the pyrolysis as well as the thermal conductivity, heat absorption, viscosity and dripping of polymer during the combustion process. In other words, graphene can improve the thermal stability of polymer and delay its ignition, and it can also inhibit fire from spreading and reduce heat release rate.

Introduction

Polymer-based composites, one of the three major engineering composite materials, are widely used in aerospace, shipbuilding, automobile, construction and other fields closely linked with people's daily lives. This is because they exhibit low weight to strength ratio as well as good physical and chemical stability, heat resistance, chemical resistance, corrosion resistance, self-lubrication and other superior properties [1, 2]. However, most of polymers, due to their organic nature, are inherently flammable and combustible. Namely, polymers burn rapidly in association with a high heat release and a quick

spreading of flame when they are exposed to fire, and they release a lot of smoke and toxic gases that have a potential threat to the safety of human life and property [3–5]. Therefore, it is imperative to reduce the flammability of polymers.

In order to avoid or reduce the flammability of polymers and expand their application, researchers have developed many strategies, such as fire retardant coating technology, flame retardant filler technology, fire retardant solution soaking and chemical grafting flame retardant technology [3, 6, 7]. Among these strategies, the flame retardant filler technology provides an acceptable compromise between cost and properties. It also brings a great flexibility to design

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materials with multifunctional properties, because flame retardant fillers usually can effectively reduce the flammability of polymeric materials.

Conventional flame retardant fillers can be simply classified into two main categories on the basis of element component: inorganic flame retardant and organic flame retardant. The former includes hydroxide, metal oxide, phosphate, silicate, etc., and they are of significance owing to their outstanding thermal stability, low cost, non-toxicity and non-secondary pollution. The latter includes halogen flame retardants, phosphorus-containing flame retardant, phosphorus-nitrogen-containing flame retardant, etc., and they are accepted widely with high efficiency and good compatibility with polymer matrix [8]. However, inorganic flame retardants are restricted by high loading, poor efficiency, poor compatibility and aggregation. Organic flame retardants like halogen flame retardants are also restricted, because they can release toxic and harmful gas in combustion to endanger people's health and the environment as well.

As one of organic flame retardant, phosphorus-containing flame retardant is low toxic but less competitive in terms of high cost and poor thermal stability. Graphene is a potential novel and "environment-friendly material" that could have special significance in engineering, because it exhibits high-flame retarding efficiency and low loading as well as good environmental acceptance [9, 10]. Graphene is a two-dimensional material composed of layers of carbon atoms arranged as a honeycomb network, and it has unique electron and phonon transport behaviour, excellent thermal conductivity ($\sim 5000 \text{ W m}^{-1} \text{ K}^{-1}$) [11], high Young's modulus ($\sim 1.0 \text{ TPa}$) and mechanical stiffness (130 GPa) [12], large theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$) [13], high mobility of charge carriers ($200000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [14] and optical transmittance ($\sim 98 \%$) [15]. This is why graphene has become a significant candidate for a variety of purposes in material science and has drawn a lot of attention in microelectronics [16], energy [17], biological medicine [18], catalysis [19], etc.

Many studies prove that graphene and its derivatives can change the pyrolysis as well as the thermal conductivity, heat absorption, viscosity and dripping of polymer. This means that they could be powerful flame retardants for polymer, because they can improve the thermal stability of polymer and delay

its ignition, and they also can inhibit fire from spreading and reduce heat release rate. Herein, we try to sum up various studies on graphene and its derivatives as effective flame retardant fillers of polymer matrices, with an emphasis on the category, flame retarding mechanism and development trend of graphene-based flame retardants.

Graphene and graphene oxide flame retardants

Graphene and graphene oxide (denoted as GO; prepared by chemical method or by treatment with acid) exhibit promising flame retardant performance. This is because they have strong barrier effect, high thermal stability and large specific surface adsorption capability that are favourable for effectively reducing heat and mass transfer.

The combustion of polymeric materials involves four key components: heat, oxygen, fuel, and free radical reaction. The flame retardancy of polymeric composite materials can be achieved by inhibiting or disrupting one or several components or circulation of these elements [4]. Graphene-based flame retardants can improve the flame retardancy of polymer through inhibiting the two key terms—heat and fuel (see Fig. 1). More specifically, graphene can work in three synergetic ways. First, graphene and GO possess unique two-dimensional layered structure and can promote the formation of a dense continuous char layer during the decomposition process. The char can act as a physical barrier to prevent heat transfer from heat source and delay the escape of pyrolysis products from substrates. The carbon skeleton of graphene and GO has a high thermal stability and can act as a template for char and promote the formation of multiple and overlapped char via the so-called "labyrinth effect". As a result, a 'tortuous path' is provided to increase the exchanging pathway of heat and mass between gaseous and condensed phases in association with the improvement in the thermal stability and fire safety of polymers [20–27]. Second, graphene and GO have a large specific surface area and can effectively adsorb flammable organic volatiles or hinder their release and diffusion during combustion; they also can provide a catalytic and carbonization platform for other materials like metallic oxide [23, 28–32]. Third, graphene and GO contain abundant reactive oxygen-

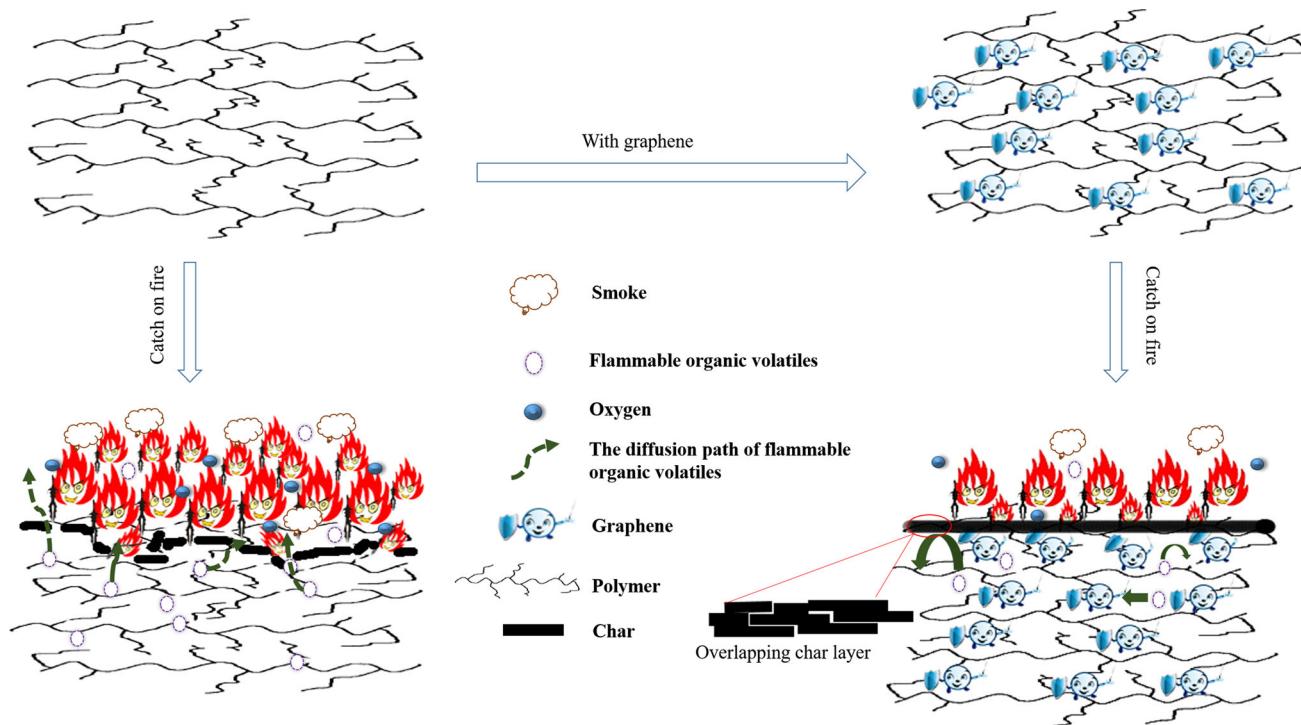


Figure 1 Schematic diagram showing the flame retarding mechanism of graphene-based flame retardant under ideal condition.

containing groups (carboxyl group at edges as well as epoxy and hydroxyl groups on the basal planes) and may find a wide range of applications in engineering. For example, the oxygen-containing groups in GO may undergo decomposition and dehydration at low temperature, thereby absorbing heat and cooling polymer substrate during combustion. Meanwhile, the gases of dehydration can dilute the concentration of oxygen around the ignition peripheral. Moreover, graphene and GO have a good compatibility and a strong interaction with polymeric molecules as well as a good thermal conductivity, and they can constitute a three-dimensional network structure in polymeric matrix. Such a three-dimensional network structure is favourable for increasing the viscosity of polymer upon exposure to heat source. It also can change the rheological behaviour of polymer and prevent its dripping, thereby hindering the release and diffusion of volatile decomposition products through the “labyrinth effect” and affecting the flame retardancy of composites (e.g., changing UL-94 classification, oxygen index (OI) and time to ignition (TTI)) [33–38].

Pure graphene is quite stable even in a natural gas flame (Fig. 2(a)), and it can significantly improve the mechanical properties, thermal stability and gas

barrier ability of polymers and reduce its flammability as well [10, 39–41]. As shown in Fig. 2(a), when the reduced GO (denoted as rGO) film is exposed to a natural gas flame for a few seconds, the burned part turns red hot, but the reaction does not propagate and can be quenched after the flame is removed. No combustion occurs even after multiple flame treatment of rGO and virgin graphene, which well corresponds to their high thermal stability. However, highly energetic GO and potassium salt by-products left from synthesis can undergo self-propagating domino-like thermal deoxygenating reaction [23, 42], which means that GO is highly flammable in the presence of contaminant like KOH. As shown in Fig. 2(b), the flame immediately triggers the self-propagating combustion of the reduced GO film in the presence of KOH salt contaminant. The time intervals between the frames are 0.32, 1.82, 2.5, 2.5 and 2.5 s from left to right, which suggests that KOH can significantly reduce the thermal stability of rGO.

