



Carbon-family materials for flame retardant polymeric materials

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ABSTRACT

As an abundant and attractive element, the emergence of new carbon-based materials brings revolutionary development in material science and technology. Carbon-based materials have spawned considerable interest for fabricating polymer composites/nanocomposites with greatly improved mechanical, thermal, gas barrier, conductivity, and flame retardant performance. In this review, the importance of carbon-based materials and the necessity of fire resistance for polymeric materials are initially introduced. Then, the fundamental flame retardant mechanisms and experimental analytical techniques are described to understand the relationship between structures and flame retardant properties. The main section is dedicated to the preparation and properties of multifunctional polymer composites/nanocomposites with carbon-based materials, with special emphasis on the flame retardant properties of these materials. A wide variety of carbon-based materials are discussed for use in flame retardant polymer nanocomposite, including graphite, graphene, carbon nanotubes, fullerenes as well as some new emerging carbon forms (carbon nitride, carbon aerogels, etc). Finally, a brief outlook at the developments in carbon-based materials for flame retardant polymeric composites is given by discussing the major progress, opportunities, and challenges.

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Contents

1. Introduction.....	24
2. Flame retardant mechanism.....	25
2.1. Condensed phase mechanisms.....	25
2.2. Gas-phase mechanisms.....	25
2.3. Characterization methods.....	25
2.3.1. Limiting oxygen index (LOI).....	25
2.3.2. UL-94 V.....	26
2.3.3. Cone calorimetry	26
2.3.4. X-ray photoelectron spectroscopy (XPS).....	26
2.3.5. Raman spectroscopy.....	26
3. Carbon-based material/polymer composites.....	26
3.1. Fullerene.....	26
3.2. Carbon nanotubes	27
3.2.1. Use of pristine CNTs	27
3.2.2. Functionalized CNTs	29
3.2.3. Combination of CNTs with other flame retardants	31
3.2.4. Flame retardant action of CNTs	32
3.3. Graphene	32
3.3.1. Utilization of pristine graphene	33
3.3.2. Organic flame retardants functionalized graphene.....	33

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3.3.3.	Inorganic/graphene hybrids.....	34
3.3.4.	Synergism between graphene and other flame retardants	36
3.3.5.	Flame retardant mechanism of graphene	37
3.4.	Graphite	37
3.4.1.	Utilization of EG or modified EG	39
3.4.2.	Synergism between EG and other flame retardants	40
3.4.3.	Flame retardant mechanism of expandable graphite	40
3.5.	Others.....	40
3.5.1.	Carbon black	40
3.5.2.	Carbon nitride	41
3.5.3.	Carbon aerogels.....	41
4.	Summary and perspectives	42
	Acknowledgements.....	43
	References	43

Nomenclature

Polymers and other organic compounds

ABS	Acrylonitrile–butadiene–styrene copolymer
APTES	3-aminopropyltriethoxysilane
BDP	Bisphenol A bis(diphenyl phosphate)
BPEA	1,2-Bis(5,5-dimethyl-1,3,2-dioxyphosphacyclohexane phosphoryl amide) ethane
DMMP	Dimethyl methylphosphonate
DOPO	9, 10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide
DPPES	2-(Diphenylphosphino) ethyltriethoxy silane
EVA	Ethylene-vinyl-acetate copolymer
HDPE	High density polyethylene
LDPE	Low density polyethylene
PA-6	Polyamide 6
PAA	Poly(acrylic acid)
PAH	Polycyclic aromatic hydrocarbon
PBS	Polybutylene succinate
PBT	Polybutylene terephthalate
PC	Polycarbonate
PDBPP	Poly(4,4-diaminodiphenylmethane-O-bicyclicpentaerythritol phosphate-phosphate)
PE	Polyethylene
PEEK	Polyetheretherketone
PEI	Polyethylenimine
PET	Polyethylene terephthalate
PLA	Polylactide
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PPA	Polyphosphamide
PPSPB	Poly(piperazine spirocyclic pentaerythritol bisphosphonate)
PS	Polystyrene
PU	Polyurethane
PUF	Polyurethane foam
PVA	Poly(vinyl alcohol)
PVC	Poly(vinyl chloride)
PVDF	Polyvinylidene fluoride
SEBS	Styrene–ethylene–butylene–styrene
SPF	Semi-rigid polyurethane foam
TPU	Thermoplastic polyurethane
UPR	Unsaturated polyester resin
WF/ABS	Wood flour/acrylonitrile–butadiene–styrene
WF/PP	Wood flour/polypropylene

WPU	Waterborne polyurethane
XLPE	Cross-linked polyethylene
<i>Fillers</i>	
APP	Ammonium polyphosphate
ATH	Alumina trihydrate
CBP	Carbon black particle
CNF	Carbon nanofiber
CNT	Carbon nanotube
EG	Expandable graphite
GO	Graphene oxide
HPCP	Hexa-phenoxy-cyclotriphosphazene
IFR	Intumescent flame retardant
LDH	Layered double hydroxide
MA	Melamine
MCAPP	Microencapsulated ammonium polyphosphate
MMT	Montmorillonite
MPP	Melamine polyphosphate
MWNT	Multi-walled carbon nanotube
PER	Pentaerythritol
POSS	Polyhedral oligomeric silsequioxane
SEP	Sepiolite nanorods
SWNT	Single-walled carbon nanotube

Characterization technique

FTIR	Fourier transformed infrared spectrometry
LOI	Limiting oxygen index
MCC	Micro-scale combustion calorimetry
Pyrolysis-GC-MS	Pyrolysis-gas chromatography-mass spectrometer
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Testing parameter

AMLR	Average mass loss rate
MLR	Mass loss rate
PHRR	Peak heat release rate
PMLR	Peak mass loss rate
SPR	Smoke production rate
THR	Total heat release
T _{max}	Temperature at maximum mass loss determined by DTG

T _{onset}	Temperature at 5% mass loss determined by TGA
TSP	Total smoke production
TSR	Total smoke release
TTI	Time to ignition

1. Introduction

Carbon-based materials comprise an attractive and fascinating family, including the naturally abundant and cost-effective graphite, and also the most expensive diamond. Whenever a new member is discovered in this family, a revolutionary development will be made in material science and technology, such as fullerene in 1985 [1], carbon nanotubes (CNTs) in 1991 [2] and graphene in 2004 [3]. Up to now, carbon-based materials include carbon black, graphite, graphene, CNT, and fullerene. These materials are not isolated from each other, but in close relationship. For example, graphene, the latest member in this family, is an atomically thick, two-dimensional (2-D) sheet (Fig. 1), regarded as the building block of all other graphitic carbon allotropes with different dimensionality [4]: 3-D graphite is made of graphene sheets stacked on top of each other with a spacing distance of 3.37 Å; 1-D CNT may be made by rolling graphene sheets; 0-D fullerenes (buckyballs) may be envisioned to be made by wrapping a part of graphene

sheet (0-D refers to the lack of translational symmetry in any dimension). Due to their extraordinary intrinsic properties and ability to be dispersed in various polymer matrices, carbon-based materials have been widely used in fabricating polymer composites/nanocomposites in order to improve the mechanical, thermal, gas barrier, conductivity, and flame retardant performances.

The utilization of synthetic polymeric materials provides numerous advantages to society in everyday life. However, a major problem arises since most of the synthetic polymers are organic and thus highly flammable. Hence, imparting fire resistance to polymeric materials has become an important and active issue in both scientific and industrial communities. For traditional flame retardant additives, a relatively high loading is usually needed to meet flame retardancy demands, that can lead to deteriorated mechanical properties. The arising of carbon-based materials provides an alternative solution to flame retardant polymer materials in the context of nanotechnology. The use of expandable graphite as a flame retardant additive for various polymeric matrices has been reported for several decades. Recently, carbon-based nanoparticles, particularly CNT and graphene, have aroused a great deal of interest due to their high flame retardant efficiency, that have opened up a new promising way to prepare multifunctional flame retardant polymeric materials.

This review article considers the most recent results regarding the use of carbon-based materials in the development of multifunctional flame retardant polymer (nano)composites. Understanding

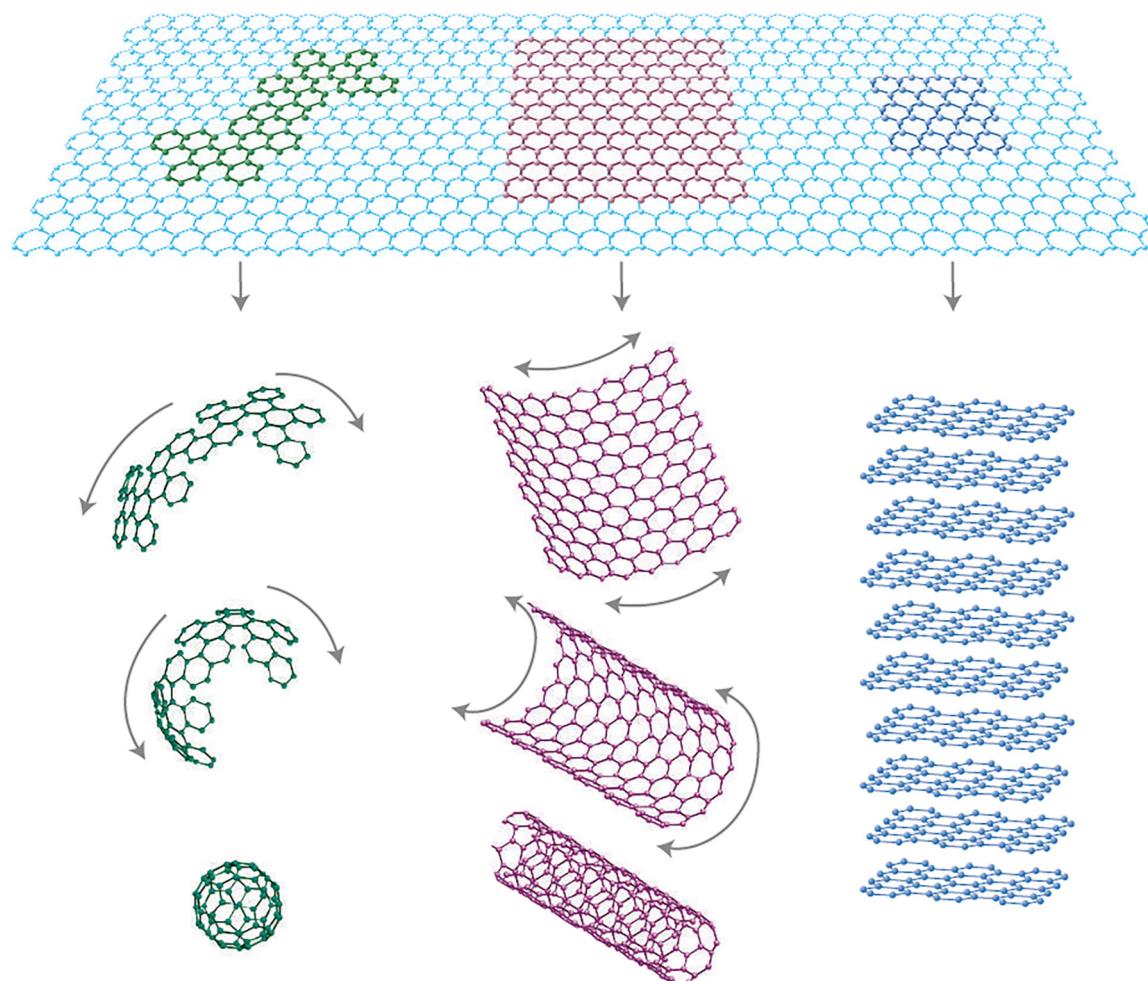


Fig. 1. Graphene, the building block of all graphitic forms, can be wrapped up into 0-D buckyballs, rolled into 1-D nanotubes, or stacked into 3-D graphite. [4], Copyright 2007.

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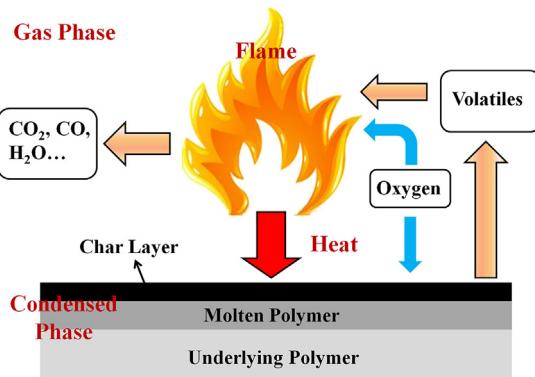


Fig. 2. Illustration of model for flame retardant actions.

the flame retardant mechanism is crucial to optimize the design of the resultant polymer (nano)composites. The flammability characteristics of the resultant polymer (nano)composites is the primary area of interest, while a number of other properties and potential applications are important including mechanical properties, thermal stability, electrical/electronic properties, and barrier properties. Finally, we give a brief comment on opportunities and challenges for future growth of this promising class of polymer (nano)composites.

2. Flame retardant mechanism

As it is well known, combustion is a complex physical and chemical process, and thereby several mechanistic principles take action simultaneously and consequently it is difficult to identify one dominant mechanism. Generally, the gas-phase and the condensed-phase actions have long been regarded as the primary effective mechanism of flame retardancy. A model for flame retardant mechanisms has been illustrated in Fig. 2. Several zones can therefore be identified as flame zone, char layer, molten polymer and underlying polymer. In the flame zone, the volatiles from polymer degradation react with oxygen in the air accompanying with generation of a variety of radicals and heat release. The char layer is the critical zone in the polymer combustion, because it controls mass and heat transfers between gas and condensed phase. In the molten polymer, also called the thermal decomposition zone, the decomposition volatiles firstly generate in this zone and afterwards migrate towards the flame zone through the microporous char layer. The underlying polymer zone is in direct contact with the molten polymer zone, but still remains intact. The flame zone is assigned to gas phase, while the other zones belong to condensed phase. If a flame retardant acts in the gas phase by radical absorption to interrupt combustion processes, it can be called gas-phase mechanism. In contrast, the condensed-phase mechanism involves that a flame retardant functions in the condensed phase through promoting char formation on the surface, that serves as a barrier to inhibit flammable volatiles from diffusing to the flame and to shield the polymer from heat and air. This section attempts to shortly review some of the principles, mechanisms and modes of action of flame retardants [5,6].

