



Carbon-family materials for flame retardant polymeric materials



Xin Wang^{a,b}, Ehsan Naderi Kalali^a, Jin-Tao Wan^a, De-Yi Wang^{a,*}

^a IMDEA Materials Institute, C/Eric Kandel, 2, 28906 Getafe, Madrid, Spain

^b State Key Laboratory of Fire Science, University of Science and Technology of China, Anhui 230026, PR China

ARTICLE INFO

Article history:

Received 23 December 2015

Received in revised form

22 November 2016

Accepted 30 January 2017

Available online 7 February 2017

Keywords:

Carbon nanotubes

Graphene

Polymer composites/nanocomposites

Flame retardancy

Flame retardant mechanism

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.

© 2017 Elsevier B.V. All rights reserved.

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.....	34

* Corresponding author.

E-mail address: deyi.wang@imdea.org (D.-Y. Wang).

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-dioxiphospacyclohexane 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	Poly lactide
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

Fillers

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

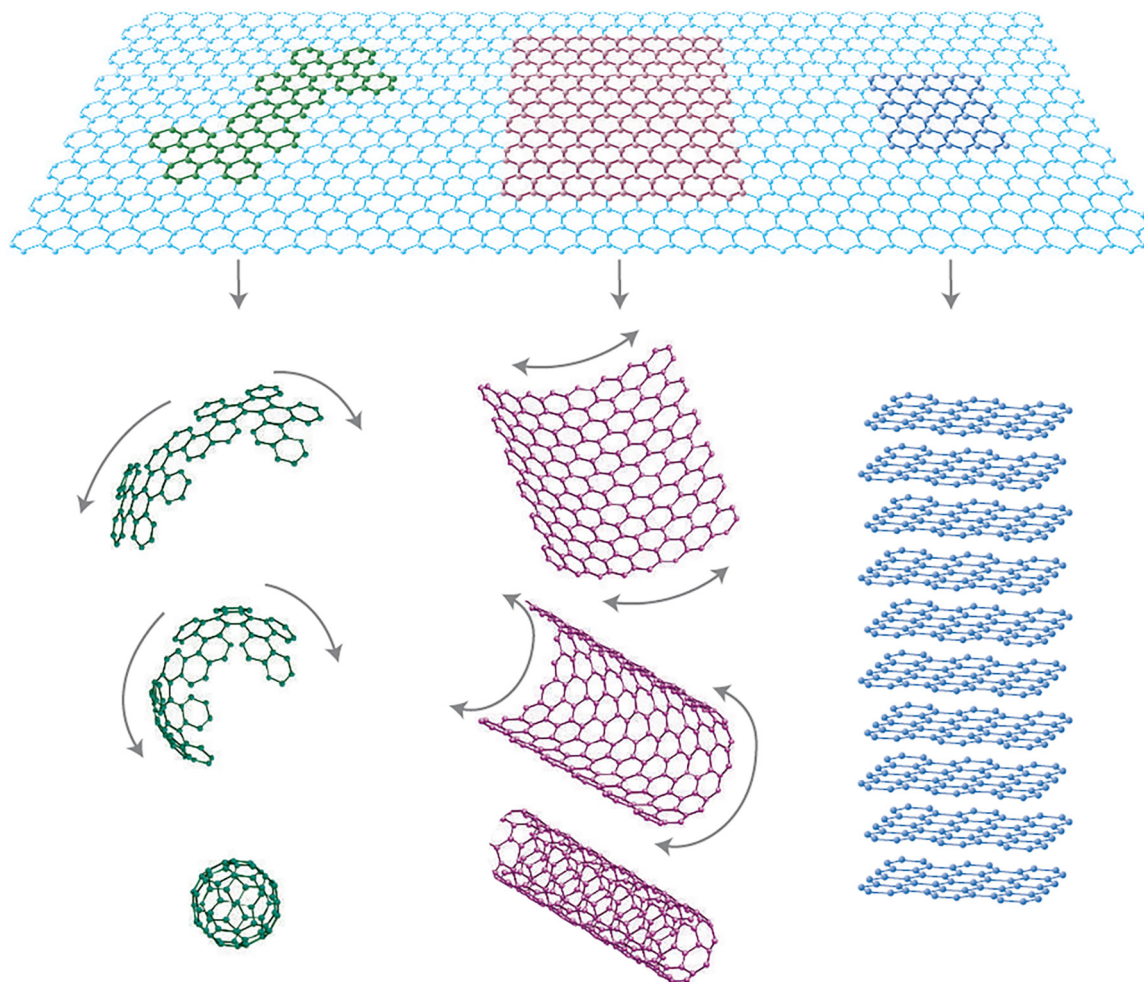


Fig. 1. Graphene, the building block of all graphitic forms, can be wrapped up into 0-D buckyballs, rolled into 1-D nanotubes, or stacked into 3-D graphite. [4], Copyright 2007.

Reproduced with permission from Nature Publishing Group.

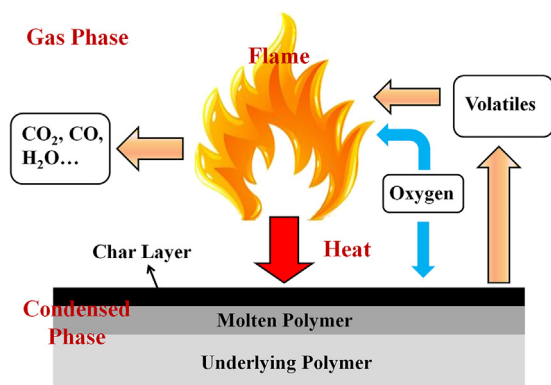


Fig. 2. Illustration of model for flame retardant actions.

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^\bullet and Br^\bullet) in the gas phase, that can react with highly reactive species (such as H^\bullet and OH^\bullet) 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 $80 \text{ mm} \times 10 \text{ mm} \times 4 \text{ mm}$ 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 $C_{\text{ox}}/C_{\text{a}}$ (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]

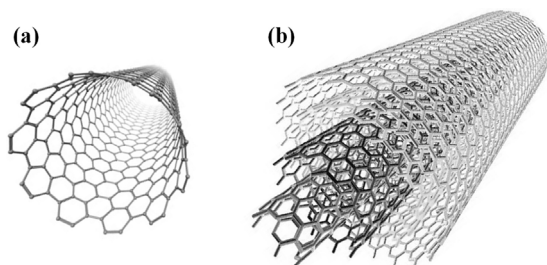


Fig. 3. Schematic representation of (a) single-walled and (b) multi-walled carbon nanotubes.

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 intumescent 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].