Huang et al. [20] studied the effect of graphene on reducing the flammability of polymer nanocomposites, and they found that, when poly(vinyl alcohol) is filled with 3 % (mass fraction; the same hereafter) graphene sheets, the peak value of heat release rate (PHRR) is reduced by 49 % (from 373 to 190 kW m⁻²)

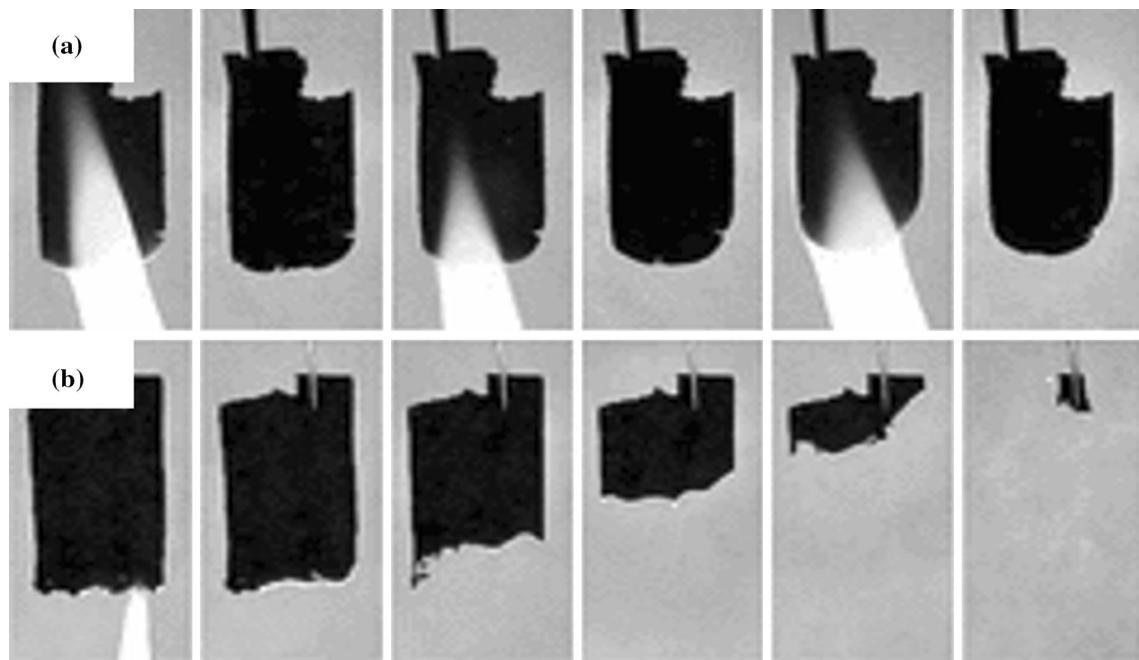


Figure 2 (a) Snapshots showing flame treatments on rGO film with intervals of 3 to 4 s. (b) Snapshots showing flame treatment on rGO contaminated with KOH salt (mass fraction: 1 %). Reproduced from ref. 42 with permission from Royal Society of Chemistry.

and the TTI is greatly increased (from 18 to 33 s). The reason might lie in that the condensed phase flame retardant can form a compact, dense and uniform char layer during combustion, thereby hindering the heat and mass transfer between gaseous and condensed phases.

Han et al. [28] reported that graphene with different degrees of oxidation and exfoliation has a significant effect on the thermal stability, dynamic viscoelasticity and mechanical properties of polymers. They found that a high oxidation degree of GO is harmful to the thermal stability and storage modulus of GO/polystyrene and graphene/polystyrene nanocomposites prepared by melt blending. In other words, it needs to eliminate O-containing functional groups and achieve uniform distribution of graphene (as an effective barrier to the permeation of flammable gases) in polymeric matrix so as to obtain optimal thermal stability of graphene/polystyrene composite. They also found that GOs or graphene can promote the carbonization on polymer surface and unburned filler, while the filler itself exhibits a high heat resistance and contributes to the formation of char residues. Therefore, filling with 5 % graphene helps to improve the flame retardancy of the polystyrene-based nanocomposites.

Previous studies also demonstrate that graphene has an eminent flame retardant performance as compared with other materials of the carbon family. Dittrich et al. [30] and Hofmann et al. [43] incorporated layered highly exfoliated thermally reduced graphene (TRGO), layered minor exfoliated-expanded graphite (EG40), spherical carbon black (CB) and multiwall carbon nanotubes (MWNT) into polypropylene (denoted as PP) at various concentrations between 0.5 and 7.5 %. They found that the effect of the fillers on the thermal stability, flow behaviour, burning behaviour and flame resistance of the polymer depends on the concentration and morphology of the fillers. Namely, a higher filler concentration favours the formation of residue structures and heat shielding counterbalance. As shown in Fig. 3, flame retarded polypropylene (PP-FR) with less than 5 % of TRGO has a higher T_{onset} (the onset temperature of decomposition) and a lower PHRR, which is because the most effective protection physical barrier with a dense and closed residue structure is formed at this level of graphene.

Dittrich et al. [44, 45] further investigated the influence of graphene on the mechanical properties, morphology, pyrolysis, rheological properties and burning behaviour of V2 PP-FR. They found that, as

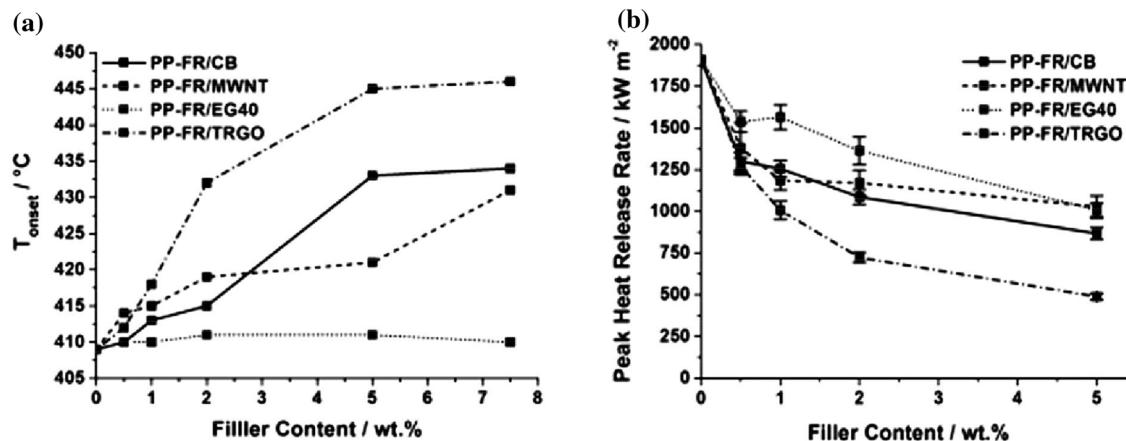


Figure 3 (a) T_{onset} of PP-FR carbon nanocomposites as a function of CB, MWNT, EG40 and TRGO concentration (0.5, 1.0, 2.0, 5.0 and 7.5 %). (b) PHRR of PP-FR carbon nanocomposites as a

function of CB, MWNT, EG40 and TRGO concentration (0.5, 1.0, 2.0 and 5.0 %). Reproduced from ref. 30 with permission from John Wiley and Sons.

compared with other carbon fillers under identical processing condition, functionalized graphene (denoted as FG) with about ten layers, and a mass fraction of 5 % exhibits more homogenous exfoliation and dispersion in PP matrix. As a result, FG filler can markedly increase the Young's modulus and yield stress of PP by 53 and 11 %, respectively. In the meantime, FG filler can shift the T_{onset} value of PP-FR (409 °C) to higher temperature (439 °C), depending on its dispersion and layer number of graphene. This is because the FG filler have a high aspect ratio and surface area and can build up an effective network structure to increase the shear stress and provide a physical hindrance against the decomposition in the early stage. The UL-94 test result indicates that the introduction of FG filler leads to a significant change in the melt flow behaviour of PP-FR and prevents PP-FR from dripping. The OI test result demonstrates that the OI is increased from 19 (of pure PP) to 21, while a carbonaceous char is formed on the top of the sample. The reason may lie in that FG can change the thermal conductivity and heat absorption of polymer matrix, thereby significantly influencing TTI which is controlled by the thermal inertia under identical condition. Besides, FG and TRGO can decrease the TTI of virgin PP (33 s) to 20 s and 23 s, which is because they can significantly increase the thermal conductivity and heat absorption and cause earlier polymer decomposition. Furthermore, the formation of effective protection layers reduces PHRR by 76 % during combustion and does not change the composition of the evolved pyrolysis gases.

The competition of the interactions, the reinforcing effect of graphene layers and the heat conduction of graphene have an obvious effect on the properties of polymeric composites. Bao et al. [35] pointed out that the thermal stability and flame retardancy of graphene are determined by its concentration, the barrier effect, the reinforcing effect of graphene nanolayers and the thermal conductivity of graphene sheets. When the concentration of graphene additive is smaller than 0.08 %, the thermal stability and combustion properties of graphene-filled polymers are mainly determined by their heat conductivity. When the graphene content is more than 0.20 % or large enough, the barrier effect is dominant to significantly reduce the PHRR and improve the flame retardancy. Liu [24] reported that the char barrier effect in epoxy resin (denoted as EP) matrix is promoted in the temperature range of 400–430 °C by graphene nanosheets (GNS) with a large surface area, and the GNS can also change the path of thermal degradation of EP thereat.

The abovementioned researches demonstrate that graphene as a potential and effective flame retardant exhibits prominent thermal and mechanical properties as well as good flame retardancy. However, there are still many challenges to develop graphene-based flame retardants. First, graphene with untreated surface has a poor dispersion in polymer matrix and is liable to agglomeration, due to its strong π - π force and weak van der Walls force. Second, the interaction between graphene sheets and the polymer matrix is so weak that the stress cannot be transmitted to

graphene effectively, thereby causing the degradation in mechanical performance. Third, 5 % of graphene filler is needed to achieve the optimal flame retardancy, but the graphene sheets at this dosage tend to agglomerate seriously. In addition, the char of graphene-filled polymers is not stable enough to form the defence system against fire, which is unfavourable for the flame retardancy performance. These challenges make graphene or GO inefficient flame retardants when used alone.