2.1. Condensed phase mechanisms

The incorporation of flame retardant additives functions in the condensed phase by formation of a protective char layer. Firstly, the increased char yield means that less material is actually burned. Secondly, the formation of char is usually accompanied by water vapor release, that could dilute the flammable volatiles. Moreover, the char layer with a low thermal conductivity could provide a

shield that suppresses the heat transfer from the heat source to the underlying polymer material. Finally, the presence of the char layer slows down the degradation rate of polymer through re-emitting most of the incident radiation back into the gas phase and reduces the “fuel flow” able to feed the flame during combustion (see Fig. 2). A typical example is the principle of phosphorus-containing additives that lead to formation of an expandable carbonaceous protective char layer. Their degradation leads to thermally stable pyro- or polyphosphoric species that catalyze polymers to form a protective barrier. A similar mechanism can be observed using boric acid based additives, inorganic borates or silicon-containing compounds [7]. Besides the char yield, the char quality as a mass- and heat-transfer barrier is also important. The char quality is affected by the graphitic carbon content, the thermal oxidative resistance and the morphological features. The carbon-based materials are found effective as “carbonifics” (char formers) in flame retardant polymer systems. The addition of carbon-based materials not only improves the char yield [8], but also enhances the compactness of the char surface and the graphitic carbon content [9].

2.2. Gas-phase mechanisms

The gas-phase activity of the flame retardants involves their interference in the combustion reaction of the polymer volatile pyrolysis products. The propagation of the volatiles oxidation (combustion) depends on pyrolysis species capability of reacting with atmospheric oxygen by the branching reaction (Eqs. (1) and (2)) [5]:



In order to slow down or stop the combustion, it is essential to inhibit the chain branching reactions. The halogen-containing compounds, usually chlorine and bromine, are well known for their inhibiting effects via the gas-phase mechanism [6]. In the gas-phase mechanism, the incorporation of halogen-containing additives preferentially releases specific radicals (e.g. Cl[•] and Br[•]) in the gas phase, that can react with highly reactive species (such as H[•] and OH[•]) to form less reactive halogen atoms. Thus, the radical reactions of the combustion process are interrupted. The exothermic processes that occur in the flame are hindered, the burning system cools, heat feedback to the polymer is reduced, pyrolysis slows and the feed of flammable gases to the flame is reduced and eventually completely suppressed.

2.3. Characterization methods

Flame retardant processes can be investigated by identifying pyrolysis species in gas phase or determination of the morphology, elemental composition and chemical structure of char produced in condensed phase. Numerous micro- or macro-scale characterization methods have been developed for clarifying the fire retardant processes. In this section, only the most commonly used laboratory test methods will be discussed.

2.3.1. Limiting oxygen index (LOI)

The LOI value is defined as the minimum oxygen concentration in the flowing mixture of oxygen/nitrogen that either maintains flame combustion of the sample for 3 min or consumes a length of 5 cm of the sample, as expressed in Eq. (3). According to ISO 4589 standard, the sample with the specimens of 80 mm × 10 mm × 4 mm is placed vertically at the center of a glass chimney and the top of the sample is ignited with a burner. The LOI test is considered to be one of the most important screening and quality control methods in research and development of flame

Table 1
Classification of materials for the UL94 Vertical burning test.

Classification	Requirements
UL-94 V0	t_1 and t_2 less than 10 s for each specimen $t_1 + t_2$ less than 50 s for the five specimens $t_2 + t_3$ less than 30 s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL-94 V1	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No afterflame or afterglow up to the holding clamp No burning drops
UL-94 V2	t_1 and t_2 less than 30 s for each specimen $t_1 + t_2$ less than 250 s for the five specimens $t_2 + t_3$ less than 60 s for each specimen No afterflame or afterglow up to the holding clamp Burning drops allowed

retarding polymer industry because of the inexpensive instrument and the relatively small sample size required. However, this test method is not suitable for evaluating real scale fire performance of a material, because the heat input is low and the simulated oxygen concentration is high.

$$\text{LOI} = \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \times 100\% \quad (3)$$

2.3.2. UL-94 V

The set of UL-94 tests has been adopted by Underwriters Laboratories as flammability tests of plastics for parts in devices and appliances. Among UL-94 tests, the UL94 Vertical test is the most commonly used method for determining the ignitability and flame-spread of plastic materials. The burner is controlled to produce a blue flame with a height of 20 mm and a power of 50 W. The distance between the top of the burner and the bottom of the specimen is kept at 10 mm. The bottom of the specimen is exposed to the flame for 10 s and then removed. The time required for the flame to extinguish is noted as the afterflame time t_1 . After extinction, the bottom of the specimen is re-exposed to the flame for another 10 s. The time required for the flame to extinguish is noted as the afterflame time t_2 , and the time required for the fire glow to disappear is noted as the afterglow time t_3 . According to the IEC 60695-11-10 standard, five parallels for each sample must be tested. The sample is classified as V0, V1 or V2 according to the criteria listed in Table 1.

2.3.3. Cone calorimetry

Cone calorimetry is one of the most effective bench-scale tests for measuring the fire behaviors of polymeric materials. The cone calorimetry test is subject to an international standard (ISO 5660). The sample is exposed to a conical radiant electrical heater, and the combustion is triggered by an electric spark. The heat release rate (HRR) is calculated by measuring the gas flow and oxygen concentration. The value of the peak heat release rate (PHRR) is regarded as one of the most important parameters for assessing the fire properties of materials. The value of total heat released (THR) is obtained from integration of the HRR versus time curve. In addition, the cone calorimetry test also enables characterization of the time to ignition (TTI), time to flameout (TOF), effective heat of combustion (EHC), mass loss during combustion, production of CO and CO₂, and total smoke released (TSR). Undoubtedly, the cone calorimetry test provides more detailed fire characteristics, that is a powerful tool to simulate flammability of materials in real-world fire conditions.

2.3.4. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is widely employed to qualitatively and quantitatively detect the chemical components of chars. XPS can identify an element in different chemical environ-

ments. For example, C in the form of C—C, C—O, C=O and C—P shows different binding energy in the XPS spectra. Therefore, it is very useful in providing a basis for the postulation of reactions that occur in the condensed phase. In the case of a mixture of melamine phosphate and a cyclic phosphonate in EVA, it has been found from the XPS results that the char is composed of phosphorus acids with P—NH bonds, that may have contributed to rapid charring [10]. Furthermore, the content of C—H and C—C in aliphatic and aromatic species, C—O (ether and/or hydroxyl group) and C=O, respectively, can be determined by XPS. The ratio of C_{ox}/C_a (C_{ox}: oxidized carbon atoms in C—O and C=O, and C_a: C—H and C—C) can be calculated to study the thermal oxidative resistance of the char [11]. Also, through comparing the content of some particular elements (such as silicon) in the exterior and interior char, the conclusion can be drawn that migration of the element during polymer decomposition may occur to form a ceramic-like layer to improve the char quality [9].

2.3.5. Raman spectroscopy

Raman spectroscopy is a widely used and powerful tool for characterizing carbonaceous materials. Generally, the Raman spectra of a char exhibit two dominant peaks at around 1590 cm⁻¹ and 1360 cm⁻¹. The former is called the G band, corresponding to the stretching vibration mode of E_{2g} symmetry in the aromatic layers of crystalline graphite, while the other is called the D band, arising from the disordered or amorphous carbon atoms [12,13]. The ratio of the integrated intensity of the G band to the D band (I_G/I_D) may be used to evaluate the degree of graphitization of the char. Basically, the higher the ratio of I_G/I_D, the better the quality of the char. The graphitized char formed during thermal degradation is crucial in the control of heat and mass transfer because it is very stable at high temperature.

Based on the discussion aforementioned, no real specific methods have been developed for carbon-based materials as fire retardants, and the fire retardant mechanistic studies for carbon-based materials remain similar to those used in other fire retardants.

3. Carbon-based material/polymer composites

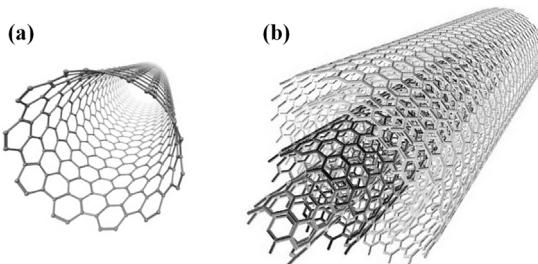
3.1. Fullerene

Fullerene, also known as “buckyball”, is an allotrope of carbon with spheroidally shaped structure. The incorporation of fullerene into a polymer matrix is an important technological accomplishment as it allows combining excellent thermal stability and good physical strength of fullerenes with the well-known advantages of polymers. However, research efforts on fullerene flame retardant polymers are still in an infant stage and only a few investigations are available. For instance, fullerene films were prepared as insulation materials, that can provide the required thermal protection by radiating heat back and, thereby, preventing the underlying substrates from burning [14]. Polypropylene (PP)/fullerene nanocomposites have been prepared via melt compounding, and results from cone calorimetry suggest that the flame retardant property of PP/fullerene nanocomposites is improved with increasing the loading level of fullerene [15]. As shown in Table 2, the PHRR of PP/fullerene nanocomposite was reduced by 46% compared to that of neat PP at the fullerene loading of 2 wt%. The flame retardant action of fullerene is believed to involve two aspects: (1) fullerene is known as a radical sponge for its high reactivity towards radicals [16], and can trap radicals in the condensed phase produced during combustion; (2) fullerene traps PP radicals during the decomposition process to form *in situ* a crosslink network that leads to a remarkable increase in both gel content and complex viscosity

Table 2

Flammability of fullerene-based PP nanocomposites.

Type of filler	Loading (wt%)	Improvement in T _{ign} (s)	Reduction in PHRR (%)	Reference
Fullerene	0.5	13	33	[15]
	1.0	15	41	
	2.0	14	46	
C ₆₀ -d-PDBPP	0.5	4	46	[18]
	1.0	6	52	
	2.0	8	59	
C ₆₀ -d-CNTs	1.0	–	71	[19]

**Fig. 3.** Schematic representation of (a) single-walled and (b) multi-walled carbon nanotubes.

of PP/fullerene nanocomposites, so this structure is called gelled-ball. The formation of gelled-ball structure may be responsible for improvement of the flame retardancy of PP in the condensed phase. Meanwhile, the incorporation of fullerene remarkably improves the thermal stability of PP in air; with 2 wt% fullerene, its T_{onset} and T_{max} were found to be 20 °C and 62 °C higher than those for PP, respectively. The improved thermal stability of the polymer nanocomposites could be attributed to the high radical scavenging efficiency of fullerene [17].

In addition to pristine fullerene, the application of functionalized or hybrid fullerenes in flame retardant polymer materials has been investigated. A dendrimer-like fullerene-decorated oligomeric intumescence flame retardant (C₆₀-d-PDBPP) has been synthesized (**Scheme 1**) [18]. The resulting C₆₀-d-PDBPP/polypropylene (PP) nanocomposites show significantly improved thermal oxidation resistance and reduced flammability compared to those of the base polymer. Furthermore, fullerene-decorated carbon nanotubes (C₆₀-d-CNTs) were fabricated and applied in flame retarding PP [19]. The PHRR observed from cone calorimetry is reduced by nearly 71% by the presence of only 1 wt% of C₆₀-d-CNTs. As summarized in **Table 2**, compared to pristine fullerenes, C₆₀-d-CNTs confer better flame retardancy to PP because of the cooperative interaction between the radical-trapping effect of the fullerene and the barrier effect of the CNT network.

3.2. Carbon nanotubes

Since their discovery in 1991, CNTs have motivated considerable activity by both academic and industrial scientists because of their high aspect ratio, nanoscale dimensions and outstanding mechanical and electrical properties. There are two main categories of CNTs, small diameter (1–2 nm) single-walled carbon nanotubes (SWNTs) and larger-diameter (10–100 nm) multi-walled carbon nanotubes (MWNTs) (**Fig. 3**). Along their main longitudinal axis, CNTs possess an ultra-high tensile strength, despite being flexible [20]. These fascinating physical properties make CNTs ideal candidate materials for fabricating multi-functional polymer nanocomposites.

3.2.1. Use of pristine CNTs

CNTs are a promising alternative to the use of conventional flame retardants. Adding a small amount (usually <5 wt%) of carbon nanotubes has been reported to reduce the fire hazards for a wide range of polymers such as PP [21,22], PE [23], EVA [23], PS [23], PLA [24], PMMA [25–27], PA-6 [28], PC [29], PEEK [30], polybenzoxazine [31] and epoxy resin [32].

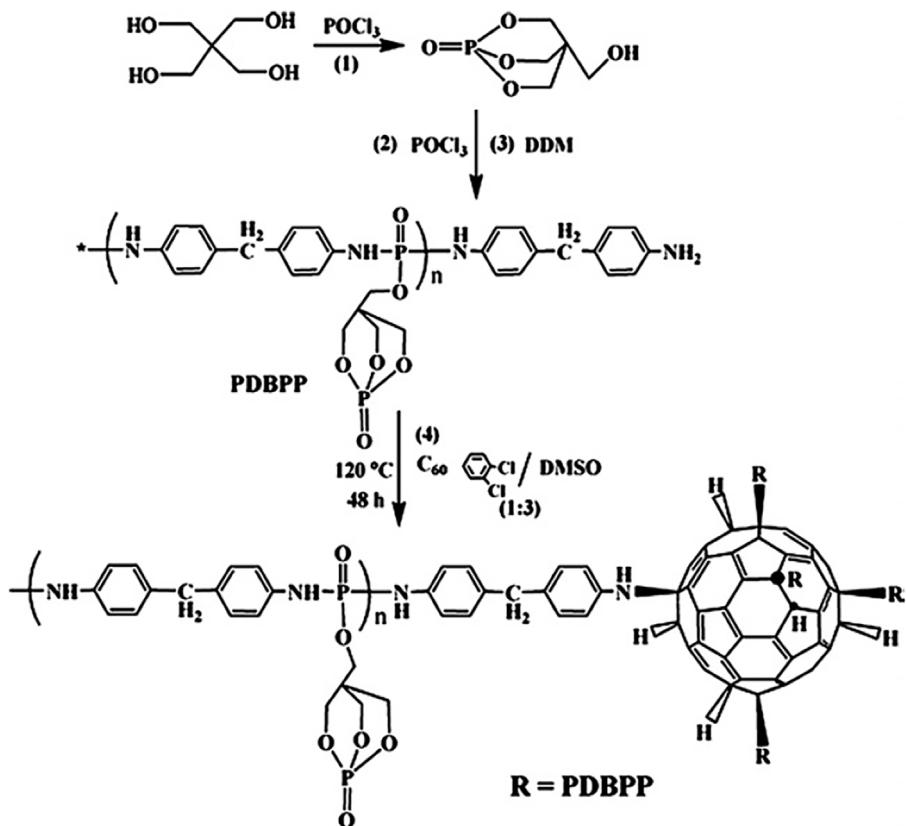
MWNT/PP composites have been prepared by melt blending without using any organic treatment or additional additives [22]. The addition of MWNT imparted high fire retardant efficiency in PP: the PHRR of the composites with 1 vol% MWNT is reduced by about 73% compared to that of PP. The influence of the type and the loading of CNTs on the flammability of PMMA has been investigated [25]. The mass loss rate for each sample tested in the gasification test is plotted in **Fig. 4a**. The mass loss rate of SWNT0.5%/PMMA was the smallest for the five samples, followed by the MWNT0.5%/PMMA. Mass loss rates for both the CNF0.5%/PMMA and the CBP0.5%/PMMA were not significantly different from that of the neat PMMA. The effectiveness of the nanotubes may be attributed to the formation of a network-structured protective layer during burning that is crucial for the significantly reduced mass loss rate, as can be seen from **Fig. 4b**.