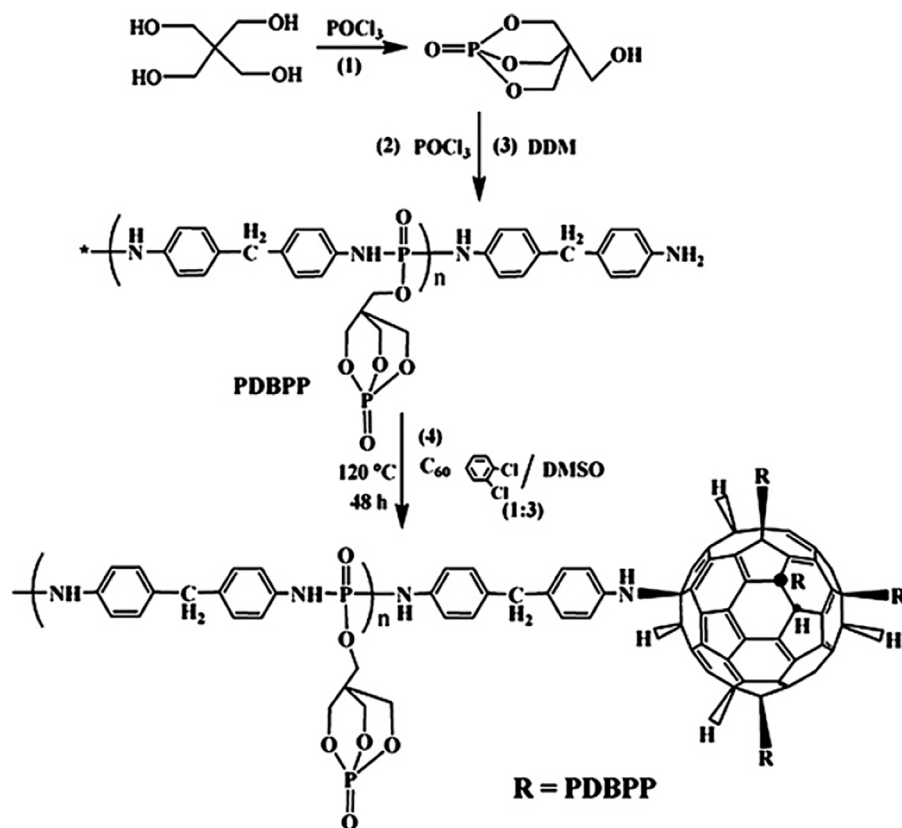
MWNT/PP composites have been prepared by melt blending without using any organic treatment or additional additives [22]. The addition of MWNT imparted high fire retardant efficiency in PP: the PHRR of the composites with 1 vol% MWNT is reduced by about 73% compared to that of PP. The influence of the 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.

Reproduced with permission from the Royal Society of Chemistry.

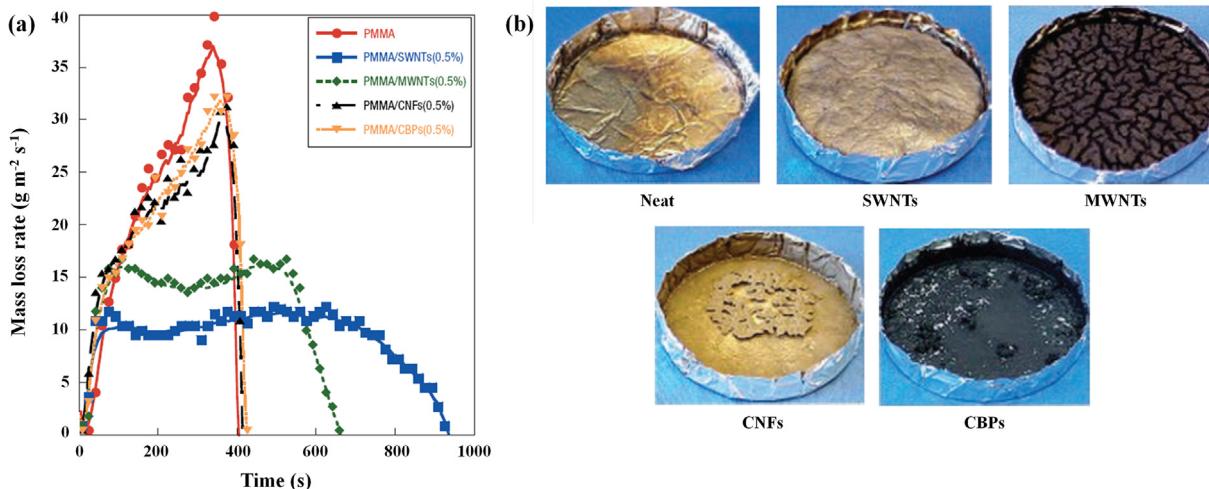


Fig. 4. a) Effects of the nanoparticle type on mass loss rate and (b) Photos of the collected residues. The tests were conducted at an external radiant flux of 50 kW/m² in nitrogen. [25], Copyright 2005.

Reproduced with permission from Nature Publishing Group.