Conventional flame retardants-graphene blending flame retardant

To solve the abovementioned problems, many researchers have made significant efforts to use graphene as an adjuvant in combination with other conventional flame retardants such as intumescent flame retardants and aluminium hydroxide [46–51], melamine polyphosphate [52], carbon black [53], layered double hydroxides (LDHs) [54], brominated polystyrene and antimony trioxide (Sb_2O_3) [55], and aluminium hypophosphite [56]. As shown in Fig. 4, the conventional flame retardants can partly prevent

graphene from agglomeration and improve the dispersion of graphene, while graphene with a high specific surface area also can enhance the dispersion and compatibility of the conventional flame retardants in polymer matrix. Furthermore, graphene with a large network of sp^2 hybridized carbon usually exhibits strong interactions with the polymer matrix of graphene-based flame retardants, and the synergistic effect between graphene and conventional flame retardants are often favourable for improving the thermal and flame retardant properties of the composites. As can be observed in Table 1, incorporating graphene with conventional flame retardants can increase the char yield and promote the formation of the successive and compact char shield, thereby effectively inhibiting the release of heat and flammable organic volatiles. It also can prolong the TTIs, thereby providing more time than conventional flame retardants alone for people escaping the fire scene. In the UL-94 test, combination graphene with conventional flame retardants can reach V0 degree, which means that the molten dripping of the polymer matrix can be suppressed, thereby inhibiting the fire from spreading. The PHRRs are reduced dramatically as compared with pure polymer matrix, which

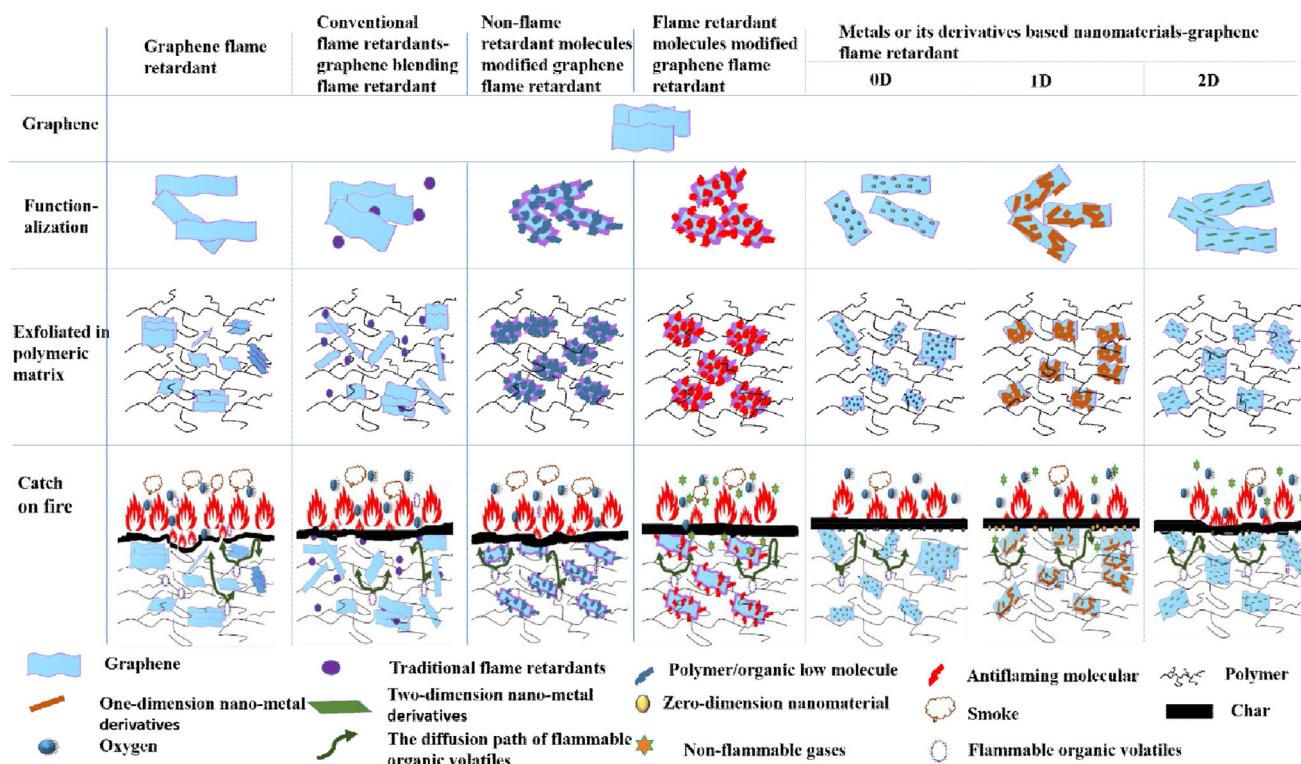


Figure 4 Schematic illustration of the action mechanism of graphene-based flame retardant.

Table 1 Effectiveness of graphene or GO combination with conventional flame retardants

Reference number	Polymer matrix	Filler	Concentration (wt%)	Heat flow (kW m ⁻²)	PHRR (kW m ⁻²)	THR (MJ m ⁻²)	CY (%)	TTI (s)	LOI (%)	UL-94	Tensile strength (MPa)
[46]	PU	—	0	—	—	—	6.5 ^b	—	22.0	Failed	6.45
		IFR ^a	20	—	—	—	—	—	29.0	V1	5.41
		IFR ^a /rGO	19/1	—	—	14.5 ^b	—	—	32.0	V1	6.18
		IFR ^a /rGO	18/2	—	—	19.3 ^b	—	—	34.0	V0	6.51
[47]	PP	—	0	50	2011	106	0	—	19	Failed	26.8
		TRGO	1	—	—	—	—	—	19	Failed	27.5
		APP	27.5	254	—	14	—	40	V0	20.9	
		APP/TRGO	27.5/1	230	—	14	—	31	V0	22.1	
		MH	59	226	75	38	—	32	V0	15.7	
		MH/TRGO	59/1	181	75	38	—	38	V0	16.8	
[48]	PP	—	0	35	1242	—	0	42	17.8	Failed	—
		IFR ^c	20	350	—	15.7	53	29.2	V1	—	
		CNTs	2	538	—	2.5	44	20.6	Failed	—	
		rGO	2	486	—	2.1	43	20.1	Failed	—	
		IFR ^c /CNTs	18/2	278	—	17.3	64	29.7	V1	—	
		IFR ^c /CNTs/rGO	18/1/1	212	—	17.8	82	31.4	V0	—	
[49]	PBS	—	0	—	—	0.4 ^b	—	23.0	Failed	30.8	
		IFR ^a	20	—	—	9.9 ^b	—	31.0	V1	25.0	
		IFR ^a /GNS	18/2	—	—	11.8 ^b	—	33.0	V0	30.5	
[50]	PMMA	—	0	35	496	67	1.2	26	17.4	Failed	18.65
		O-LDHs/BPEA	5/10	308	52	12.7	27	26.1	V2	14.59	
		rGO	1	376	66	2.4	29	20.5	Failed	20.31	
		O-LDHs/BPEA/rGO	5/10/1	273	50	18.1	32	28.2	V1	17.34	
[52]	PVA	—	0	35	373	58	12.9 ^b	18	19.2	Failed	57.2
		Graphene	1	214	55	11.6 ^b	25	23.4	Failed	63.2	
		MPP	10	297	38	16.3 ^b	48	25.7	Failed	42.4	
		Graphene/MPP	1/10	148	36	18.5 ^b	53	29.6	V0	53.6	
		Graphene/MPP	1/20	114	18	21.5 ^b	70	33.4	V0	44.7	

NOTE: The data of PHRR, THR and CY are obtained from cone calorimeter test at the heat flow listed in table

A synergic effect can be observed between the conventional flame retardants and graphene or GO

CY refers to char yield; APP refers to ammonium polyphosphate; MH refers to magnesium hydroxide; CNTs refer to carbon nanotubes; PBS refers to poly(butylene succinate); GNS refers to graphene nanosheets; PMMA refers to poly(methyl methacrylate); O-LDHs refers to organics-modified LDHs; BPEA refers to 1,2-bis(5,5-dimethyl-1,3,2-dioxyphospacyclohexane phosphoryl amide) ethane; MPP refers to melamine polyphosphate

^a Refers to intumescent flame retardant (contains microencapsulated ammonium polyphosphate (MCAPP)/melamine (MA) blend at a mass ratio of 2:1)

^b Refers to the data obtained from TGA testing at 600 °C

^c Is made up of 80 % APP and 20 % pentaerythritol

means that polymer composites are more secure in case of fire. For example, Gavgani et al. [46] reported that the intumescent flame retardant polyurethane (IFRPU) prepared with rGO (dosage: 0.2 %), melamine and microencapsulated ammonium polyphosphate exhibits not only compensated thermal stability and mechanical properties but also improved

antidripping properties (indicated by a UL-94 V0 rating and self-extinguishing) as well as increased storage modulus, char yield and thermal stability. The reason lies in that rGO is well dispersed with little agglomeration (Fig. 5a) and exfoliated in the IFRPU composites, thereby preventing the migration and increasing the dispersion of the intumescence

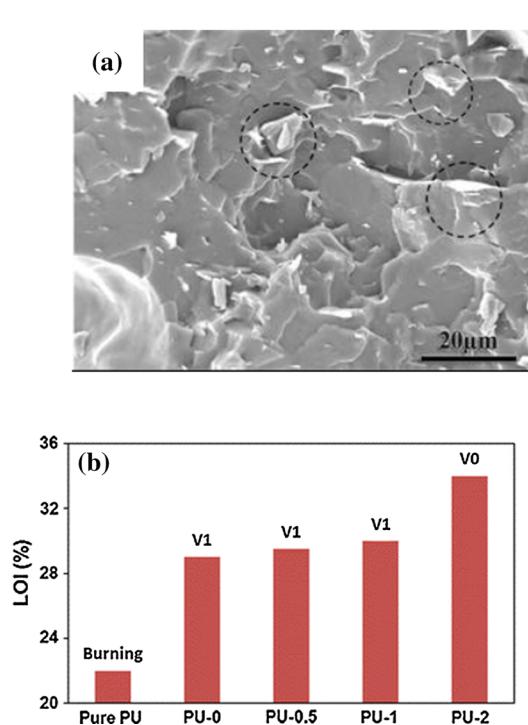


Figure 5 (a) Scanning electron microscopic (SEM) images of PU-2 with 2 % rGO and 18 % IFR; circles stand for regions where PU chains are adhered to the pulled-out rGO owing to strong interactions. (b) The flame retardancy of IFRPU/rGO composites (PU-0 concentration with 20 % IFR, PU-0.5 concentration with

Samples	LOI (%)	UL-94 rating	Dripping	Time of burning
Pure PU	22.0	Burning	Yes	42
PU-0	22.9	V1	Yes	78
PU-0.5	31	V1	No	Self-extinguished
PU-1	32	V1	No	Self-extinguished
PU-2	34	V0	No	Self-extinguished
Samples	Tensile strength (Mpa)	Elongation at break (%)	Modulus	Shore A hardness
Pure PU	6.45	385.34	5.46	75
PU-0	5.41	321.87	6.23	77
PU-0.5	5.75	288.24	8.53	80
PU-1	6.18	249.63	13.17	86
PU-2	6.51	218.91	16.56	92

19.5 % IFR and 0.5 % rGO, and PU-1 concentration with 19 % IFR and 1 % rGO). (c) Effect of rGO on the LOI values and UL-94 results of pure PU and IFRPU composites. (d) Mechanical properties of pure PU and IFRPU/rGO composites. Reproduced from ref. 46 with permission from Springer.

flame retardant. The low dosage of rGO, compared with that of conventional intumescence flame retardant (18 %), indicates it is an effective strategy to combine different flame retardants to acquire synergistic flame retarding effect.