The influence of the dispersion state of the CNT in the polymer matrix on the flame retardant properties has also been investigated [33]. It was found that the incorporation of only 0.5 wt% of SWNT uniformly dispersed in PMMA led to a considerable decrease in the PHRR (**Fig. 5a**) in comparison to that for pristine PMMA. In contrast, the flammability of PMMA compositions containing poorly dispersed SWNT proved to be similar to that of unfilled PMMA, without any significant reduction in the PHRR.

The loading of CNTs also affects the flammability of the PMMA nanocomposites [33]. For the PMMA nanocomposites with good CNTs dispersion, the addition of 0.1 wt% of SWNTs leads to a very slight reduction in the PHRR of PMMA, while a 25% reduction is attained by the addition of 0.2 wt% of SWNTs. More than 50% reduction in PHRR is achieved with the incorporation of 0.5 wt% of SWNTs (**Fig. 5b**). These results indicate that a significant reduction in nanocomposite flammability required a sufficient CNT concentration to form a compact and continual char layer on the surface of the degrading polymer. When the SWNTs loading is 1.0 wt%, the resultant PMMA nanocomposite shows a higher PHRR than its counterpart containing 0.5 wt% of SWNTs. The lowest heat release rate is attained for the PMMA nanocomposite containing 0.5 wt% of SWNTs, most likely due to a balance between shielding effects and thermal conductivity [21]. The effect of the average size of MWNT on the flammability of EVA has been studied [34]. The results obtained from cone calorimetry tests showed a notable increase in the time to ignition for EVA composite containing 3 wt% of crushed MWNT, in contrast to that for its counterpart with the equivalent MWNT loading (**Fig. 6**). Interestingly, partial substitution of MWNT by crushed MWNT also caused an increase in the time to ignition (**Fig. 6**). This behavior has been attributed to the chemical reactivity of radical species present at the surface/extremities of crushed MWNTs.

In addition to the suppression of the heat release rate and the mass loss rate during combustion, the incorporation of MWNT also promotes low flame spread rate and an anti-dripping effect for polymer undergoing degradation (**Fig. 7**) [35]. The anti-dripping phenomenon was also observed for PA-6/MWNT nanocomposites [28]. It was reported that the increased melt viscosity of the nanocomposites was responsible for the dripping suppression.

A comparative study of CNTs and other nanofillers (such as MMT and LDH) on the flammability of polymers has been carried out as well [32]. Addition of just 0.0025 mass fraction of highly aligned MWNTs resulted in a 45% reduction in the peak



Scheme 1. Schematic illustration of synthetic route of PDBPP decorating fullerene. [18], Copyright 2009.

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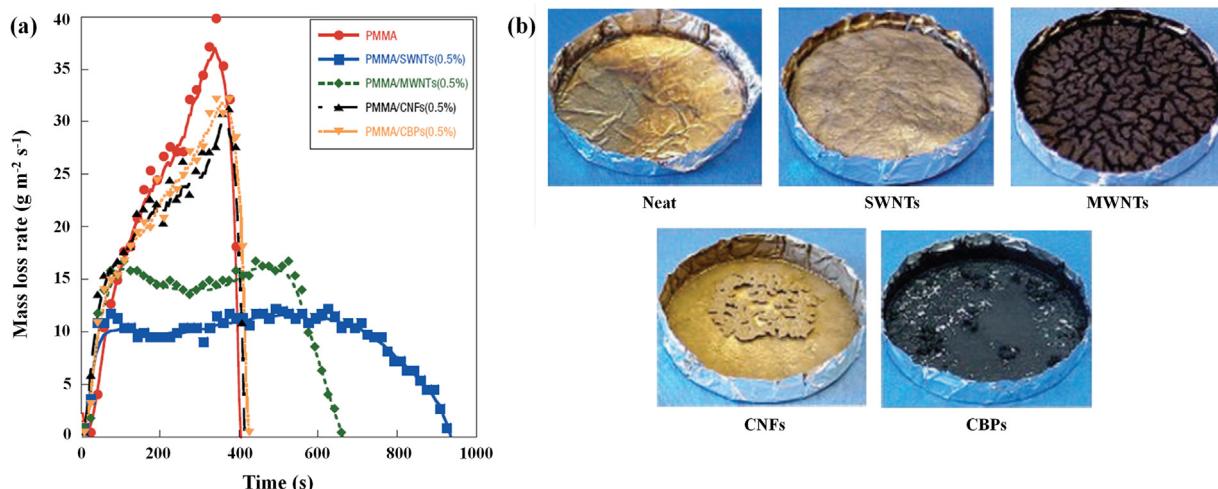


Fig. 4. a) Effects of the nanoparticle type on mass loss rate and (b) Photos of the collected residues. The tests were conducted at an external radiant flux of 50 kW/m^2 in nitrogen. [25], Copyright 2005.

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mass loss rate (PMLR) during the gasification test of MWNT/epoxy composites; reduced PMLR could be also achieved for MMT/epoxy nanocomposites, but required much higher MMT loading [32]. The superior flame retardant performance of MWNT/epoxy composites was probably due to the good char integrity (no visible cracks on the char surface of MWNT/epoxy samples) after combustion, as shown in Fig. 8. These observations are consistent with the results reported elsewhere [23].

Besides improving the fire resistance, the inclusion of CNTs also positively influenced other properties of the resultant

nanocomposites. MWNT/silicone-based foamy nanocomposites were prepared via mechanical blending without any previous functionalization treatment [36]. The LOI of the nanocomposites increased with the MWNT content, attaining the self-extinguishing grade at a low mass fraction of the MWNTs (0.5 wt%). The superior flame retardancy could be ascribed to the improved thermal stability, the high char yield and the reduced mass loss rate observed from TGA experiments (Fig. 9). This improvement in thermal stability can be attributed to that dispersed CNTs may hinder the flux of degradation products, delaying the onset of degradation, while the

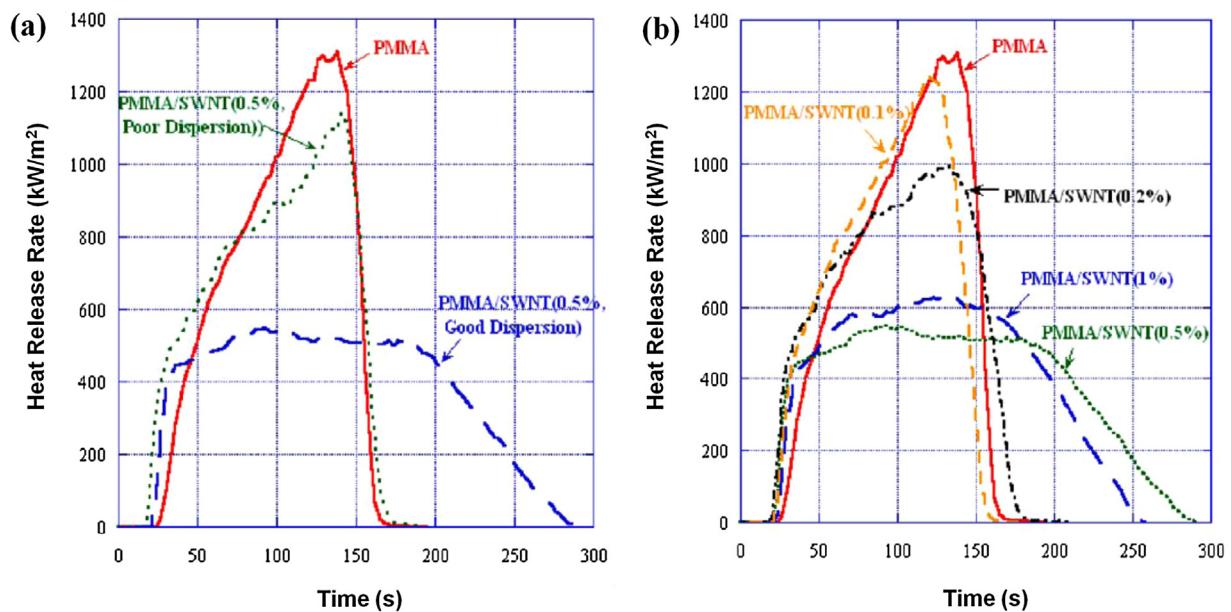


Fig. 5. HRR curves of PMMA containing SWNT: (a) effects of SWNT dispersion and (b) SWNT concentration (50 kW/m²). [33], Copyright 2004. Reproduced with permission from Elsevier Ltd.

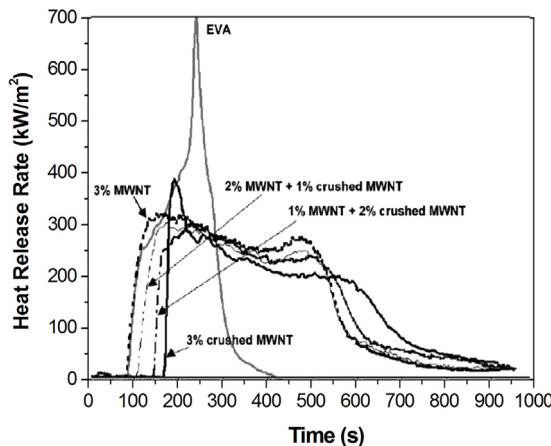


Fig. 6. The effect of the content of crushed MWNTs on the HRR of the EVA composites during the cone calorimetry experiments (35 kW/m²). [6], Copyright 2008.

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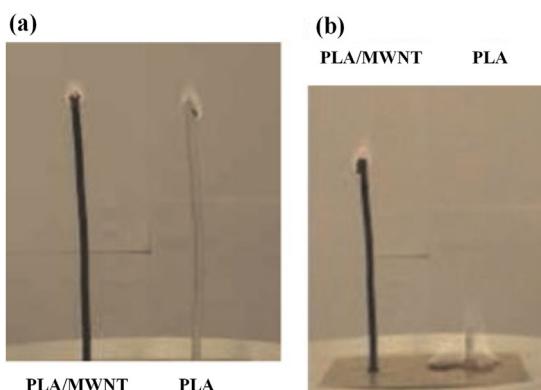


Fig. 7. Flammability test of virgin PLA and PLA/MWNT (a) at the ignition (b) and after 15 s [35], Copyright 2010.

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thermally stable CNT network behaves as a char promoter and thus results in a higher char yield. Multifunctional SWNT/cellulose composite paper was fabricated using simple papermaking techniques [37]. The resulting SWNT/cellulose composite paper showed an electrical conductivity of 3×10^{-2} S cm⁻¹ and a reduced peak heat release rate in cone calorimetry tests. MWNT/polybenzoxazine nanocomposites were prepared by using a solventless method varying the MWNT amount from 0.1 to 1.0 wt% [31]. Rheological and electrical percolation thresholds were obtained for MWNT content lower than 0.1 wt% suggesting that there is good affinity between MWNTs and polybenzoxazine matrices. Also, the incorporation of MWNTs simultaneously improved the thermo-mechanical and flame retardant properties of the nanocomposites.

Recently, carbon nanotube buckypapers have been fabricated by the simple filtration of carbon nanotube suspensions and subsequently applied as an inherent flame-retardant shield to the polymeric material surface [38–41]. Mixed SWNT and MWNT buckypaper was incorporated onto the surface of polyimide/carbon fibre composites via a compression moulding method [40]. Compared to direct mixing of carbon nanotubes into the resin, the use of buckypaper is more efficient in fire retardancy improvement. In the MWNT buckypaper/epoxy/carbon composites, significant reduction in the PHRR by more than 60% and the smoke generation by 50% was also observed [39]. The dense nanotube networks and the small pore size within the buckypaper (Fig. 10) provide low gas and heat permeability, that are responsible for the improved flame retardancy.

3.2.2. Functionalized CNTs

Functionalization can significantly improve the dispersion state of CNTs within polymer matrices and enhance the interaction between CNTs and polymer matrices, and thereby reinforce the resultant composites with consequent remarkable improvement in performance. Generally, three strategies are mainly employed to obtain the flame retardant functionalized CNT/polymer nanocomposites:

- Surface modification of CNTs by coupling agents to improve the dispersion state of CNTs within polymer matrices.

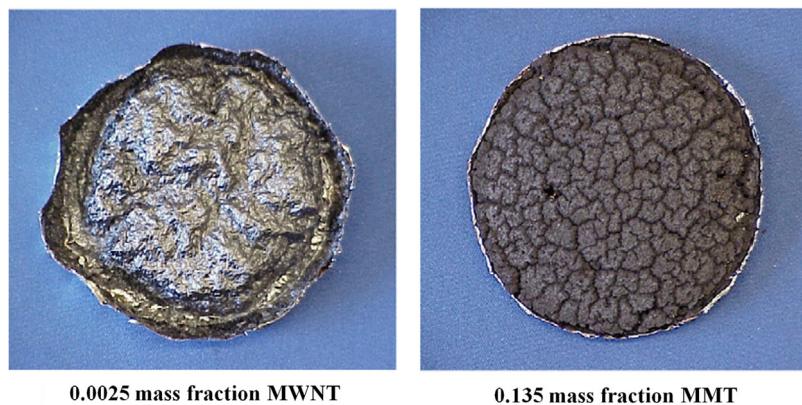


Fig. 8. Residue for MWNT/epoxy and MMT/epoxy samples after gasification test. Unlike MMT/epoxy residue, MWNT/epoxy shows good residue integrity. [32], Copyright 2010.

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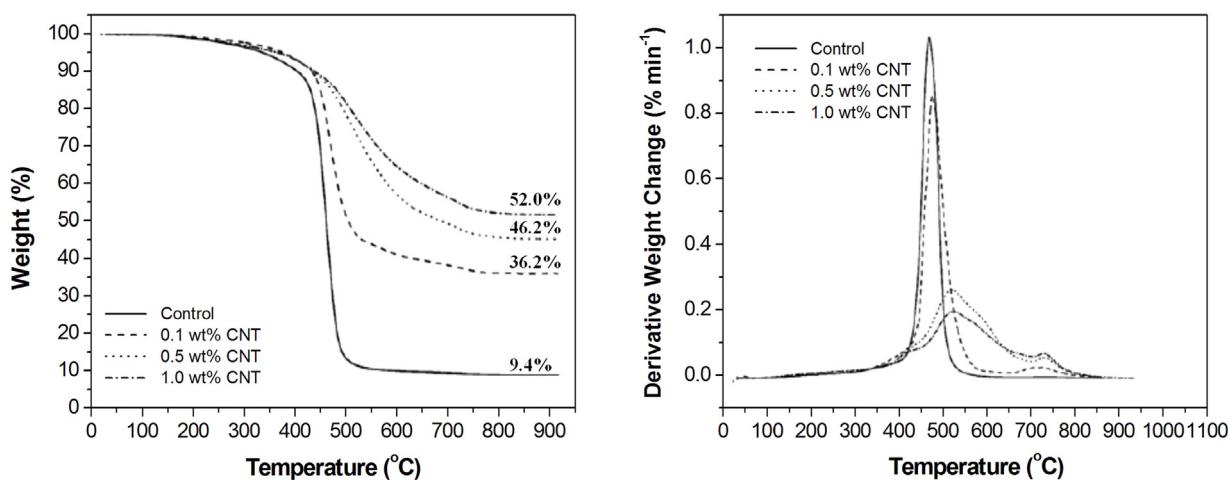


Fig. 9. Thermogravimetric results of the silicone-based foams containing different loading of MWNTs. [36], Copyright 2008.