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

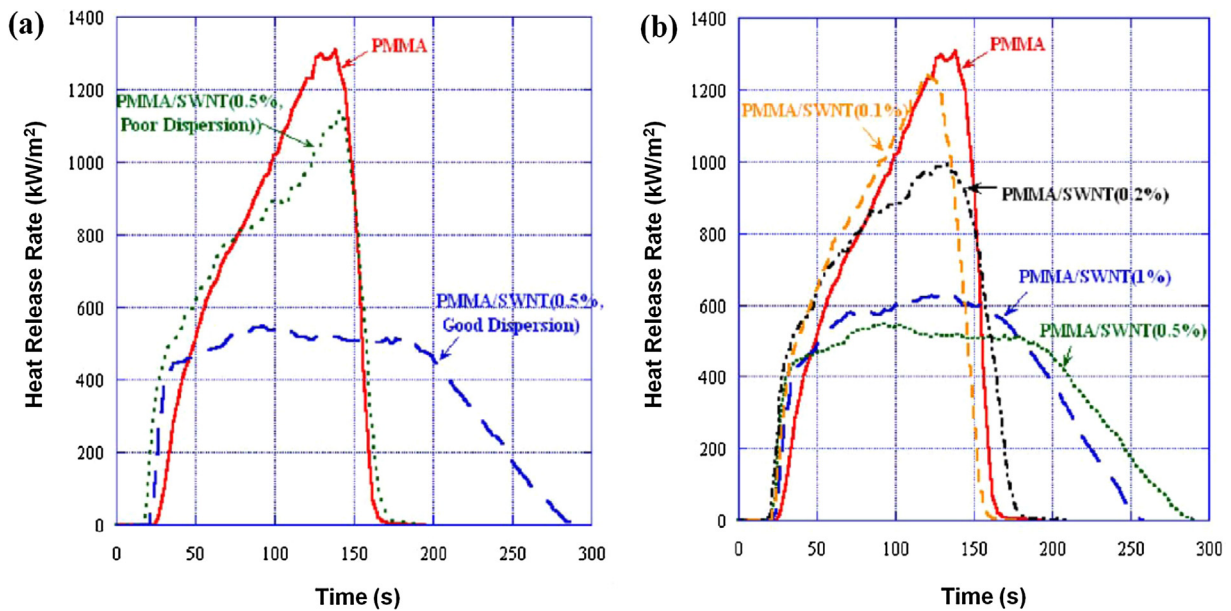


Fig. 5. HRR curves of PMMA containing SWNT: (a) effects of SWNT dispersion and (b) SWNT concentration (50 kW/m^2). [33], Copyright 2004.

Reproduced with permission from Elsevier Ltd.

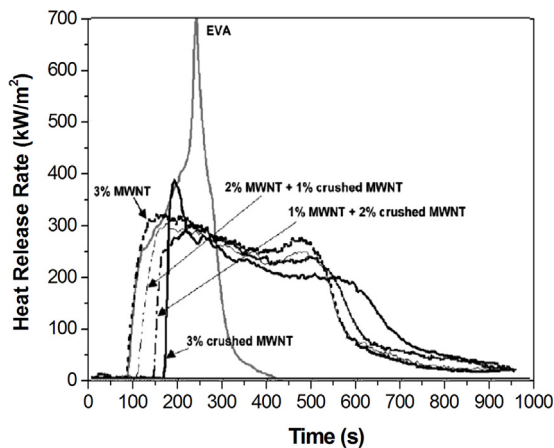


Fig. 6. The effect of the content of crushed MWNTs on the HRR of the EVA composites during the cone calorimetry experiments (35 kW/m^2). [6], Copyright 2008.

Reproduced with permission from Elsevier Ltd.