Wang et al. [49] used graphene as a synergist to enhance the fire resistance of intumescence flame retardant poly(butylene succinate) (IFRPBS). They found that adding 2 % graphene to IFRPBS with 18 % IFR further increases LOI to 33 (adding 20 % IFR alone gives an LOI of 30). Because the incorporation of graphene further increases the viscosity of the molten polymer, the graphene/IFRPBS composite exhibits excellent antidripping properties, and its UL-94 reaches V0 degree (see Fig. 6). Further study reveals that graphene with the unique structure has a synergistic function with IFR, and the synergistic function can help to increase the char yields and the thermal stability of the char at high temperature. Such a synergistic flame retardancy is also reported by Huang et al. [50]. By incorporating intumescence

flame retardants (IFRs), graphene and LDHs via in situ polymerization, they prepared intumescence flame retardant poly(methyl methacrylate) (PMMA) nanocomposite. They found that graphene (1 %) and LDHs (5 %) in the as-prepared intercalated/exfoliated nanocomposite exhibit uniform dispersion and very little deterioration of the mechanical properties of the polymer-based composites. More importantly, the presence of LDHs and GNS enhances the compact and dense intumescence char, thereby obviously improving the flame retardant properties of the composites.

Combining graphene with conventional flame retardants can significantly reduce the usage of graphene and conventional flame retardants and obtain a better fire resistant performance. However, the additive concentration is still high, and except for tensile stress, the combination will either deteriorate or make no contribution to the mechanical properties of polymers (see Table 1). Therefore, efforts still need to be made to improve the dispersion and thermo-

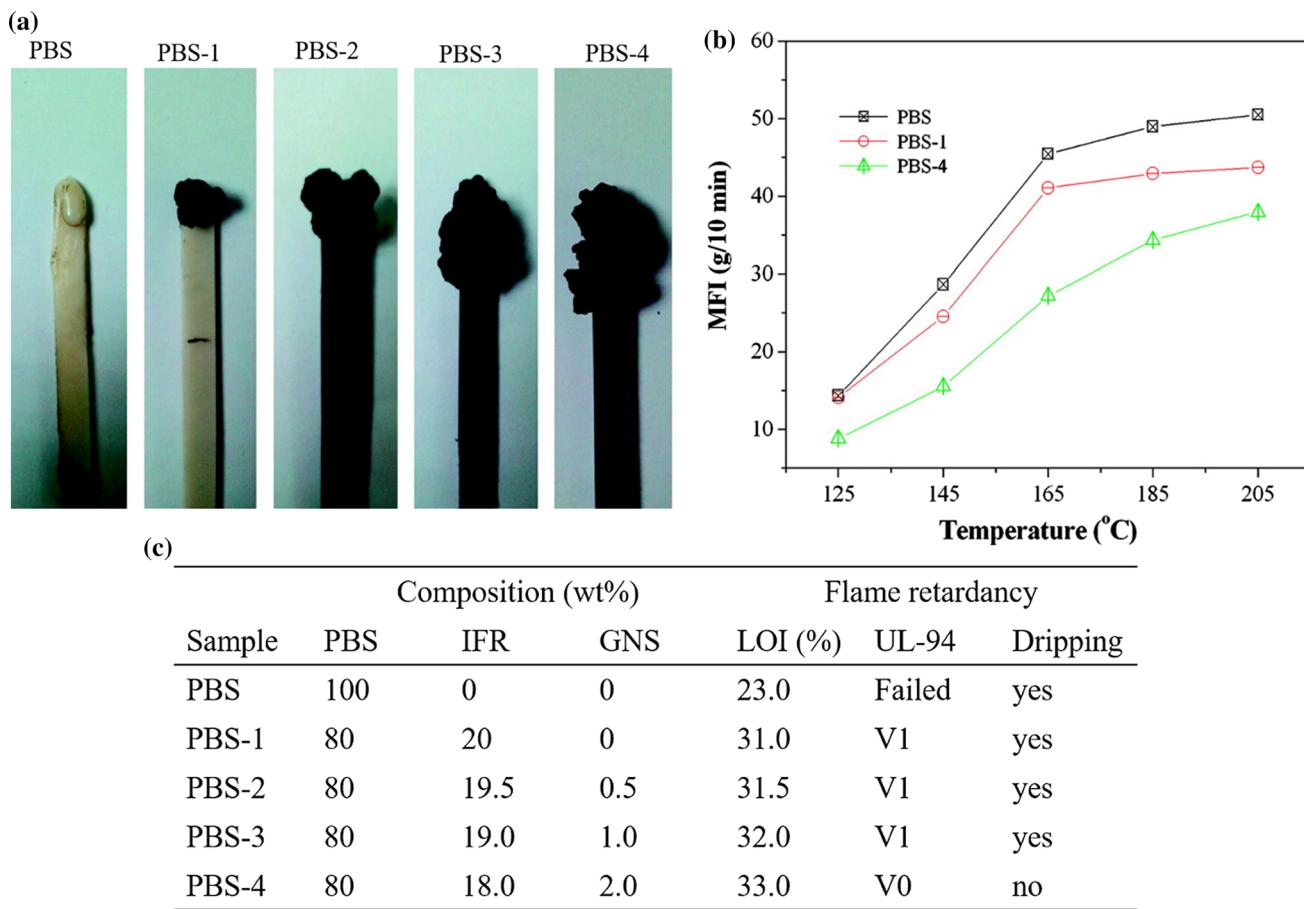


Figure 6 (a) Photos of char residues of samples after combustion, showing that the incorporation of graphene with IFRPBS could improve the char yields. (b) Melt flow index values for PBS, PBS-1 and PBS-4 composites, showing that the viscosity of molten

polymer increases with the addition of graphene. (c) The flame retardancy of PBS and IFRPBS/graphene systems. Reproduced from ref. 49. Copyright © 2011, American Chemical Society.

oxidation stability of graphene, thereby enhancing both the mechanical properties and flame retardancy of the polymer composites.

Graphene-based composites flame retardants

As mentioned above, it is easy to create functional graphene-based composites [42]. Because the combination of graphene and secondary components may result in remarkably improved fire retardant performance, a number of strategies have been proposed for the construction of graphene-based composites, and graphene-based composite flame retardants have attracted significant attention.

There are three major advantages to construct graphene-based nanocomposites. First, graphene has

a unique basal two-dimensional (2D) layer structure. This makes it possible to load micro-nanostructure materials such as nanotube, nanorod and nanoparticles with the size ranging from a few nanometers to several hundred nanometers, thereby affording 2D layer structure. The 2D structure of graphene can provide more possibilities to achieve covalent attachment and non-covalent adsorption of various functional molecules. Second, graphene has a high surface area and can form stable dispersion in various solvents. This makes it possible to synthesize graphene-based nanocomposites by simple methods. The interfacial contact of graphene and GO with other components can be improved, and the aggregation of the secondary components can be effectively prevented while some unique properties at nanoscale are preserved. The secondary components attached to the surface of graphene and GO sheets

could act as a separator between the sheets, thereby increasing the exfoliation and minimizing the restacking. Finally, the abundant oxygen-containing groups on the surface of GO provide more active sites for covalent attachment and non-covalent adsorption. In view of these advantages of graphene and GO, we can rationally speculate that organic molecules or inorganic nanomaterials can be functionalized on graphene sheets via covalent bonding such as free radical reactions of carbon–carbon double bonds and cycloaddition reaction or covalent reaction with oxygen-containing groups. There are also no-covalent interactions attributed to π - π stacking, hydrogen bonding and van der Walls forces. This makes it feasible to construct a broad of new graphene-based nanocomposite flame retardants which can be classified as molecules-modified graphene composite flame retardants and inorganic-nanomaterials graphene composite flame retardants.

Molecules-modified graphene composite flame retardants

Molecules, such as polymeric molecules and inorganic acid molecules, can be grafted onto the planes of graphene sheets, forming molecules-modified graphene composite flame retardants. The addition of these molecules can prolong the distance and restrain the aggregation of the layers of graphene, thereby increasing its dispersion and compatibility with polymer matrices. This leads to more favourable mechanical properties, thermal stability and flame retardant performance. Such a grafting technology, with either flame retardant molecules or non-flame retardant molecules, could be powerful in enhancing the mechanical properties and thermal stability of graphene.

The non-flame retardant molecules are used to modify graphene aiming to improve the dispersion and thermal stability of graphene; they can be further subdivided into polymeric molecules and low organic molecules approximately.

Several reviews have been published on polymeric molecules-modified graphene-based nanocomposites [42, 57]. It has been found that the polymeric graphene-based composites usually exhibit improved mechanical properties, thermal stability and flame retardant performance [31, 32, 58–61]. This is because polymeric molecules, such as polyethylene glycol

mono-methyl ether 750 [59], polypropylene [58, 62], polyurethane [31, 60], poly(vinyl alcohol) [61] and poly(ethylene glycol) bis-amines [63], can be grafted onto the planes and edges of graphene sheets to improve the interfacial interaction between graphene and polymer matrix and achieve good dispersion of graphene in polymer matrix. For example, Cao et al. [58] incorporated polypropylene on the sheets of GO (PP-g-GOs) to compatibilize commercially important polyolefin-based polymer blends. They found that PP-g-GOs act as the multifunctional filler for PP/PPO blends, which not only improves the compatibility of PP/PPO but also enhances the flame retardancy and thermal strength. The flame retarding effect of PP-g-GOs and the ausgezeichnet dispersion of the PPO phase jointly function to account for notably improved flame retardancy. With the incorporation of 1.5 % PP-g-GOs into PP, the PHRR value is decreased from 1204 (pure PP) to 788 W·g⁻¹; the temperature for the PHRR value is increased by about 7 °C.