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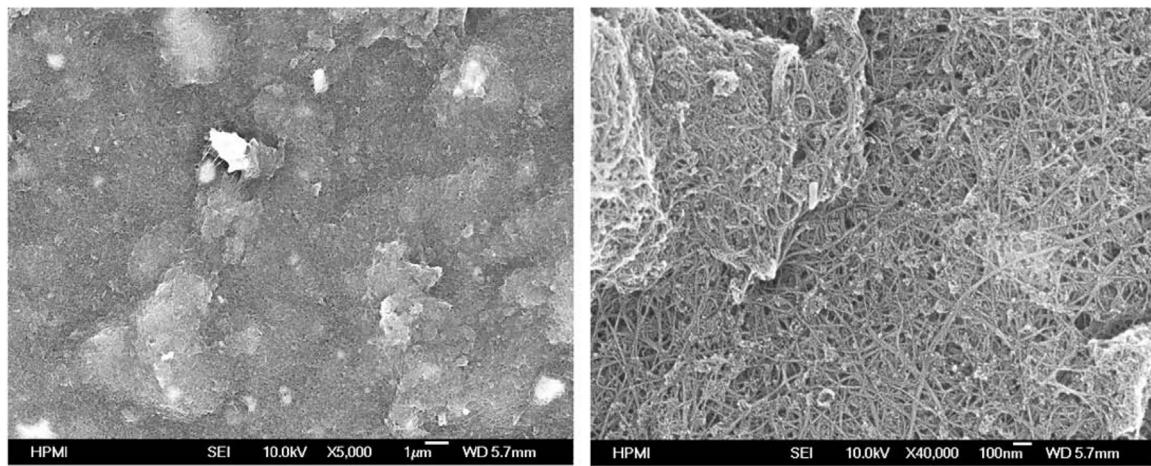


Fig. 10. SEM images of MWNT buckypaper. Left: low magnification; right: high magnification. [39], Copyright 2010.

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- Covalent linkage of organic flame retardants to CNTs to improve the char yield of polymers undergoing degradation as part of combustion process.
- Hybridization of CNTs by inorganic particles to create flame retardant improvement.

Recently, several coupling agents have been covalently linked to CNTs. The functionalized CNT can be incorporated into various polymers such as PP [42], epoxy [43], EVA [44], ABS [45] and cotton [46,47]. For an epoxy composite containing 9 wt% of functionalized CNT, the LOI is increased to 27% and the UL-94 V-0 rating,

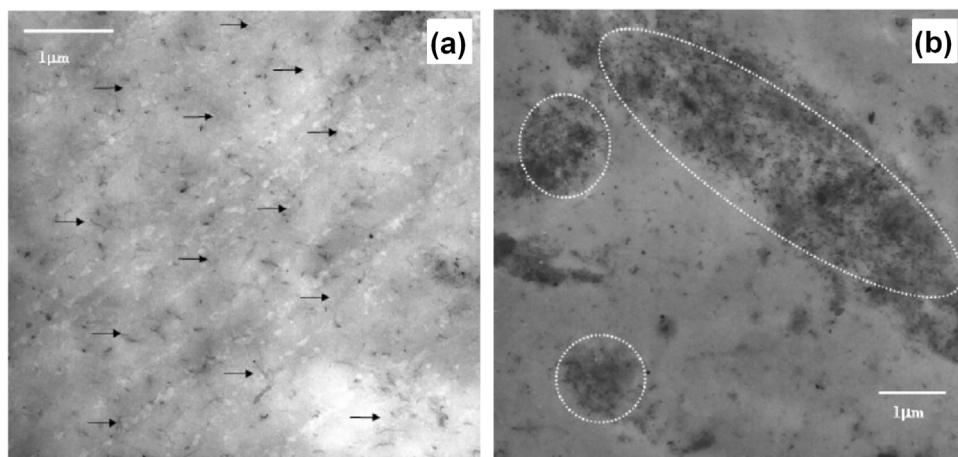


Fig. 11. TEM images of the two nanocomposites at low magnification: (a) EVA + 3 wt% functionalized MWNTs, (b) EVA + 3 wt% MWNTs (arrows in (a) indicate the location of individually spread nanotubes, while dotted curves in (b) highlight aggregates). [50], Copyright 2007. Reproduced with permission from WILEY-VCH Verlag GmbH & Co.

Table 3
Comparison of CNTs and Functionalized CNTs in lowering PHRR of polymers.

Polymer Type	Loading (wt%)	Reduction in PHRR (%)		Reference
		CNTs	Functionalized CNTs	
EVA	2	11.2	24.4	[56]
UPR	–	49.1	72.0	[58]
PVDF	3	53.6	57.7	[61]

and the char yield at 750 °C is increased by 46.94% [43]. Significant reduction in the burning rate has also been reported for polyvinylphosphonic acid/MWNTs/cotton composites compared to that for cotton alone [46].

Generation of composites from CNTs with covalent linked organic flame retardants has been demonstrated to improve the flame retardant efficiency for various polymers including PP [48], ABS [49], EVA [50–52], PC [53], epoxy [54], and cyanate ester [55]. In order to form the covalent linkage between organic flame retardants and CNTs, surface treatment of CNTs must be conducted. Usually, pristine CNTs can be hydroxylated using potassium hydroxide and ethanol [48] or carboxylated by an acid-oxidation procedure [49]. After surface treatment, the CNTs with active groups could be grafted to organic flame retardants. For example, carboxyl-functionalized MWNTs have been prepared and then treated with SOCl₂ to form carbonyl chloride followed by treatment with an amino-terminated flame retardant [49]. The functionalization of CNTs facilitates their dispersion into a polymer matrix (Fig. 11), and enhances interfacial adhesion between the CNT and the polymer. Genuine composites may be formed, as indicated by an increase of the Young's modulus and flame resistance compared to those for compositions containing unfunctionalized CNTs [50].

Another emerging approach used to functionalize CNTs is hybridization of CNTs using inorganic particles. Phosphazene/CNT [56,57], POSS/CNT [58], LDH/CNT [59], silica/CNT [60], zirconia/CNT [61] and aluminum nitride/CNT [62] hybrids have been synthesized and applied to the generation of flame retardant polymer composites. Composites produced using these hybrids exhibit superior enhancement over those containing pristine CNTs in terms of flame retardant properties (Table 3) as well as other performance parameters such as the thermal stability and dielectric properties [61].

3.2.3. Combination of CNTs with other flame retardants

CNT/polymer nanocomposites exhibit low flammability in terms of heat release rate but it fails to other burning measure-

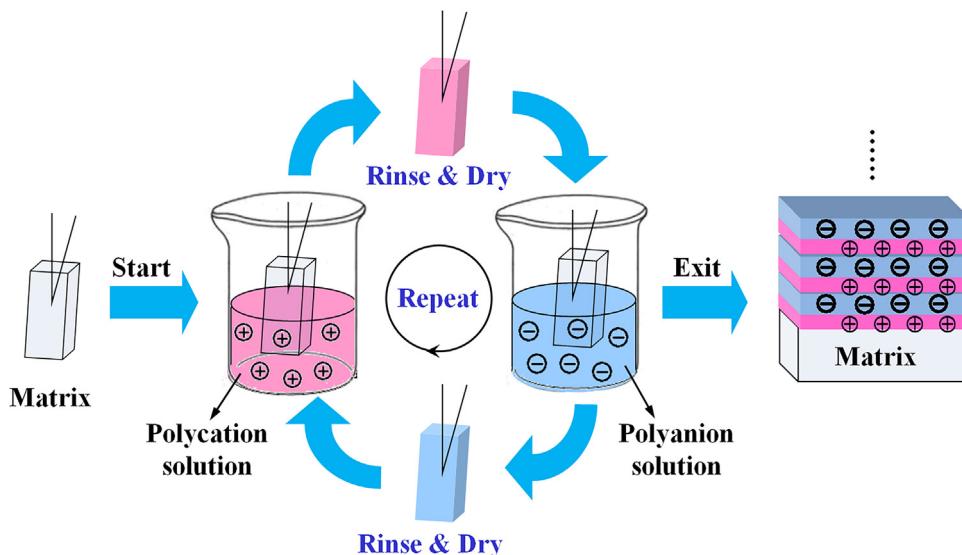
ments, particularly LOI and UL-94 tests [29]. Hence, CNTs are combined with other flame retardant additives in order to create a synergistic effect. Table 4 summarizes the flame retardant performance of some polymer nanocomposites based on CNTs and other flame retardants. Synergistic effect on improving the flame retardancy of polymer composites by incorporating CNTs has been demonstrated for PE [63,64], PP [65–67], PS [68], PET [69], PBT [70], PMMA [71,72], EVA [73], SEBS [74] and epoxy resin [75]. For PET composites, the UL-94 V-0 rating has been achieved with the co-addition of 5 wt% MWNTs and 7 wt% BDP; meanwhile, the percolation threshold of the CNT/BDP/PET composites is decreased to 0.28 vol% from 0.86 vol% for the CNT/PET composites, indicating that the dispersion of CNTs within PET matrix is effectively improved with the assistance of BDP [69]. The combination of 3 wt% CNT and 5 wt% BDP also exhibits effective improvement in SEBS composites: the UL-94 tests of the resultant composite achieve V-0 rating; compared to pure SEBS, the tensile strength and elastic modulus are simultaneously increased by 114% and 225%, respectively [74]. In addition to organic flame retardants, CNTs could also create synergism with inorganic fillers such as clay [76,77] or aluminum phosphinate [70]. The synergism of carbon nanotubes and clay for improving flame retardancy of ABS is attributed to that the presence of clay promotes the graphitization degree of the char together with MWNTs, as evidenced by Raman spectroscopy [76]. The synergistic efficiency on the flame retardancy in composites correlates with the size of CNTs. It is found that the short MWNTs (1–2 μm) produce superior flame retardant properties over the long ones (0.5–40 μm) in terms of PHRR and MLR [72]. It is worthy to note that sometimes an antagonistic effect occurs between CNTs and other flame retardant additives instead of a synergistic effect [65,71]. It is proposed that the deteriorated flame retardance induced by the combination of CNTs and organophosphorus flame-retardants may be resulted from the decreased char yield and the poor quality of the chars.

Most recently, CNTs together with other additives have been utilized to design highly efficient flame retardant coatings on surface of polymers via layer-by-layer assembly. Generally, pristine CNTs are difficult to disperse in aqueous solutions due to large aspect ratio. Therefore, surface modification such as amination or carboxylation makes CNTs ionically charged for electrostatic layer-by-layer assembly. Scheme 2 shows a general procedure of depositing multi-layered coatings on surface of polymer substrate via layer-by-layer assembly. The carbon nanotubes network created by the layer-by-layer process significantly reduces the flammability of PU foam with respect to a 35% reduction in PHRR and prevents pool fire

Table 4

Synergistic effect of CNT and other flame retardants in various polymer composites.

Polymer	Type and loading of CNT	Type and loading of synergist	Highlights	Reference
LDPE	MWNT (3 wt%)	Ni ₂ O ₃ (5 wt%)	73% reduction in PHRR observed from cone calorimetry, char yield of 13.7 wt%	[64]
PP	Chlorinated CNT (3 wt%)	Ni ₂ O ₃ (5 wt%)	73% reduction in PHRR observed from cone calorimetry, char yield of 54.3 wt%	[67]
PS	MWNT, 2 wt%	Decabromodiphenyl oxide (8.3 wt%)/Sb ₂ O ₃ (1.7 wt%)	71% reduction in PHRR and 57% reduction in THR observed from cone calorimetry	[68]
PET	MWNT (5 wt%)	BDP (7 wt%)	LOI value of 25.2%, UL-94 V-0 rating (3.2 mm), and no dripping	[69]
PBT	MWNT (0.5 wt%)	Aluminum phosphinate (9.5 wt%)	66% reduction in PHRR observed from cone calorimetry, UL-94 V-0 rating (3.2 mm)	[70]
PMMA	MWNT (1.5 wt%)	Decabromodiphenyl ether (20 wt%) + Sb ₂ O ₃ (5 wt%)	74% reduction in PHRR observed from cone calorimetry, UL-94 V-0 rating (3.2 mm)	[72]
SEBS	MWNT (3 wt%)	BDP (5 wt%)	LOI value of 25.5%, and UL-94 V-0 rating (3.2 mm)	[74]
ABS	MWNT (1 wt%)	Clay (1 wt%)	56% reduction in PHRR observed from cone calorimetry	[76]

**Scheme 2.** Illustration of layer-by-layer deposition for CNT/polymer multi-layered coating by an alternating submersion in a cationic solution and an anionic solution with washing between each solution.

by forming a protective layer [78]. In another study [79], a more significant reduction in PHRR (69%) has been observed in the flame retardant PU foam using a multi-layered coating composed of MMT and CNTs, at a low coating mass gain of 4.1 wt%. A new flame retardant nanocoating composed of amino-functionalized MWNT (MWNT-NH₂) and APP are deposited on ramie fabric [80], and the presence of the nanocoating leads to a relatively slow fire spread rate on the ramie fabric. This new and innovative multi-layered coating methodology provides a promising flame retardant treatment for current polymeric materials; however, the negative influence of coatings on hand feeling and appearance of fabrics or foams is still a controversial issue currently.

3.2.4. Flame retardant action of CNTs

Based on the above observations, the flame retardant actions of CNT/polymer nanocomposites involve the condensed phase action. In the condensed phase, a protective char layer covering the entire sample surface is formed that acts as insulative barrier and reducing volatiles escaping to the flame. The formation of a continuous layer, without any cracks or holes, is due to the formation of so-called three-dimensional network structure when the content of CNTs reached a threshold value. Otherwise, the breakdown of the char layers produces large crevasses and cracks that provide bypasses for the heat and mass transfer between flame and burning poly-

mers. In addition, it is reported that the CNTs play an important role in the reduction of the PHRR by forming good quality char containing graphitic carbon demonstrated by Raman [76] and XRD spectra [81]. Dubois and co-workers [34] assume that the reaction between the radicals produced at the surface of crushed MWNTs and the radicals formed during EVA thermal degradation probably occurs that is responsible for the decrease in the amount of volatile products and the delay of materials ignition in the cone calorimetry. However, this phenomenon is only observed in the case of crushed MWNTs; for most of flame retardant CNT/polymer nanocomposites, the radicals' reaction is rarely reported.