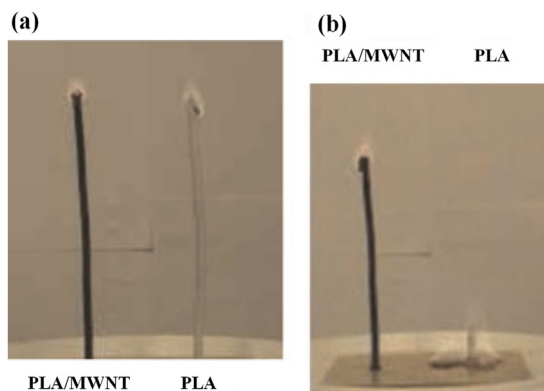


Fig. 7. Flammability test of virgin PLA and PLA/MWNT (a) at the ignition (b) and after 15 s [35], Copyright 2010.

Reproduced with permission from John Wiley & Sons, Ltd.

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 $3 \times 10^{-2} \text{ S cm}^{-1}$ 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.

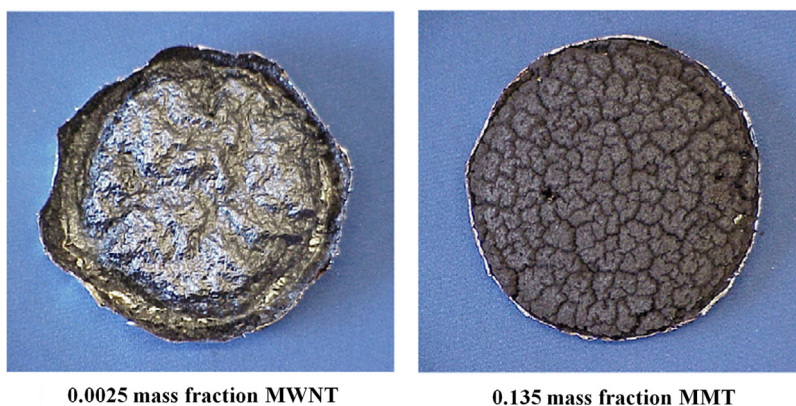


Fig. 8. Residue for MWNT/epoxy and MMT/epoxy samples after gasification test. Unlike MMT/epoxy residue, MWNT/epoxy shows good residue integrity. [32], Copyright 2010.

Reproduced with permission from Elsevier Ltd.

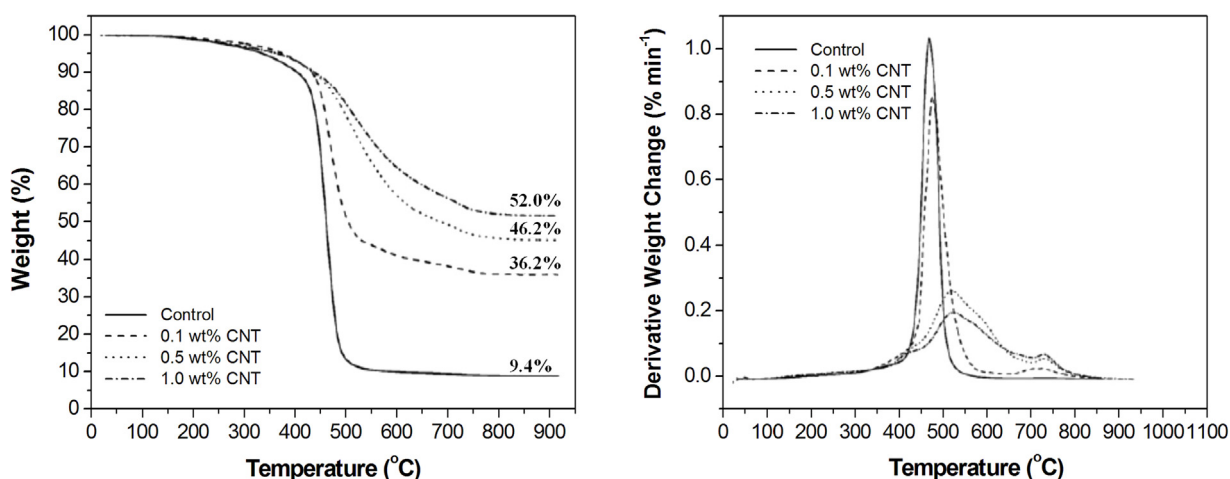


Fig. 9. Thermogravimetric results of the silicone-based foams containing different loading of MWNTs. [36], Copyright 2008. Reproduced with permission from the Royal Society of Chemistry.