Small organic molecules, such as organosilicon compounds [64–68], cetyltrimethyl ammonium bromide [69] and pentaerythritol [70], are modified or adsorbed onto the planes and edges of graphene sheets to create organic-small molecule graphene composites. The incorporated small organic molecules act as a bridge between graphene and polymer matrices and form a network structure, thereby increasing the dispersion of graphene and improving the mechanical properties of the composites. Wang et al. [66] adopted a simple refluxing process to simultaneously reduce and surface functionalize GO with octa-aminophenyl polyhedral oligomeric silsesquioxanes (OapPOSS). They found that OapPOSS provides the active sites to link rGO with the polymeric matrix, resulting in the enhanced interfacial interaction between the functionalized graphene and epoxy as well as the improved dispersion of rGO in the epoxy composites. Namely, the adsorption, the barrier effect and the graphitized carbons promoted by GO, as well as the synergistic effect of OapPOSS contribute to improving the thermal oxidative resistance of the char layer. As a result, the thermal stability and flame retardant performance of epoxy composites with 2.0 % of incorporated OapPOSS-rGO are dramatically enhanced. As shown in Fig. 7 (d, e, f), with the incorporation of 2.0 % of OapPOSS-rGO, the peak heat release rate, total heat release and CO production rate values of OapPOSS-rGO/EP are

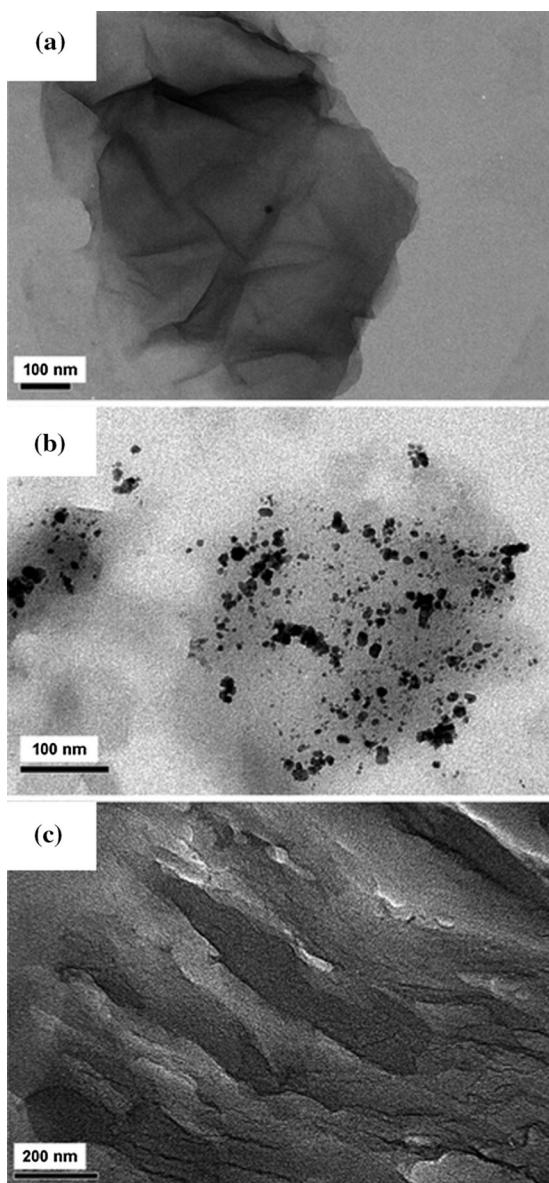
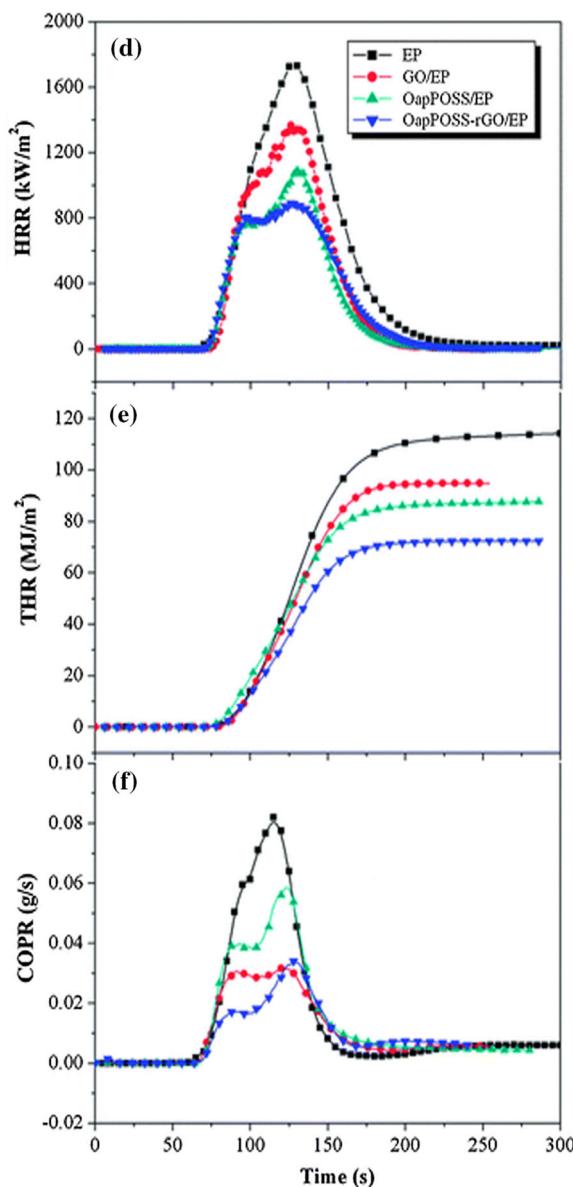


Figure 7 Transmission electron microscopic (TEM) images of (a) GO, (b) OapPOSS-rGO (OapPOSS refers to octa-aminophenyl polyhedral oligomeric silsesquioxanes) and (c) OapPOSS-rGO–EP composites (rGO has good dispersion in epoxy resin (denoted as EP) composites and shows no obvious aggregation) as well as heat



release rate (HRR, e), total heat release (THR, f) and CO production rate (COPR, g) versus time curves of epoxy and its composites. Reproduced from ref. 66 with permission from Royal Society of Chemistry.

significantly reduced by 49, 37 and 58 %, respectively, compared to those of pure epoxy.

Flame retardant molecules can be used to functionalize graphene or GO (similar to organic functionalization). These molecules restrict the restacking of graphene and GO sheets and enhance the compatibility of graphene in polymer matrices. Such a strategy combines the flame retardant properties of graphene and the secondary components, providing

nanocomposite flame retardants that exhibit preferable flame retardant performance. The flame retardant graphene-based nanocomposite flame retardants can be classified into three categories: inorganic acids molecules graphene-nanocomposite flame retardants, P-, Si- or N-containing molecules graphene-nanocomposite flame retardants and conventional-organic flame retardant molecules graphene-nanocomposite flame retardants.

Phosphoric acid [71–73] and phosphomolybdic acid [74] are examples of the substances that can be used to make inorganic acid graphene-nanocomposite flame retardants. They attach to graphene and disrupt the interfaces between graphene sheets, improving the dispersion of graphene in polymer matrices. Moreover, the inorganic acids can act as char-forming catalysts in the condensed phase, enhancing the barrier effect of graphene. Kim et al. [71] obtained an eco-friendly flame retardant, graphene phosphonic acid (GPA), which was prepared by covalently attaching phosphorus to the edges of graphene nanoplatelets via a chemical-ball milling method. They found that phosphonic acid can be transformed to pyrophosphonic acid and metaphosphonic acid which can catalyse the formation of protective char. As a result, GPA exhibits high dispersibility in various polar solvents as well as good flame retardancy. As shown in Fig. 8, GPA supports the formation of a protective layer on the surface of Hanji (a handmade paper from Korea), and hence GPA/Hanji (Hanji treated with GPA) has superior flame retardancy.

The second category of flame retardant graphene-nanocomposite flame retardants is the P-, Si- or N-containing molecules graphene-nanocomposite flame retardants. They are formed from substances that can be covalently bonded to graphene, such as hexachlorocyclotriphosphazene (HCCP) [75], phenyl dichlorophosphate (PDCP) [76], hyperbranched

cyclotriphosphazene polymer [77, 78], organophosphorus oligomer [79], N-aminoethyl piperazine [80], silicon-phosphorus oligomer [81], phenyl-bis-(triethoxysilylpropyl) phosphamide [82], ionic liquid-containing phosphonium [83] and 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo [2.2.2] octane (PEPA) [84]. Bao et al. [75] made use of in situ polymerization to functionalize GO with HCCP which acts as a char-catalysing agent (Fig. 9). They found that the functionalized GO (FGO) is well dispersed in polystyrene (PS). The physical barrier effects and the strong interfacial interactions between FGO and the PS matrices account for the dramatically decreased HRR, THR, peak CO₂ release rate and peak CO release compared with those of pure PS. Guo et al. [76] developed a new approach for preparing functionalized GO using PDCP with flame retardant elements to improve the flame retardancy of the polymer. They found that FGO exhibits good dispersion in EP without large aggregation and contributes to the increase of the thermal stability, onset temperature and maximum weight loss temperature of EP composites. The flame retardant performance of the composites is also improved, possibly because the layered effect of GO contributes to enhancing the flame retardancy and promoting the char formation. They also confirmed that graphene and functionalized graphite oxide are more effective than GO in improving the flame retardant properties and provide a maximum PHRR of 23.7 and 43.9 %, respectively, at 5 % loading.