3.3. Graphene

Graphene, as a new member of carbon allotropes discovered by the exfoliation of graphite in 2004 [3], has been arousing tremendous attention and research interest in the scientific community. With the unique structure of a 2-D monolayer of sp² hybridized carbon atoms, graphene has shown exceptional physical properties, such as ultrahigh specific surface area (calculated value, ~2630 m² g⁻¹) [82], excellent Young's modulus (~1000 GPa) and fracture strength (~125 GPa) [83], high electronic conductivity (~200 000 cm² V⁻¹ s⁻¹) [84], good thermal conductivity (~5000 W m⁻¹ K⁻¹) [85], and fascinating transport

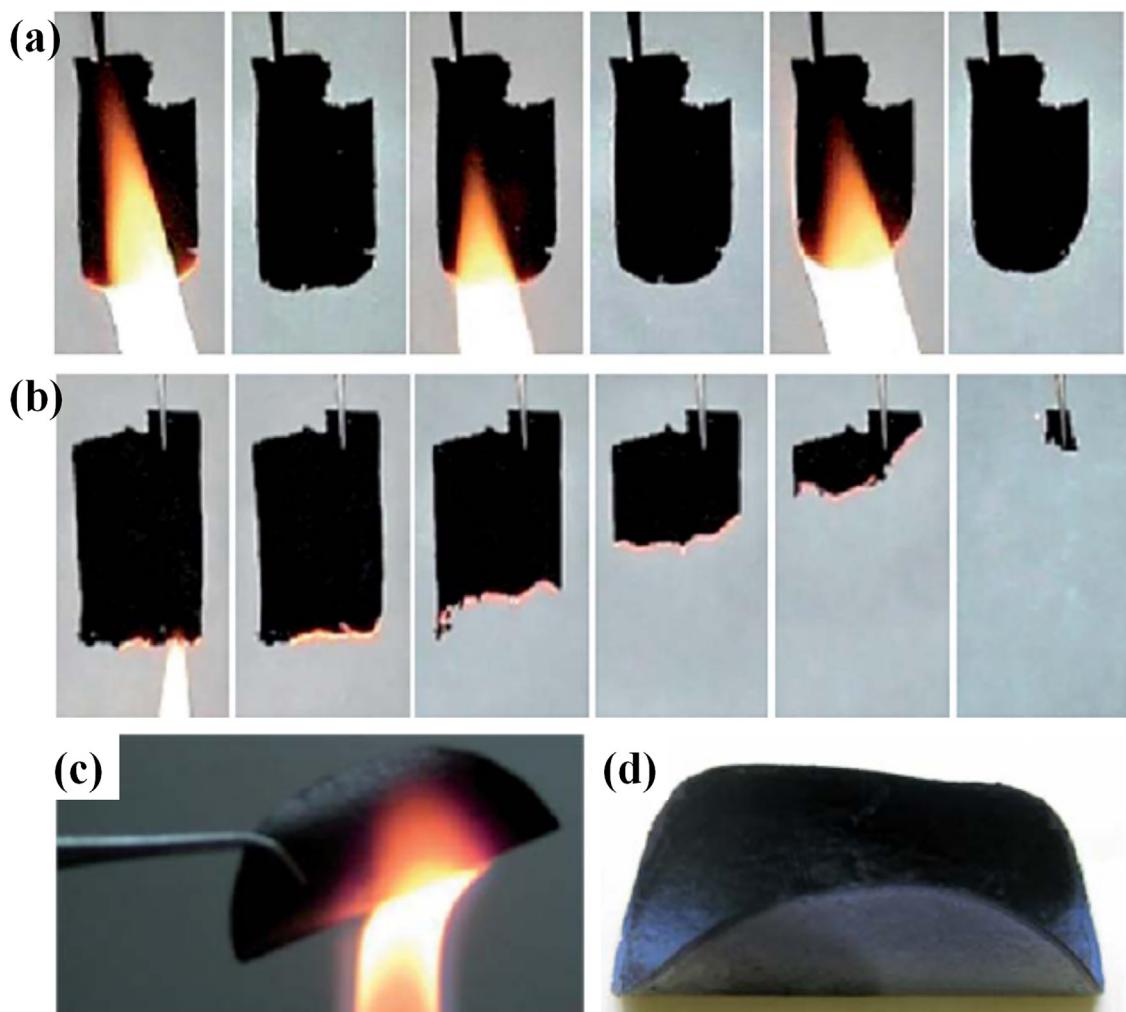


Fig. 12. (a) Snapshots showing flame treatments on reduced graphene oxide film with intervals of 3–4 s. The film was first exposed to a natural gas flame for a few seconds. The burned part turned red hot but didn't propagate, and was quenched after the flame was removed; (b) Snapshots showing flame treatment on a reduced graphene oxide contaminated with KOH salts (1 wt%). The flame immediately triggered the self-propagating combustion in the film, which suggests that potassium salts can significantly reduce the thermal stability of reduced graphene oxide. Time intervals between the frames are 0.32 s, 1.82 s, 2.5 s, 2.5 s and 2.5 s, from left to right [87]. Copyright 2011. (c) Photographs of the MMT-reduced graphene oxide hybrid films (with initial thickness of 0.05 mm) exposed to open flame; (d) Digital image showing the MMT-reduced graphene oxide hybrid film after flame treatment. [88]. Copyright 2011. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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phenomena [86]. These fascinating properties make graphene one promising nanofiller to be employed in nanocomposites for many multi-functional applications. In this section, the properties of graphene-based polymer nanocomposites will be summarized and discussed with special emphasis on the flame retardant behavior.

3.3.1. Utilization of pristine graphene

Graphene with high purity is quite stable against combustion when exposed to a natural gas flame for a few seconds. The burned part turns red hot but does not spread, and is quenched after the removal of the flame, clearly indicating the high intrinsic flame resistance of graphene (Fig. 12a) [87]. However, the presence of potassium salt impurities makes graphene oxide (GO) become highly flammable. A gentle touch with a hot spot could trigger catastrophic and total combustion of such GO films (Fig. 12b) [87]. Recently, a simple and efficient approach to fabricate flexible multifunctional free-standing MMT-graphene hybrid films via vacuum filtration has been reported [88]. This MMT-graphene hybrid film shows excellent flexibility, electrical conductivity and fire retardant properties, as shown in Fig. 12c and 12d. Besides, graphene phos-

phonic acid has been prepared by a simple method of ball-milling graphite with red phosphorus that is demonstrated as an effective flame retardant [89].

Due to its good intrinsic flame retardant property, pristine graphene has been utilized directly to prepare flame retardant polymer composites via melt compounding or solution blending methods. Flame retardant polypropylene composites based on graphene and other carbon materials by melt-extrusion have been prepared [90]. In contrast to other nano- and micron-sized carbon fillers such as expanded graphite, nano-scaled carbon black, and multiwall carbon nanotubes, only graphene afford uniform dispersion combined with simultaneously improved stiffness (+80%), electrical conductivity ($3 \times 10^{-5} \text{ S cm}^{-1}$) and enhanced flame retardancy of PP, as evidenced by the reduced PHRR (-76%). Graphene/WPU nanocomposites prepared from solution blending method show good flame retardant and smoke suppression behaviors with a significant reduction in total smoke release (25% reduction with 1 wt% graphene) and a lower PHRR and THR [91].

The flame retardant effect in polymer composites correlates with the oxidation degree of GO. It has been revealed that excessive

Table 5

Flammability of functionalized graphene-based polymer nanocomposites.

Polymer	Loading of functionalized graphene (wt%)	Main results	Reference
Epoxy	10	Improvement in char yield to 30.2% from 16.7% (pure epoxy) and 21.1% (GO/epoxy); increase in LOI to 26% from 20% (pure epoxy) and 23% (GO/epoxy).	[97]
Epoxy	10	LOI value of 36%, UL-94 V-0 rating (3.2 mm); for pristine graphene/epoxy composite, LOI value of 26%, fail in UL-94 test (3.2 mm).	[98]
XLPE	3	29% reduction in PHRR observed from cone calorimetry, while it is 9% for GO/XLPE.	[99]
PP	20	67% and 24% reduction in PHRR and THR, respectively, while those are 48% and 20% for PPA/PP composites	[100]
Epoxy	8	41% and 50% reduction in PHRR and THR, respectively, while those are 35% and 46% for PPA/epoxy composites	[101]
EVA	1	46% reduction in PHRR and TTI of 75 s observed from cone calorimetry, whereas those are 31% and 61 s in the case of graphene/EVA	[102]
Epoxy	1	45% reduction in PHRR observed from pyrolysis-combustion flow calorimetry, while that of GO/epoxy is only 18%.	[103]

oxidation was detrimental to the fire retardant effect of GO because it caused a GO with weak intumescence ability [92]. GO with different oxidation degrees and graphene as flame retardants for polystyrene has been investigated [93]. It is found that both the thermal stability and the reduction in PHRR decrease with increasing the oxygen groups in GOs or graphene. The best fire retardancy is observed with 5 wt% of the graphene, in which case the reduction in the PHRR is almost 50% as compared to PS.

Pristine graphene or GO has been also incorporated into flame retardant thermosetting resins, such as epoxy resin [94] and polybenzoxazine [95]. An interesting phenomenon has been observed in graphene/epoxy composites: the PHRR displays an increase trend compared with that of pure epoxy resins, despite an increased LOI value and a reduced THR simultaneously [94]. This phenomenon is attributed to the balance between the effect of thermal conductivity and the barrier property of graphene.

3.3.2. Organic flame retardants functionalized graphene

As a precursor of graphene, GO contains abundant functional groups such as epoxy, hydroxyl, carboxyl and $-C=C-$ groups at the edge area and basal planes [96], that provides many active sites for fabricating functionalized graphene. The surface modification makes hydrophilic GO hydrophobic (Fig. 13) [97], that facilitates the dispersion of the graphene sheets in the polymer matrix.

The grafting-based approach has been widely used to prepare organic flame retardants functionalized graphene. In this strategy, a two-step procedure can usually be employed to establish covalent linkage between organic flame retardants and graphene or GO: (i) provide organic flame retardants with functionalities that enable them to react with either graphene or GO; (ii) functionalized GO need to be reduced to functionalized graphene in the presence of reducing agents. Sometimes, simultaneous functionalization and reduction of GO could be realized if the modifier also serves as a reducing agent. Table 5 lists some typical organic flame retardants functionalized graphene and their application in polymer composites. Recently, 9, 10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [97], 2-(diphenylphosphino)ethyltriethoxy silane (DPPES) [98], hyperbranched flame retardant [99], polyphosphamide (PPA) [100,101], and poly(piperazine spirocyclic pentaerythritol bisphosphonate) (PPSPB) [102] have been grafted to GO in order to overcome the challenge of GO in its burn-out limits. As expected, organic flame retardants functionalized graphene sheets exhibit superior flame retardant properties compared with either organic flame retardants or pristine graphene as far as LOI, UL-94 rating and PHRR are concerned. For example, epoxy composites with 10 wt% of DPPES-graphene could pass UL-94 V-0 rating, whereas its counterparts

with the equivalent loading of either DPPES or graphene cannot [98].

Another emerging approach used to functionalize graphene with flame retardants is sol-gel chemistry. In general, the silane coupling agent firstly reacts with flame retardants to produce siloxane-containing flame retardants; the silane coupling agent meanwhile reacts with graphene or GO; subsequently, siloxane-containing flame retardants are grafted to silane modified graphene or GO via the hydrolysis and the condensation of siloxane. A typical fabricating procedure of functionalized GO/PMMA composites is depicted in Scheme 3. Through this approach, various silicon- and phosphorus-containing flame retardants functionalized graphene or GO have been synthesized and demonstrated to be effective in reducing the flammability of various polymers, such as epoxy resins [103,104], polyurea [105], PVA [106] and PMMA [107].

3.3.3. Inorganic/graphene hybrids

In addition to covalent functionalization, various inorganic/graphene hybrids, including LDH/graphene and metal oxide/graphene, have been synthesized via non-covalent modification. The formation mechanism of LDH/graphene hybrids is schematically illustrated in Scheme 4. The formation process is depicted as follows: firstly, graphite oxide is sufficiently exfoliated into graphene oxide by sonication; secondly, the metal cations are attached onto the negatively charged graphene oxide by electrostatic attraction; thirdly, the graphene oxide is reduced to graphene; finally, graphene sheets decorated by the metal cations are self-assembled into LDH/graphene hybrid nanostructure due to the hydrophobic nature of graphene. The formation mechanism of metal oxide/graphene hybrids is similar. The attachment of LDH or metal oxide nanoparticles may prevent the graphene sheets from aggregation during preparation of polymer nanocomposites.