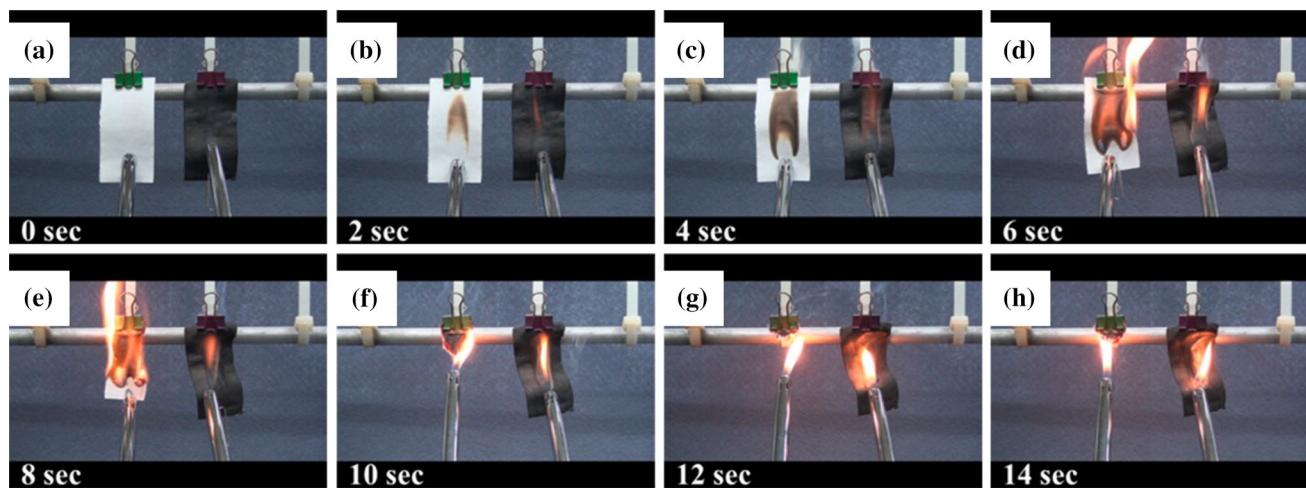


Figure 8 Snapshots of flame treatments of Hanji (left) and GPA/Hanji (right) with respect to time in second: (a–h) 0–14 s. GPA/Hanji has a superior flame retardancy, due to the key role of GPA

which supports the protective layer formation on the surface of Hanji. Reproduced from ref. 71 with permission. Copyright 2014, American Chemical Society.

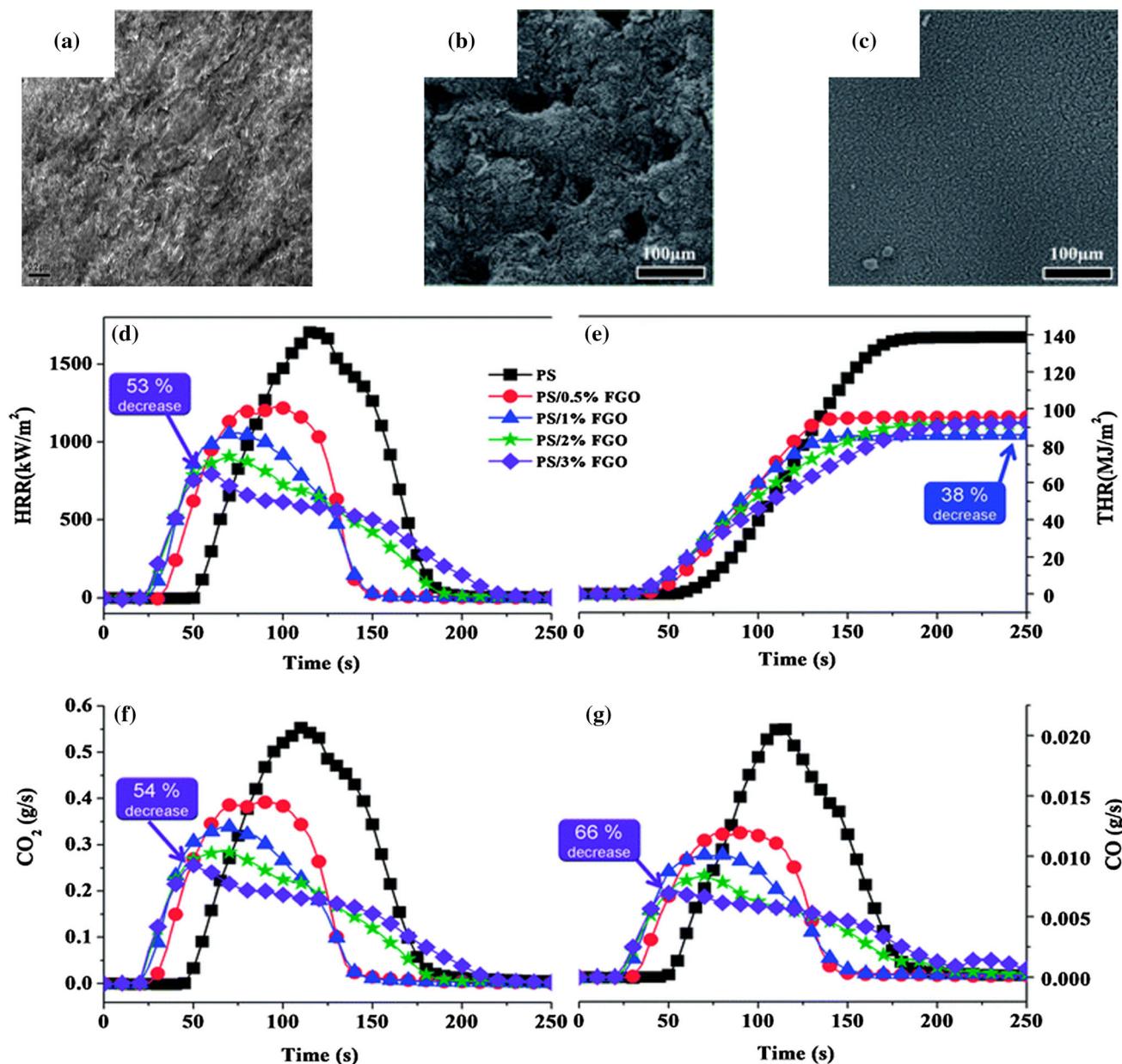


Figure 9 (a) TEM photographs of the ultrathin section of PS/3 % FGO: the FGO exhibits good dispersion and shows no obvious aggregation. (b) and (c) SEM profiles of PS/2 % FGO and PS/3 % FGO for the observations of char: a continuous and compact char is formed on the outer surface of PS/3 % FGO. Cone calorimeter

test results: (d) HRR curves; (e) THR curves; (f) CO₂ yield; and (g) CO yield. Due to the effect of FGO, the HRR, THR, peak CO₂ release rate and peak CO release are decreased by 53, 38, 54 and 66 % as compared with those of pure PS. Reproduced from ref.75 with permission from Royal Society of Chemistry.

The third category of flame retardant graphene-nanocomposite flame retardants refers to conventional-organic flame retardant molecules graphene-nanocomposite flame retardants. They include conventional-organic flame retardants such as phosphorus-containing organic flame retardants [40, 85–87],

phosphorus- and nitrogen-containing organic flame retardants [88–93], and phosphorus- and silicon-containing-organic flame retardants [94, 95]. These organic flame retardants can functionalize graphene by inserting covalently bonded molecules between the layers of graphene (intercalation). Liao et al. [85]

Table 2 Effectiveness of molecule-modified graphene-nanocomposite flame retardants

Reference number	Polymer matrix	Filler	Concentration (wt%)	Heat flow (kW m ⁻²)	Decrease (%)		Increase (%)			LOI
					PHRR	THR	Tensile stress	CY	TTI	
[74]	PP	rGO	2	35	14.4	12.7	17.4	–	–12.5	–
		PMoA-rGO	2		18.9	16.2	23.0	–	–28.1	–
		PMoA-rGO	3		23.0	16.2	22.6	–	–21.9	–
[76]	EP	GO	5	45	24.2	14.0	–	14.2	–	–
		GNS	–		45.5	20.8	–	19.4	–	–
		PDCP-GO	–		43.9	23.7	–	22.4	–	–
[78]	PE	GO	1	35	8.4	–3.3	–	–	–16.6	19.0
		GO	1		8.9	–1.9	–	–	–1.5	19.0
		HGO	3		28.0	2.7	–	–	–6.1	19.5
		HGO	3		28.7	5.6	–	–	–21.2	20.5
[86]	PP	GO	2	35	6.2	–6.7	–	–	–34	–
		MA-GO	–		29.0	2.7	–	–	–34	–
[88]	EVA	rGO	0.5	35	21.4	5.6	–	–	1.8	–
		PPSPB-rGO	–		33.6	16.9	–	–	22.8	–
		rGO	1		31.4	14.5	–	–	7.0	–
		PPSPB-rGO	–		46.2	21.8	–	–	31.6	–
[89]	PP	FRs	20	35	48.3	19.7	–	–	27.8	–
		FRs/GO	18/2		60.6	19.2	–	–	18.5	–
		FRs-FGO	20		66.9	22.4	–	–	22.2	–
[91]	EP	PPA	8	35	35.1	45.8	–14.2	–	–	29.0
		PPA-g-GNS	–		41.3	49.6	41.8	–	–	30.5
[94]	EP	GON	10	–	–	–	42.3 ^a	–	26	–
		DPPES	–	–	–	–	–4.0 ^a	–	26	–
		DPPES-GON	–	–	–	–	71.8 ^a	–	36	–
[95]	EP	FRs(DOPO)	5	35	–	–	–	–	–	28.5
		FRs(DOPO)-rGO	–		35.0	–	–	–	–	29.5

NOTE: The date of PHRR, THR and CY are obtained from cone calorimeter test at the heat flow listed in table

A synergic effect can be observed between the second phase and graphene or GO

CY refers to Char yield; IFR refers to intumescent flame retardant; XLPE refers to PMoA refers to phosphomolybdic acid; PDCP refers to distilled phenyl dichlorophosphate; FRs-FGO refers to 4,4-diaminodiphenyl methane and spirocyclic pentaerythritol bisphosphonate disphosphoryl chloride functioned on GN; DPPES refers to 2-(diphenylphosphino)ethyltriethoxy silane; PBTP refers to phenyl-bis-(triethoxysilylpropyl) phosphamide

^a Refers to the data obtained from TGA testing

The decrease and increase percentages (%) in relevant properties are based on the untreated polymeric matrix

prepared 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide-reduced GO (DOPO-rGO) by allowing epoxy-ring groups to react with reduced graphene; they found that the phosphorus and GO layer structures of DOPO-rGO cause a continuous and stable protective char layer that acts as a thermal insulator and mass transport barrier, thereby increasing char yield and LOI. Huang et al. [88] grafted the intumescent flame retardant poly(piperazine spirocyclic pentaerythritol bisphosphonate

onto the surface of graphene (PPSPB-GO) and incorporated it into ethylene vinyl acetate copolymer (EVA). With the assistance of TEM observations, they found that most GO in the grafted PPSPB composite exhibits an exfoliated structure, but most rGO sheets used alone are agglomerated, which indicates that PPSPB-rGO has good dispersion in the EVA matrix. Thermal analysis shows that 1 % addition of PPSPB-rGO to EVA promotes the thermal stability obviously. The decomposition temperature of the

composite is about 20 °C higher than that of pure EVA. Also, 1 % PPSPB-rGO/EVA composites have a lower PHRR (about 56 % reduction) and THR (about 24 % reduction) compared with pure EVA, and the TTI also rises from 57 to 75 s. Furthermore, the yields of toxic gas are much lower than that of virgin EVA. Wang et al. [91] functionalized graphene with polyphosphamide (PPA) and obtained a flame retardant that can be incorporated into epoxy resin. Table 2 summarizes the effectiveness of flame retardant molecules graphene-nanocomposite flame retardants, where a synergic effect is observed between the secondary phase and graphene or GO, and incorporation of various fillers increases the tensile strength of the EP matrices by about 42 %. Besides, the addition of 8 % PPA-g-GNS reduces the failure strength of EP, due to the absence of graphene, leading to weak interaction between PPA-g-GNS and EP matrix. Furthermore, the LOI value of the EP composites rises to 30.5 upon the addition of 8 % PPA-g-GNS, and the PHRR values are reduced by about 42 % compared to that of pure EP. In general, the enhanced fire resistant properties of the polymer composites can be attributed to the formation of the stable, successive and compact char layers promoted by PPA and graphene.

Generally, a synergistic flame retardant mechanism covering the condensed phase mechanism and the gas phase mechanism is cited to explain the prominent flame retardant performance of graphene-doped polymer matrices composites (Fig. 4). For example, P-containing molecules can be converted into phosphoric acid, facilitating the dehydration and carbonization of polymers during combustion. Also, the phosphate groups in the phosphorus-rich residues combine with graphene in the condensed phase, increasing char yield and providing a continuous and compact char layer with an overlapping network structure that hinders heat and mass transfer. Free radicals, such as PO_\cdot , PO_2^\cdot and HPO_\cdot that are converted from phosphate groups, can catch $\text{H}\cdot$ and $\text{HO}\cdot$ free radicals formed in the combustion of polymer matrices in the gas phase and interrupt the decomposition reaction, improving the thermal stability and fire retardancy of polymers [71, 78, 85, 89, 91, 95–97]. N-containing molecules decomposed at low temperature accompanying with the release of non-flammable gases, such as nitrogen and water vapour that can absorb heat from polymeric matrices and cool down the matrices. These non-flammable gases also

decrease the concentration of oxygen around the fire, and they can act as gas phase barriers to enhance the flame retardant performance of polymer [98, 99]. Si-containing flame retardants can form stable -Si-C- and -Si-O-C- bonds with graphene and polymer matrices to form a reticular structure during combustion. This increases the melt viscosity, restrains the molten drops and prevents the fire from spreading. The final decomposition products, silicate and silicon dioxide, are absorbed on the surface of the char and reinforce the thermal stability of the char layer, so as a result, the thermal stability and flame retardant properties of the composite are enhanced [67, 68, 94, 100, 101]. As expected, the combination of P-containing, N-containing, Si-containing and P-N-containing or Si-P-containing molecules with graphene may result in a synergic action in the condensed and gas phases, thereby improving the thermal stability and fire retardancy of composites (see Table 2).

Inorganic-nanomaterials graphene-based composite flame retardants

Nanotechnology is one of the most important technologies of the 21st century and has brought significant innovations in many fields. When materials have a size that is decreased to nanoscale, they usually exhibit unique physical and chemical characteristics compared to bulk counterparts, such as the small size effect, the surface and the boundary effect. Nanotechnology also provides new strategies and methods for designing and manufacturing high-performance graphene-based nanocomposites. Nanomaterials, like nanoscale graphene, exhibit a high aspect ratio and can effectively reinforce polymers even at low loading levels. Moreover, inorganic nanomaterials can act as barriers to improve the thermal stability of polymeric composites, broadening the application scope of polymers [102, 103]. Because inorganic nanomaterials are commonly believed to be eco-friendly, developing inorganic-nanomaterials-doped-composite flame retardants is of particular significance. Furthermore, inorganic nanomaterials, in combination with graphene, will enable the reduction of the overall filler content, leading to improved flame retardancy as well as more favourable mechanical and/or processing properties [104, 105]. In addition, inorganic

Table 3 Effectiveness of inorganic-nanomaterials graphene-nanocomposite flame retardants

Reference number	Polymeric matrix	Filler	Concentration (%)	Heat flow (kW m ⁻²)	Decrease (%)				Increase (%)	
					PHRR	THR	TSR	COP	CY	TTI
[108]	EP	GNS	2	35	30.1	17.0	13.3	—	−33.3	—
		Ce-MnO ₂			44.3	25.6	27.7	—	400.0	—
		Ce-MnO ₂ /GNS			53.7	35.5	41.2	—	466.7	—
[115]	PP	Graphene	—	35	16.2	−24.1	−52.1	−17.3	12.5	2.6
		NiO/graphene			27.3	4.2	−3.1	−12.6	50.0	−7.9
		NiCe _x O _y /graphene			37.4	17.3	36.3	49.5	425	−18.4
[119]	PMMA	RGO	2	35	16.8	—	—	79.1	133.3	—
		NiAl-LDH			13.2	—	—	74.7	300.0	—
		RGO-LDH			25.1	—	—	98.8	516.7	—
[122]	EP	GNS	2	35	31.0	17.0	21.5	—	—	—
		ZnS			26.6	8.1	13.8	—	—	—
		ZnS/GNS			46.8	27.5	62.8	—	—	—
[124]	EP	GNS	2	35	28.4	19.5	23.4	—	—	—
		MoS ₂			20.2	13.1	15.8	—	—	—
		MoS ₂ /GNS			45.8	25.3	30.5	—	—	—
[135]	EP	MWCNT	(2.5) ^a	35	24.7	29.1	26.0	—	—	2.2
		MWCNT/GNP			32.8	36.9	38.1	—	—	4.4
		MWCNT/GNP			34.9	40.2	43.2	—	—	0
[140]	PF	GO	0.5	35	5.8	−12.9	—	—	3.1 ^b	35.3
		SiO ₂			26.4	32.3	—	—	5.1 ^b	29.4
		SiO ₂ /GO			5.4	0	—	—	5.3 ^b	58.8
		SiO ₂ /GO			21.4	6.5	—	—	5.5 ^b	58.8
[145]	PVA	Graphene	2	35	44.0	19.0	—	—	—	61
		Mt			18.7	0	—	—	—	33
		Mt/graphene			49.1	19.0	—	—	—	156
[147]	PA6	GO	—	35	7.4	10.1	16.9	—	—	−10
		HNTs			4.4	5.3	2.1	—	—	10
		HNTs-d-rGO			11.3	20.3	10.8	—	—	−2.7

NOTE: The data of PHRR, THR and CY are obtained from cone calorimeter test at the heat flow listed in table

A synergic effect can be observed between the second phase and graphene or GO

PMMA Refers to poly(methyl methacrylate); MWCNT refers to carbon nanotube; GNP refers to graphene nanoplatelets; Mt refers to montmorillonite; HNTs refers to halloysite nanotubes; COP refers to CO yield

^a Means that the ratio is the content of GNP in hierarchical membrane

^b Refers to the data collected from TGA data; PF refers to phenolic

The decrease and increase percentages (%) in relevant properties are based on the untreated polymeric matrix

nanomaterials may act as secondary components to increase the exfoliation and minimize the agglomeration of graphene and GO, thereby improving the dispersion of graphene and GO in polymer matrices nanocomposites. Table 3 shows that the char yields of composites are much higher than that of pure polymer matrices, which could be due to the synergistic effect that supports and promotes the formation of more stable char with continuous and compact physical barrier. Due to the formation of the physical barrier, the PHRR, THR and TSR decrease, which

means that the fire security of the composites is enhanced.

Many studies of inorganic-nanomaterials graphene composite flame retardants have been published in recent years. These studies mainly focus on metals or metal derivative-based nanomaterials, carbon-based nanomaterials and silica-based nanomaterials.

Metals or metal derivative-based nanomaterials include metal oxides, metal hydroxides and other metallic compounds, such as Co₃O₄ [106], SnO₂ [107], Ce-MnO₂ [108], TiO₂ [109, 110], CuO [111], NiO [106],

Sb_2O_3 [112], Fe_3O_4 [113], $\text{Fe}@\text{Fe}_2\text{O}_3$ [114], NiCe_xO_y [115], ZrO_2 [116], Ni(OH)_2 [116], MnCo_2O_4 [38], FeOOH [117], AlOOH [118], NiAl-LDH [119] (LDH represents to layered double hydroxide), NiFe-LDH [120], Co(OH)_2 [121], ZnS [122], ZnCO_3 [123], MoS_2 [124], $\text{Al}(\text{H}_2\text{PO}_2)_3$ [125], ferrocene (Fc) [126], zirconium organophosphate [127], nano- Sb_2O_3 [128] and zinc hydroxystannate [129, 130]. They can also be classified into zero-dimensional nanoparticles, one-dimensional nanowires/nanorods/nanotubes and two-dimensional nanoplates/nanobelts. Usually, nanometals and/or their derivatives in polymeric matrices also act as smoke-suppression materials [107, 131]. Table 3 shows that these materials decrease the TSR and COP significantly. The nanometals and/or their derivatives also act as char-forming catalysts as well as the support of char, thereby promoting the formation of residual inorganic carbonaceous protection layers with high stability. Furthermore, at the same temperature range or below the temperature at which polymer is decomposed, they can remove heat by releasing water vapour and can decrease the concentration of both combustible gases and oxygen.