Hu and coworkers have done much innovative work on the application of LDH/graphene and metal oxide/graphene into flame retardant polymer nanocomposites [108], as summarized in Table 6. Incorporation of metal oxide/graphene hybrids results in significant thermal stabilization of polymer: a 37 and 27 °C increment in the temperature of 5% mass loss is observed for $\text{SnO}_2/\text{graphene-epoxy}$ and $\text{Co}_3\text{O}_4/\text{graphene-epoxy}$ with 2 wt% of the fillers, respectively, compared to that for pure epoxy resins [108–116]. LDH/graphene and metal oxide/graphene hybrids also have been demonstrated to be effective in lowering the fire hazards of various polymers such as epoxy [108,112,113,115,116], PMMA [109], PBT [114], PLA [111], PBS [111], and PA-6 [110]. With only 2 wt% of LDH/graphene or metal oxide/graphene hybrid, the PHRR value is decreased by at least 30% for most polymer composites. The significant reduction in heat release rate may be attributed to the formation of a good insulating char layer with high con-

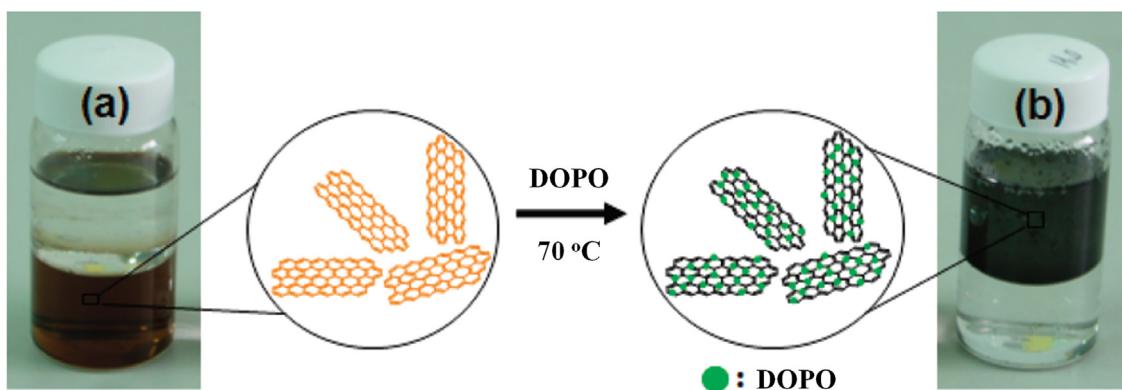
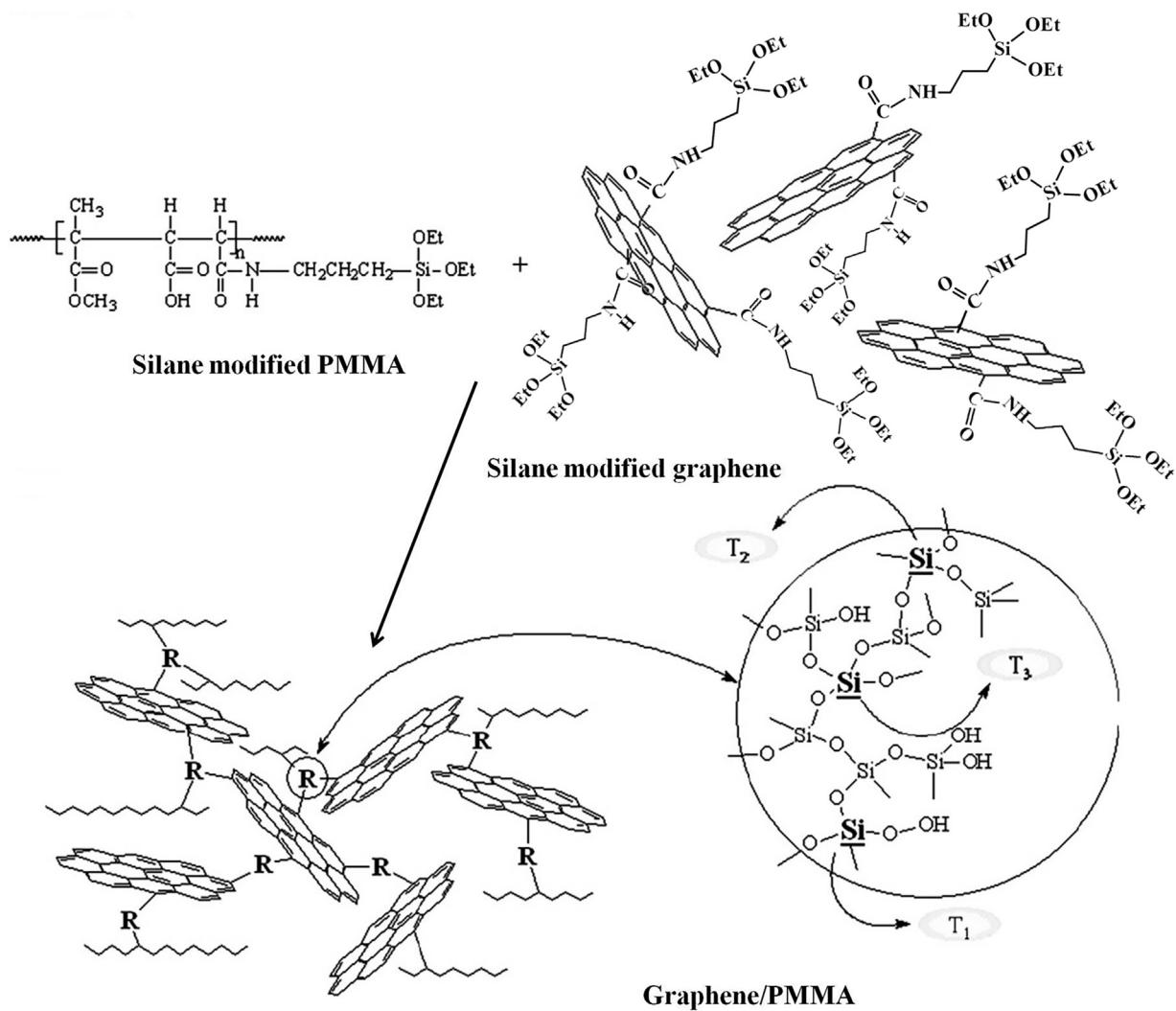


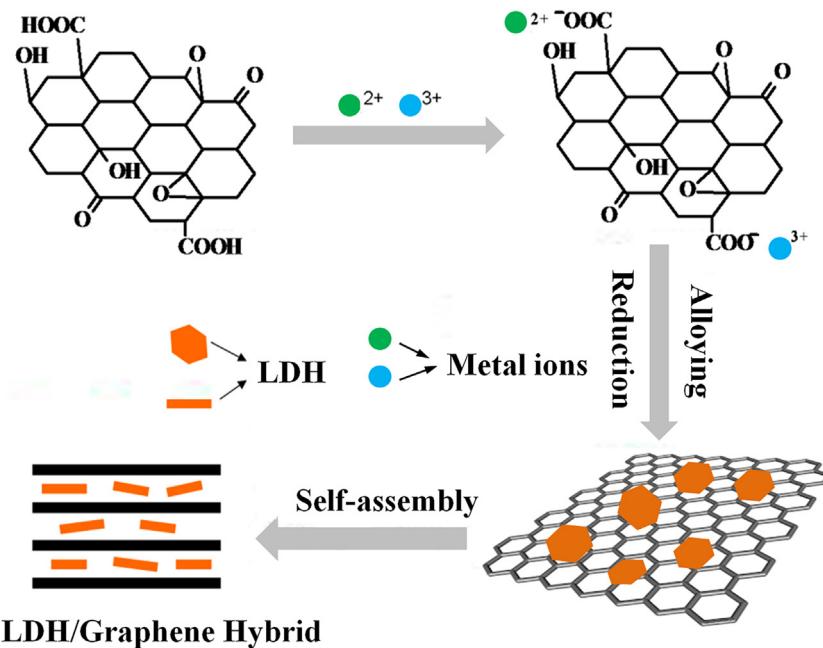
Fig. 13. Photographs of (a) GO and (b) DOPO-reduced GO dispersions in water (bottom) and toluene (top) for 1 month. [97]. Copyright 2012. Reproduced with permission from the American Chemical Society.



Scheme 3. Preparation route of functionalized graphene/PMMA composites via sol-gel technique. [107]. Copyright 2012. Reproduced with permission from Elsevier Ltd.

tent of graphitized carbons (as evidenced by Raman spectra) and thermal oxidative resistance (as evidenced by XPS), that could effectively inhibit oxygen permeation, heat and mass transfer, and prevent combustible gas escape from the degradation zone to feed flame. In addition to the heat-related fire hazards, incorporation of LDH/graphene or metal oxide/graphene hybrid also leads to sup-

pressed smoke production and reduced smoke toxicity compared to pristine graphene [113]. The smoke suppression may be attributed to the reduced amount of the organic volatiles degraded from polymers, since organic volatiles are the major source of smoke particles [117]. Furthermore, some metal oxide/graphene hybrid such as Co₃O₄/graphene shows great effectiveness in reducing the CO con-



Scheme 4. Schematic illustration of the formation mechanism of LDH/graphene hybrid.

Table 6

Flammability of polymer filled with LDH/graphene or metal oxide/graphene hybrids.

Polymer	Type of filler	Main results	Reference
Epoxy	Co_3O_4 /graphene, SnO_2 /graphene	29% and 27% reduction in PHRR of Co_3O_4 /graphene-epoxy and SnO_2 /graphene-epoxy composites, respectively.	[108]
PMMA	NiAl-LDH/graphene	25% reduction in PHRR observed from cone calorimetry, which is superior over either NiAl-LDH or pristine graphene.	[109]
PA-6	Co_3O_4 /graphene, NiO /graphene	11% and 23% reduction in PHRR of Co_3O_4 /graphene-PA-6 and NiO /graphene-PA-6 composites, respectively.	[110]
PBS, PLA	Co_3O_4 /graphene	31% and 40% reduction in PHRR of PBS and PLA composites, respectively; the addition of Co_3O_4 /graphene significantly decreased the release of carbon monoxide.	[111]
Epoxy	MoS_2 /graphene	46% and 25% reduction in PHRR and THR, respectively; an 53 °C increment in the onset thermal degradation temperature (air)	[112]
Epoxy	NiFe-LDH/graphene	61% and 60% reduction in PHRR and THR, respectively, which are much better than either NiFe-LDH or pristine graphene.	[113]
PBT	MnCo_2O_4 /graphene	37% and 36% reduction in PHRR and SPR, respectively, observed from cone calorimetry.	[114]
Epoxy	ZnS/graphene	47% and 27% reduction in PHRR and THR, respectively, accompanying with a 63% decrease in TSP	[115]
Epoxy	Ce-doped MnO_2 /graphene	54% and 41% reduction in PHRR and TSR, respectively, observed from cone calorimetry.	[116]

centration during combustion due to its high catalytic activity for CO oxidation [108,111].

3.3.4. Synergism between graphene and other flame retardants

Although organic flame retardants functionalized graphene and inorganic/graphene hybrids have been demonstrated to be effective in lowering the heat release rate of polymers, most of these composites fail in LOI and UL-94 tests. In order to meet industrial requirement, graphene has been used as a synergist for flame retarding polymers in combination with a wide variety of conventional flame retardants. Table 7 summarizes some synergistic system between graphene and other flame retardants in recent years. Striking multiple synergies created by combining graphene and CNTs have been observed: with 0.5 wt% of graphene and 0.5 wt% of CNT, the PHRR and AMLR of PP composite are decreased by 73% and 38%, respectively, that are superior over its counterparts with 1.0 wt% of graphene or CNT [118]. Remarkable synergistic effects in their tensile strength (+14.3%) and Young's modulus (+27.1%), electrical conductivity (+32.3%) and thermal conductivity

(+34.6%) are also observed. However, the improvement in thermal conductivity leads to an increase in PHRR of graphene-based polymer composites sometimes [119]. As aforementioned, the optimal flame retardancy may be a balance between the thermal conductivity and the barrier effect of graphene that is similar to that of CNTs.

Very recently, thermally insulating and fire-retardant lightweight anisotropic foams have been prepared based on nanocellulose and GO, together with sepiolite nanorods (SEP) [125]. UL-94 vertical burning tests show that nanocellulose-based composite foams with an optimized addition of GO (10 wt%) and SEP (10 wt%) display very good fire retardancy, where the flame does not self-propagate (Fig. 14). Foams with suboptimal composition, that is, with no GO or low SEP content, exhibit some fire retardancy, but shrink much more than the nanocomposite foams with optimal composition, indicating the existence of synergism between GO and SEP.

The combination of graphene with other flame retardants also exhibits excellent anti-dripping properties during the combustion

Table 7

Synergistic effect of graphene with other additives on flame retardant properties of polymer composites.

Polymer	Loading of graphene	Type and loading of synergist	Highlights	Reference
PP	0.5 wt%	CNT (0.5 wt%)	73% and 38% reduction in PHRR and AMLR, respectively, observed from cone calorimetry.	[118]
ABS	2 wt%	Co(OH) ₂ (4 wt%)	30% reduction in PHRR observed from cone calorimetry, and 45.1% and 40.5% increase in tensile strength and bending strength of the ABS composites, respectively; Elongation at break is reduced to 3.7% from 28.0% for virgin ABS.	[119]
PE	0.2 wt%	ATH (40 wt%)	18% reduction in PHRR compared to that of PE/ATH composite observed from cone calorimetry	[120]
PU	2 wt%	MCAPP (12 wt%) and MA (6 wt%)	LOI value increased from 22.0% to 34.0% accompanying with excellent antidripping properties as well as UL-94 V-0 rating.	[121]
PBS	2 wt%	APP (12 wt%) and MA (6 wt%)	LOI value increased to 33.0% from 23.0% for pure PBS as well as UL-94 V-0 rating.	[122]
PMMA	1 wt%	LDH (5 wt%) and BPEA (10 wt%)	45% reduction in PHRR observed from cone calorimetry, UL-94 V-1 rating.	[123]
PP	1 wt%	CNT (1 wt%), MPP (14.4 wt%) and PER (3.6 wt%)	LOI value of 31.4%, UL-94 V-0 rating, and 83% reduction in PHRR observed from cone calorimetry.	[124]

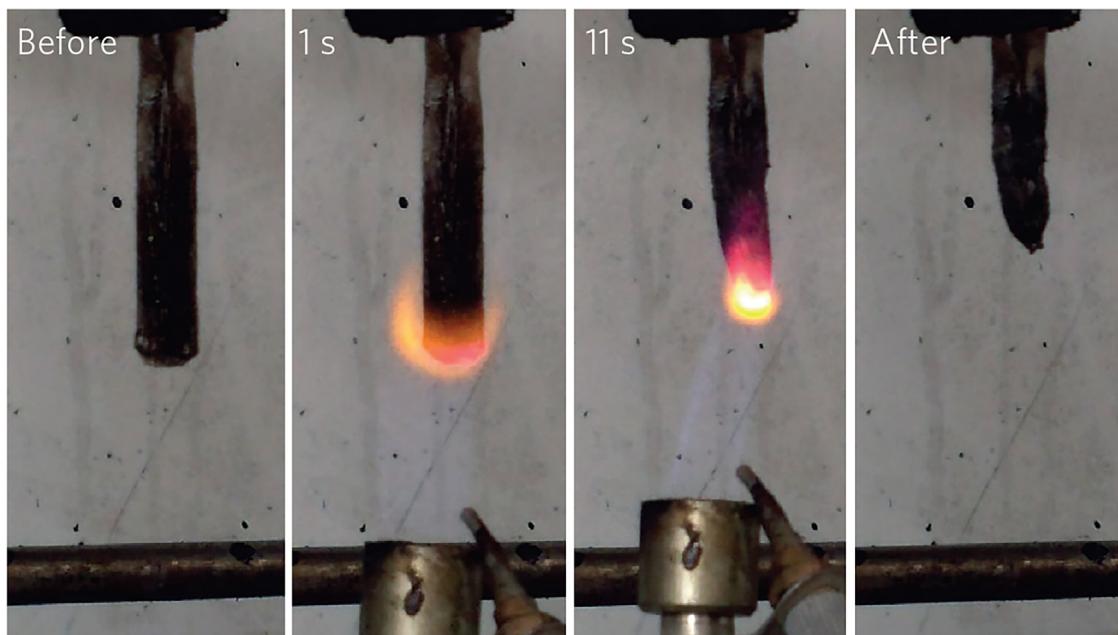


Fig. 14. Vertical burning test (UL94) of a nanocomposite foam containing 77% CNF, 10% graphene oxide, 10% SEP and 3% boric acid (in wt%). The panel shows the foam before the test, after 11 s of application of a methane flame, and the foam after the test, showing high fire retardancy. [125], Copyright 2014. Reproduced with permission from Nature Publishing Group.

of polymers. For instance, a UL-94 V-0 PBS composite with excellent anti-dripping behavior is obtained for a formulation of 18 wt% IFR and 2 wt% graphene [122]. Melt flow index measurement indicates that the presence of graphene significantly enhances the melt viscosity and thus restrains the melt dripping. Similar anti-dripping behavior has also been reported in the case of intumescence flame retardant polyurethane with 0.5–2.0 wt% of graphene [121].

3.3.5. Flame retardant mechanism of graphene

The flame retardant action of graphene is mainly focused on its influence on the structure and yield of the char formed. The 2-D fillers like nano-clays with good barrier properties have been already reported for some time [126,127]. Since GO or graphene possesses platelet morphology, it has potential application as an alternative to nano-clay that could improve the barrier performance of polymers during the thermal degradation process. According to a recent study, defect-free graphene sheets are impermeable to all gas molecules [128]. The incorporation of graphene can provide a so-called “tortuous path” effect that significantly alters the diffusion path of pyrolysis products, thus resulting in significantly reduced mass loss rate, as illustrated in Fig. 15 [129].

Effective dispersion of the graphene platelets may further enhance barrier properties of polymeric hosts, while high aspect ratio can be achieved [129]. Furthermore, the graphene can promote the formation of a compact, dense and uniform char layer in condensed phase during the combustion of polymer matrix. Such a structured char layer effectively inhibits the internal thermal decomposition products into the flame zone and the permeation of oxygen and heat into the underlying of polymer matrix [130].

In the condensed phase, graphene may absorb polycyclic aromatic hydrocarbon (PAH) species and these active PAH species propagate on the graphene that serve as a template of micro-char [101]. Finally, numerous micro-chars assemble together to form a continuous and compact char layer (*Scheme 5*).

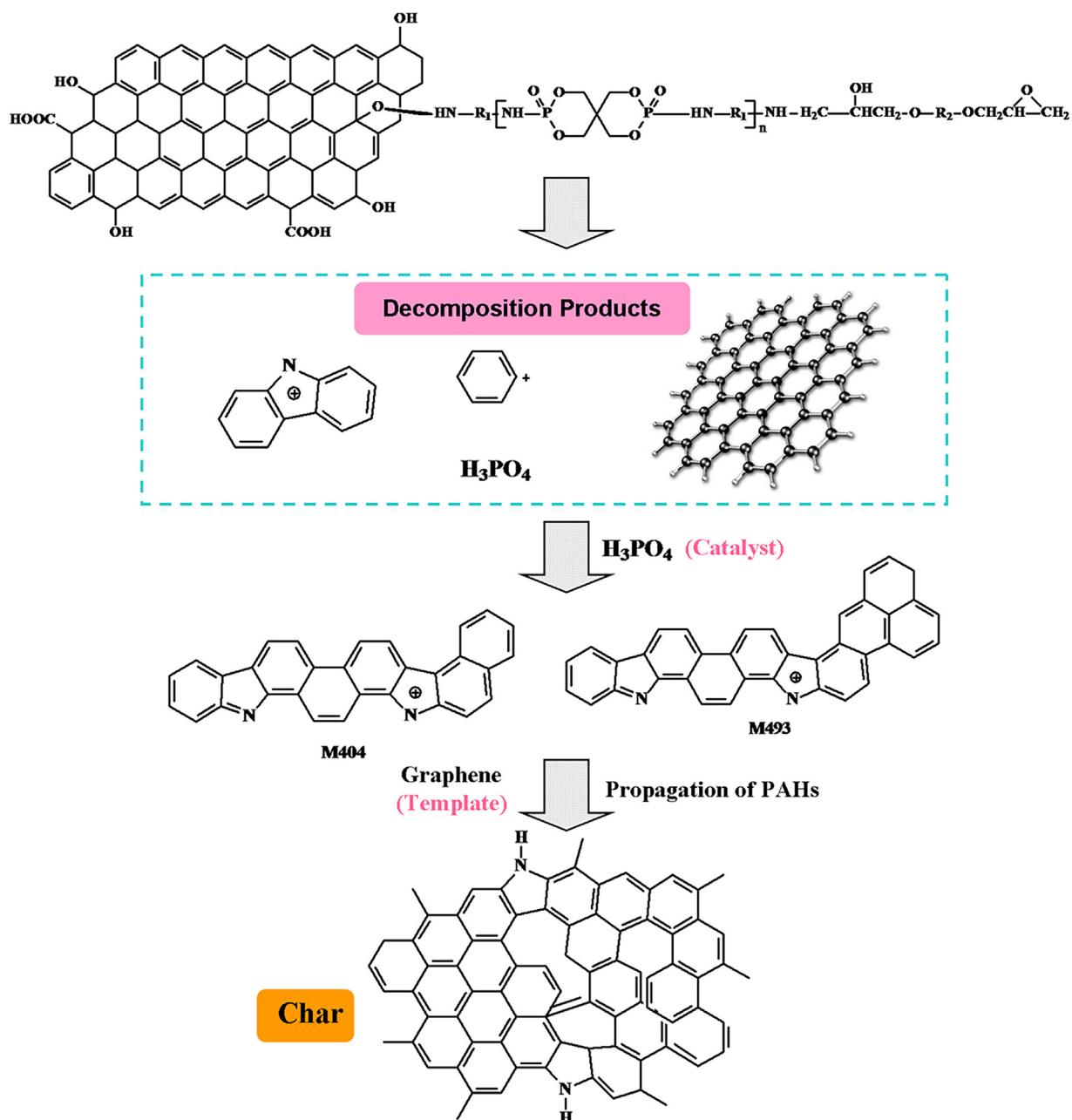
3.4. Graphite

Graphite is a layered mineral made up of stacked graphene sheets where carbon atoms within the layered nano-sheets form hexagonal cells through covalent bonds, with successive carbon layers connected by Van der Waals forces. However, pristine graphite is rarely used in flame retardant polymers since the carbon



Permeation path imposed by nanoflatelet modification of polymer composites

Fig. 15. Permeation path imposed by graphene nanoflatelet modification of polymer composites.



Scheme 5. The possible mechanism of the char formation for PPA-g-graphene/epoxy composites. [101], Copyright 2014. Reproduced with permission from the Royal Society of Chemistry.

flakes in natural graphite stack so compactly that the penetration of the resin matrix into the slots of the graphite sheets is very difficult. Instead, expandable graphite (EG) prepared from natural graphite

by chemical treatment has been widely used as flame retardant for a wide range of polymers due to its easy exfoliation in a polymer matrix.

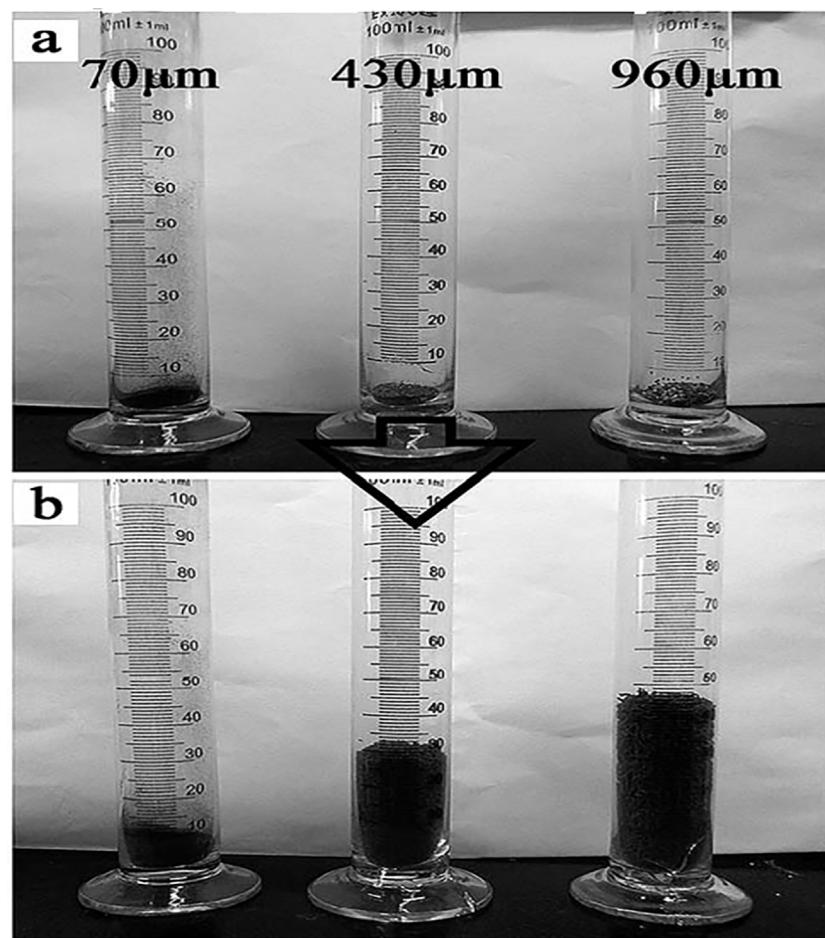


Fig. 16. Digital photos of three kinds of EG particles: (a) original and (b) after heat treatment. Lower size EG particles display lower volume expansion ratio. [140], Copyright 2014.

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3.4.1. Utilization of EG or modified EG

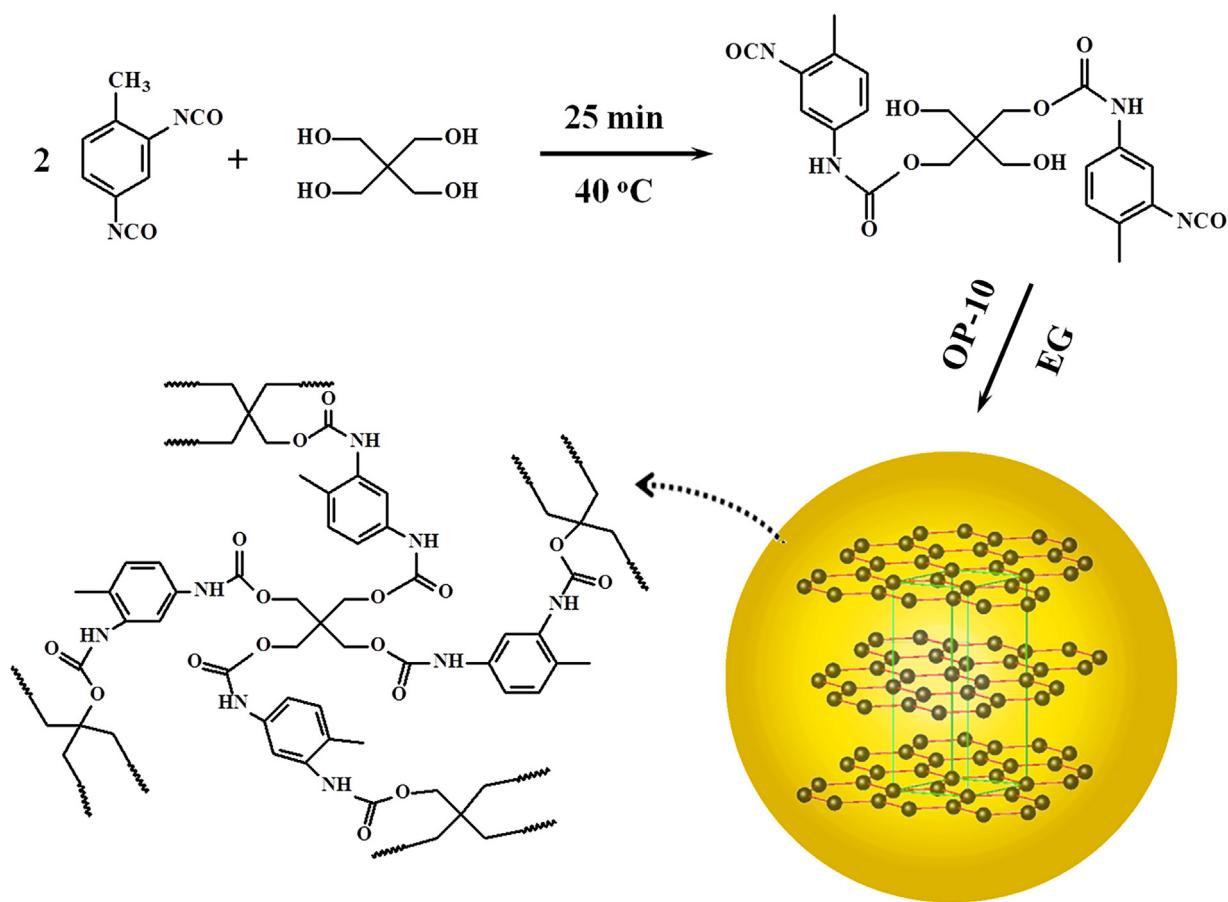
As a type of graphite intercalation compound, EG is in general prepared by exposing flake graphite to concentrated sulphuric acid in combination with strong oxidizers such hydrogen peroxide or potassium permanganate [131–137].

Under these conditions graphite is oxidized and meanwhile sulphate anions are inserted into the graphite sheets. EG retains most outstanding characteristics of natural graphite, such as low price, abundance, electrical conductivity, reinforcement of mechanical properties of polymers. One of the most important aspects of EG is its flame retardancy. It is convenient to blend EG with polymers since EG is commercially available fire retardant. EG/PA-6 and clay/PA-6 composites have been prepared by a melt-compounding method, and EG show significant reductions in PHRR (~60% compared to neat polyamide 6) and MLR, slightly superior over that obtained for organoclay composites [138]. An approach to prepare EG using a hydrothermal method has been reported, and the PHRR values of the composites containing 30 wt% of EG are notably lower than those of the pure HDPE resin and the composites containing 30 wt% of natural graphite [139].

The size of EG particle affects the flame retardant property of polymers. The influence of the nominal particle sizes (70 μm, 430 μm and 960 μm) of EG on the properties of water-blown semi-rigid polyurethane foams (SPFs) has been investigated [140]. Horizontal burning tests demonstrate that the EG-430 μm and EG-960 μm with various loadings could effectively suppress the fire spread rate of the SPF; however, EG-70 μm shows almost no

effect on the improvement in flame retardant properties of SPF. The flame retardancy of the composite is enhanced with increasing the EG size that is attributed to the formation of an insulating char layer with the increase in volume of expanded graphite (Fig. 16) [140]. Similar observation has also been reported, but the mechanical properties of PU foam decrease with increasing the EG loading due to the poor compatibility between EG and polymer matrix [141].

In order to improve the compatibility between EG and polymer matrix, two strategies have mainly been employed: sol-gel method and micro-encapsulation technology. In the sol-gel method, EG and pre-polymer (such as epoxy resin, polyurethane, etc.) or monomer are functionalized by the silane coupling agent, before hydrolysis and condensation between the siloxanes to form a covalent linkage between EG and polymer matrix. Using this method, EG/epoxy [142] and EG/PMMA [143,144] composites have been prepared and showed effective flame retardant behaviors. Recently, another approach that has been utilized to improve the interfacial adhesion between EG particles and polymer matrix is microencapsulation technology. Polyurethane micro-encapsulated EG has been prepared and applied in EVA composites, as shown in Scheme 6, and the resultant composites passed UL-94 V-0 rating, even after being treated with 70 °C water for 168 h [145]. Due to the good interfacial adhesion between fillers and EVA matrix, EVA composites containing micro-encapsulated EG show superior mechanical and dynamic mechanical thermal properties over their counterparts containing un-modified EG. In other studies, EG micro-encapsulated by



Scheme 6. Schematic diagram for the preparation of PU microcapsuled EG, OP-10: polyoxyethylene octylphenol ether. [145], Copyright 2011. Reproduced with permission from the American Chemical Society.

methyl methacrylate-acrylic acid copolymer [146] or melamine-formaldehyde resin [147] has been demonstrated to be effective in flame retardant rigid PU foam.