Zero-dimensional nanoparticles, such as Co_3O_4 , SnO_2 and TiO_2 , can be deposited on the surface of graphene, and their aggregation can be prevented and their shape can be controlled by *in situ* growth. The studies on resultant graphene–inorganic nanocomposites are reviewed elsewhere [132, 133]. Naturally, if the adsorption of graphene is enhanced and the contact area of metal derivatives is increased, the catalytic effect of metal derivatives will be enhanced, thereby promoting the formation of residue char, inhibiting the release of smoke and improving the flame retardant performance of the composite flame retardants. Jiang et al. [108] fabricated Ce-doped MnO_2 graphene hybrid sheets by utilizing an electrostatic interaction between Ce-doped MnO_2 and GNS. They found that Ce-doped MnO_2 with different sizes are attached to the surface of graphene, and the graphene sheets retain a wrinkle shape in the EP matrices (see Fig. 10). With a 2 % addition of GNS, the PHRR of GNS-EP is decreased by about 30.0 %, and the incorporation of Ce- MnO_2 -GNS to EP reduces the PHRR value by about 53.7 %. They also found that Ce- MnO_2 -GNS has remarkable smoke-suppression performance and can reduce the TSR by about 41.1 %. They attribute the good flame retardant performance of Ce- MnO_2 -GNS to the

synergistic effect between GNS and Ce- MnO_2 . Such a synergistic effect can promote the formation of a compact residual char layer in the EP-based nanocomposite; Ce- MnO_2 acts as a char catalyst and reduces the chain length of pyrolysis product that can easily catalyse carbonization. GNS can extend the contact time of degraded products with metal oxide catalysts by absorption and can act as a platform for micro-char during combustion. One-dimensional nanowires/nanorods/nanotubes, such as Co(OH)_2 and Ni(OH)_2 , have good compatibility and dispersion in polymeric matrices. They can form three-dimensional nano-hybrid networks that enhance the interaction between flame retardant fillers and polymeric matrices. Hong et al. [121], using three kinds of metal hydroxide nanorods (MHR) combined with GNS as the fillers, prepared acrylonitrile–butadiene–styrene (ABS) copolymer composites and studied their mechanical, thermal and flame retardant effects. They found that the as-prepared ABS copolymer composites exhibit good mechanical, thermal and flame retardant properties, which is attributed to the good dispersion of the fillers in the polymeric matrices and the formation of a 3D network structure, and the catalytic action of MHR. Two-dimensional nanoplates/nanobelts, such as LDH, MoS_2 , and AlOOH, can be inserted into the layers of graphene to endow graphene with high exfoliation, thereby improving the barrier effect of the graphene. Wang et al. [120] using NiFe-LDH/GNS hybrids (prepared by one-pot *in situ* solvothermal procedure) as the fillers, successfully reduced the fire hazard of epoxy resin-based composites. They found that NiFe-LDH/GNS has a disordered structure whose NiFe-LDH nanosheets lie on the surface of GNS, and the synergism effect of NiFe-LDH and graphene in the gaseous and condensed phases is responsible for the great improvement in the flame retardant performance of the EP-based composite.

Carbon-based nanomaterials such as carbon nanotube [134, 135], nanodiamond [136] and C_{60} [137] are generally considered to be eco-friendly materials with remarkable thermal characteristics, mechanical properties and flame retardancy. The use of carbon family materials to enhance the mechanical properties of polymer has been studied for a long time, but few studies are concerned about the effectiveness of carbon materials as a barrier in promoting the thermal stability of polymer and in inhibiting fire of flame retardants [104, 138, 139]. In fact, for C_{60} , not only act

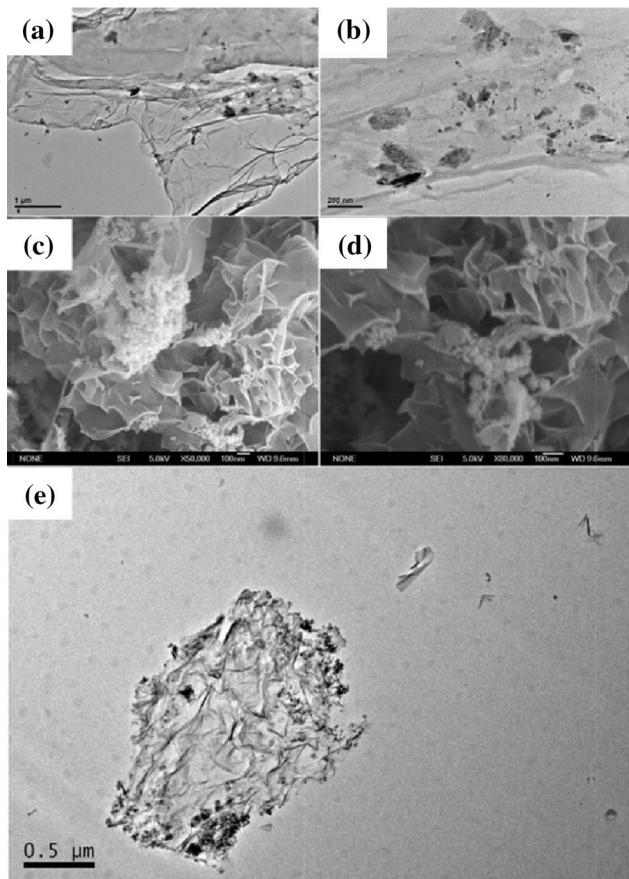
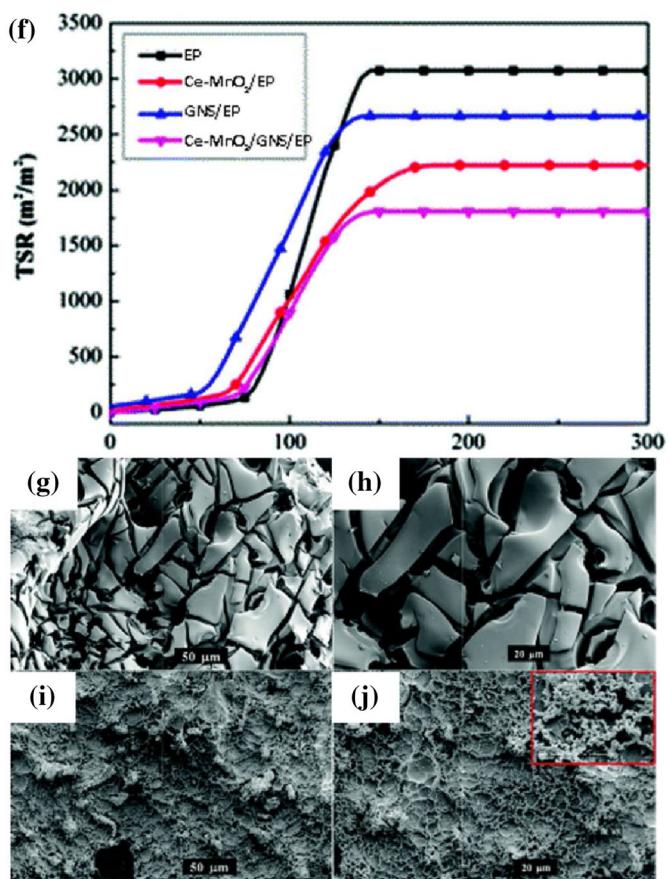


Figure 10 TEM and SEM images of Ce-MnO₂-GNS hybrid (a–d), TEM image of Ce-MnO₂-GNS-EP ultrathin section (e), TSR curves for EP and its composites obtained from cone calorimetry

as the fortifiers for graphene and barriers but also have a free radical trapping effect in polymeric matrices. Song et al. [137] incorporated C₆₀ into graphene via three-step reactions, and they found that the as-prepared C₆₀@graphene exhibits uniform dispersion in PP matrices while the C₆₀ on the surface of GNs can prevent their aggregation. As a result, the interaction of nanofiller and polymer matrices is effectively improved and the mechanical properties of the PP-based composite are enhanced, thanks to the free radical-trapping effect of C₆₀ and the thermal barrier effect of graphene layers.

Silica-based materials, such as silica nanospheres [140], silica [141, 142], silicon nanoparticle [143] and silica-containing mineral nanomaterials (such as sepiolite nanorods [144], montmorillonite [145, 146], halloysite nanotubes [147], and tubular clay [148]), can be combined with silicates. Most of them exhibit a layer structure for the silica-containing mineral nanomaterials. In the presence of silicates, a



test (f) and SEM images of the surface morphology of the residue of EP (g, i) and Ce-MnO₂-GNS-EP (h, j). Reproduced from ref.108 with permission from Royal Society of Chemistry.

multilayered carbonaceous-silicate structure is formed on the surface of composites during combustion. When silica-containing mineral nanomaterials are combined with graphene and used as the flame retardant fillers, their dispersion in and compatibility with polymer matrices is improved, and the silicates lead to resistance to thermo-oxidative decomposition of graphene and promote the formation of a continuous and compact residual superficial char layer during combustion. The resulting residual char layer acts as a strong physical barrier to protect the substrate from heat and oxygen effectively, thereby slowing down the escape of flammable volatiles generated during polymer degradation as well as ameliorating the thermal stability, mechanical performance and flame retardancy. Li et al. [147], using rGO decorated with halloysite nanotubes (HNTs-d-rGO) as the flame retardant filler, prepared a novel PA6-based flame retardant, and they claimed that the reduced PHRR and THR of the nylon-based

composite are attributed to barrier effect of the uniform dispersion and network structure of the filler in the polymeric matrices.

Conclusions and challenges

In conclusion, because graphene and its derivatives have the advantages of being halogen free, high efficiency and rich abundance of raw materials, they are promising of “green” flame retardants. Although there are still many challenges to be met before graphene can be used alone as flame retardant, the use of graphene as adjuvant in combination with a flame retardant is promising. Specifically, inorganic-nano-materials graphene composites flame retardants are of particular significance, because they can be readily fabricated with environmentally benign procedures, such as solution deposition method, sol-gel processing, template method, hydrothermal/solvothermal technique, covalent grafting and non-covalent interactions. Their thermal, mechanical and flame retardant properties can be effectively improved even at low loading with the assistance of the synergetic effects among different components. This is why graphene, as significant adjuvant, in combination with inorganic nanomaterials may be a promising candidate of flame retardant.

However, it still remains a challenge to develop graphene flame retardants with controllable dispersion, lower loading in polymer matrices and superior properties. In this respect, it could be a promising strategy to combine graphene with other inorganic flame retardants. The secondary component can inhibit the aggregation of graphene and exert synergism with graphene, thereby enhancing the interface interaction between graphene and polymer matrices and improving the mechanical properties, thermal stability and flame retardancy of the composite flame retardants. Despite the rapid development of inorganic-nanomaterials graphene composite flame retardants, some issues are still unresolved. Namely, it needs to further study the interaction between inorganic nanomaterials and graphene and the dispersion of inorganic nanomaterial graphene composite flame retardants in polymer matrix, thereby obtaining optimized mechanical and flame retardancy properties. It also needs to reveal the exact mechanism that is responsible for the synergistic flame retardant effect of different components,

thereby increasing the efficiency of inorganic nano-materials as flame retardant fillers.

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Compliance with ethical standards

Conflict of Interest The authors declare that they have no conflict of interest.

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