3.4.2. Synergism between EG and other flame retardants

Although EG is an inexpensive and abundant flame retardant additive, it has obvious disadvantages: one is high loading required for a satisfactory flame retardant level that leads to a deleterious effect on the mechanical properties of polymer matrix; another is the thermally unstable char layers formed during combustion. Therefore, EG needs to be combined with other flame retardants to achieve a high flame retardant efficiency. A number of studies have been conducted on EG filled flame retardant polymers, giving satisfactory fire resistance for some polymers, such as PUF [148–153], PLA [154–156], PE [157–161], PP [162,163], PET [164], PMMA [165], PVC [166], EVA [167], ABS [168,169], polyurea [170], phenolic resins [171], etc. Table 8 lists the flame retardant performance of some polymer composites based on the combination of EG and other flame retardants. Due to the volume expansion nature of EG during combustion, EG has been widely combined with phosphorus-containing compounds to form intumescence flame retardant system for polymers where an intumescence and stable char layer could be generated.

3.4.3. Flame retardant mechanism of expandable graphite

Based on the preceding discussion, the utilization of EG as a flame retardant benefits from its layered structure ('physical' barrier action) and intumescence/blowing effect ('chemical' action) in the condensed phase. When exposed to heat, EG, expands hun-

dred times its initial volume and generates a "worm-like" structure layer on the surface of the materials [140,172,173]. Such a layer of graphite can prevent heat and oxygen permeating into the polymer matrix, thus improving the fire resistance. The suggested action by which EG/PLA composites function involves the formation of a porous carbonaceous layer that serves as a physical barrier to both mass and heat transfer (Fig. 17a). TEM observations reveal the presence of layered graphite nanolayers of different dimension in the char residue after burning (Fig. 17b) [174]. As expected, the graphite expansion and the presence of graphite nanolayers suffocate the flames through inhibiting the heat and mass transfer between underlying polymer and flame zone.

3.5. Others

In addition to these allotropes described in the preceding, other carbon-based materials such as carbon black, carbon nitride, and carbon aerogels have also been investigated in flame retardant polymer nanocomposites, and the current progress in this area will be summarized and discussed in this section.

3.5.1. Carbon black

Like graphite, carbon black is an abundant, low density, electrical conductive and low cost filler that has been widely used in fabricating polymer composites. Previous study indicates that the inclusion of 10 wt% of carbon black not only dramatically enhances the thermal stability of PP composites both under nitrogen (+41 °C in T_{5wt%}) and in air (+69 °C in T_{5wt%}), but also improves flame retardancy in terms of a 74% reduction in PHRR observed from cone

Table 8

Synergistic effect of EG with other additives on flame retardant properties of polymer composites.

Polymer	Loading of EG	Type and loading of synergist	Highlights	Reference
PUF	10 wt%	HPCP (15 wt%)	71% reduction in PHRR compared to that of PUF observed from cone calorimetry	[148]
PUF	12.8 wt%	DMMP (3.2 wt%)	65% and 58% reduction in PHRR and THR, respectively, compared to those of PUF.	[150]
PLA	11.25 wt%	APP (3.75 wt%)	LOI value of 36.5% and V-0 rating in UL-94 tests, greatly improved flame retardant properties compared to composites with APP or EG alone.	[155]
WF/PP	10 wt%	IFR (15 wt%)	77% reduction in PHRR relative to the control sample, LOI value of 38.8%, UL-94 V-0 rating.	[163]
PET	2.5 wt%	Clay (2.5 wt%)	56% and 25% reduction in PHRR and TSR, respectively, observed from cone calorimetry.	[164]
PVC	5 wt%	Phosphate ester (Reefos 50) (60 phr)	Reduction in PHRR from 325 to 63 kW/m ² and THR from 55 to only 10.7 MJ/m ² .	[166]
WF/ABS	12.5 wt%	APP (7.5 wt%)	LOI of 34.2% and a V-0 rating were achieved, whereas LOI values of the samples with EG and APP alone were only 30.5% and 24.5%, respectively.	[168]
ABS	11.25 wt%	APP (3.75 wt%)	LOI value of 31% and UL-94 V-0 rating were achieved, while the samples containing EG and APP alone only passed V-1 rating at the same loading.	[169]

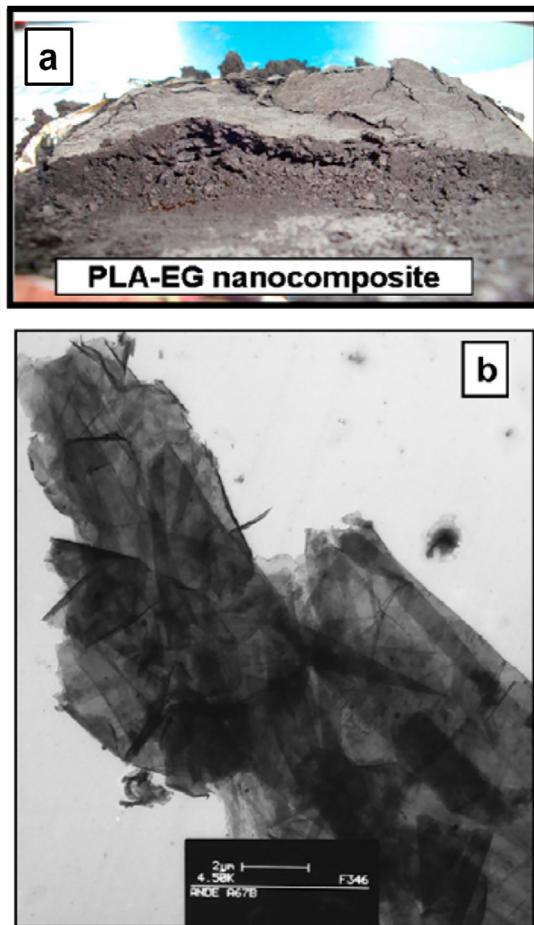


Fig. 17. (a) Illustration of the char formed in PLA-EG composite during cone calorimeter testing and (b) TEM image realized on the char of PLA-EG composite. [174], Copyright 2010.

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calorimetry [175]. The enhanced behavior may be attributed to the trapping of peroxy radicals by carbon black nanoparticles at elevated temperature to form a gelled-ball cross-linked network, as evidenced by the rheological properties, that serves as a barrier to both mass and heat transfer. Besides the sole use of carbon black,

it is also used as synergist with other flame retardant additives. The combination of carbon black and Ni₂O₃ reveals more efficient than carbon black or Ni₂O₃ individually to enhance the char yield of PLA as well as improvement in the char structure [176]. Synergistic effects have also been observed between carbon black and CNT [177] or graphene [178] in flame retardant polyolefins.

3.5.2. Carbon nitride

Graphitic carbon nitride is a stacked two-dimensional material consisting of C, N, and some impurity H. In contrast to the majority of carbon-based materials, it has electron-rich properties, and basic surface functionalities owing to the existence of N and H atoms [179,180]. It is thereby considered as a potential candidate to complement carbon in material applications. Previous study implies that graphitic carbon nitride endows sodium alginate nanocomposites with enhanced thermal stability and mechanical properties [181]. Copper cobaltate/graphitic carbon nitride (named C-CuCo₂O₄) hybrids are synthesized by a facile hydrothermal method and then incorporated into the thermoplastic polyurethane (TPU) using a melt compounding approach [182]. The incorporation of C-CuCo₂O₄ not only suppresses the PHRR (-37% compared to that of the control TPU), but also reduces the smoke toxicity including CO concentration during combustion. Improvements in the thermal stability and the flame retardancy could be ascribed to the physical barrier effect of graphitic carbon nitride nanosheets and the catalytic activity of CO from copper cobaltate. Up to now, the utilization of graphitic carbon nitride or its derivatives as flame retardants is rarely reported and further investigation is warranted.

3.5.3. Carbon aerogels

Carbon aerogels have shown a thriving development over the last few decades due to their advantages of ultralight weight, high porosity, large specific surface area and high electrical conductivity [183]. A facile route to produce carbon aerogels by pyrolysis of regenerated cellulose aerogels has been reported, giving a product that displays multifunctionality of hydrophobic properties, electrical conductivity, and fire resistance (Fig. 18) [184]. As may be seen, these carbon aerogels do not support any burning when exposed to the flame of alcohol burner, implying superior fire retardant behavior. Carbon aerogels based on bacterial cellulose pellicles [185] or graphene oxide [186] with similar strong fire resistance have also been reported. These multifunctional carbon aerogels will provide a brand new platform for many potential applications such as 3D electrode materials, advanced sensors and catalyst supports.

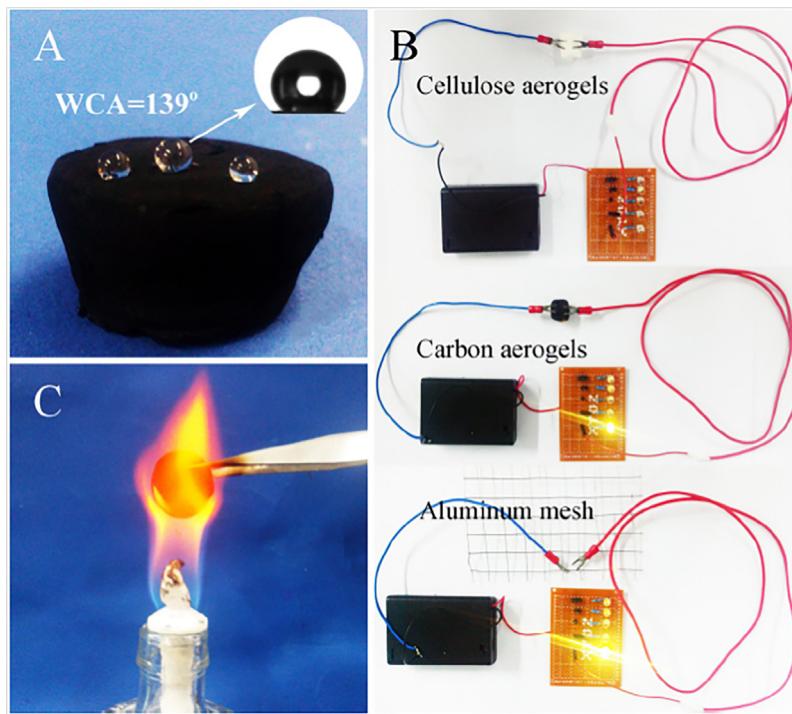


Fig. 18. (A) Hydrophobic carbon aerogel with several water drops on the surface, and the inset shows the water contact angle measurement. (B) Snapshots of electrical tests of the cellulose aerogel, the carbon aerogel and the aluminum mesh in a circuit. (C) Digital photograph of the carbon aerogel in a hot flame of an alcohol burner. [184], Copyright 2014.

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4. Summary and perspectives

Carbon-based materials have been widely used in fabricating polymer composites over the past few decades. In contrast to conventional flame retardants, the incorporation of carbon-based materials can improve the fire retardancy of polymers as well as the mechanical properties, thermal stability, thermal conductivity and electrical conductivity, promising behavior for the development of high performance polymer (nano)composites. For instance, in the case of graphene/polymer nanocomposites, the significant reduction in PHRR and TSP were observed at a very low graphene content (≤ 5 wt%). Regarding the flame retardant efficiency of the carbon-based additives, a comparative study on the influence of various carbon-based additives including thermally reduced graphite oxide (TRGO), multi-layer graphene (MLG250), carbon black (CB), multi-wall nanotubes (MWNT) and expanded graphite (EG) on the flame retardancy and mechanical properties of isotactic polypropylene has been carried out recently [187]. The reduction in PHRR follows the order: PP/EG < PP/MWNT < PP/CB < PP/MLG250 < PP/TRGO. This indicates that MLG250 or TRGO consisting of few graphene layers is most efficient in reducing heat release of polymer materials. The high flame retardant efficiency of MLG250 and TRGO is attributed to a well-exfoliated layered morphology to be favorable over spherical particles, tubes and platelets of other carbon-based additives.

The general principles of the action of carbon-based materials as flame retardants do not significantly differ from the conventional retardants. There are two main routes in which the burning process can be retarded: (1) the addition of carbon-based materials is beneficial to the formation of a protective layer. In most studies, it can be concluded that incorporating carbon-based fillers gives rise to the formation of a continual and compact char layer (without obvious cracks and holes) on the surface of burned polymer materials, that can shield the underlying materials against flame and meanwhile slow down the “fuel flow” (flammable gases derived

from the degradation of the material) able to feed the flame. (2) Some carbon-based materials, such as fullerenes, CNTs and carbon black, can absorb highly active radicals so that the chain reaction of combustion process is interrupted.

However, pristine carbon-based fillers are incompatible with organic polymers and cannot form homogeneous composites, resulting in inferior behavior. In order to overcome this obstacle, surface modification of carbon-based fillers has been adopted to improve the dispersion state of carbon-based fillers in polymer matrices and their interfacial interaction. Surface modification of carbon-based fillers using a range of techniques has been carried out by different research groups with various organo modifiers. Among these reported techniques, the sol-gel method and the hybridization are the very common ways to produce carbon-based filler/polymer composites with good dispersion state. In the future, functionalization and hybridization of carbon based material may be important approaches to further enhance the impact of carbon family material on the fire retardancy and other properties of polymer composites due to the improved interfacial interaction, multifunction, and synergistic effect between varied elements.

Up to now, only a few carbon-based materials, such as graphite and carbon black, have been used into industrial production of flame retardant polymer composites, due to their abundant resource and low cost. The application of other carbon-based materials, such as CNT, graphene, fullerene, etc., in the field of flame retardant polymer composites is mainly at the stage of laboratory experiments or at very early stages of some industrial application. However, such a situation might be completely changed with the large-scale production of CNT or graphene in the foreseen future, because some new techniques using low cost materials to prepare CNT or graphene have been developed. Currently, most of graphene/polymer or CNT/polymer nanocomposites are prepared based on a solvent dispersible method to obtain uniform dispersion, but that is not suitable for industrial applications. However,

the combination of carbon-based materials with the commercial flame retardants has displayed excellent comprehensive properties in polymer composites, that is promising to be commercialized in the future. The discovery of carbon-based materials as flame retardant additives has opened a new dimension for developing fire-safe polymer composite materials in both scientific research and industrial applications.

Acknowledgements

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