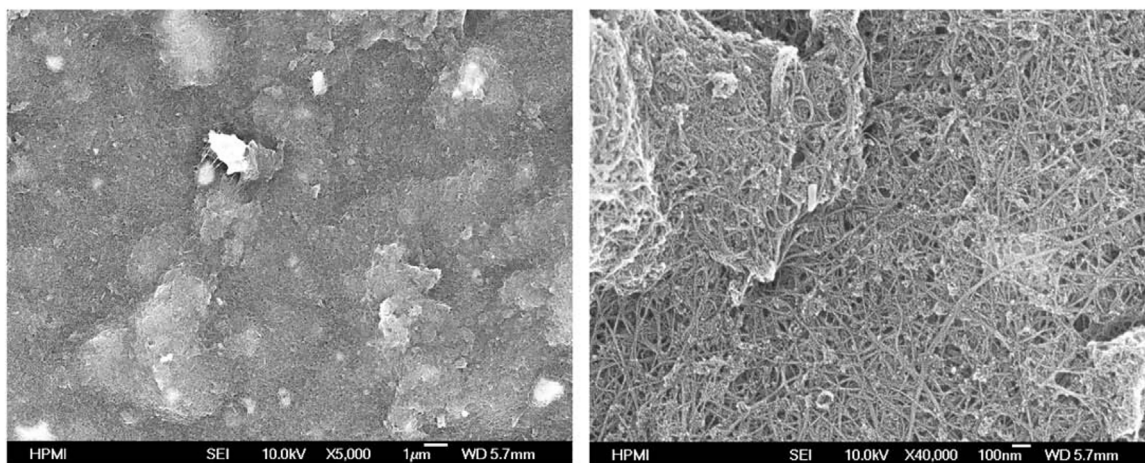


Fig. 10. SEM images of MWNT buckypaper. Left: low magnification; right: high magnification. [39], Copyright 2010. Reproduced with permission from Elsevier Ltd.

- 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,

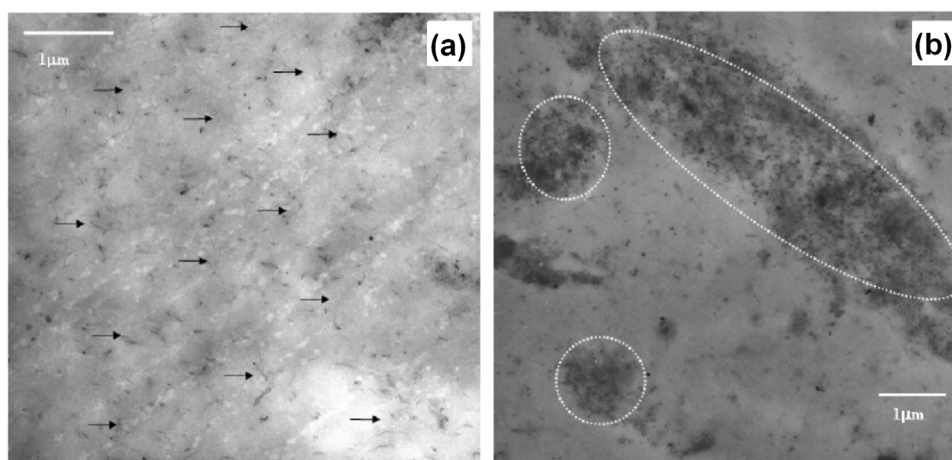


Fig. 11. TEM images of the two nanocomposites at low magnification: (a) EVA + 3 wt% functionalized MWNTs, (b) EVA + 3 wt% MWNTs (arrows in (a) indicate the location of individually spread nanotubes, while dotted curves in (b) highlight aggregates). [50], Copyright 2007.

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 SOCl_2 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

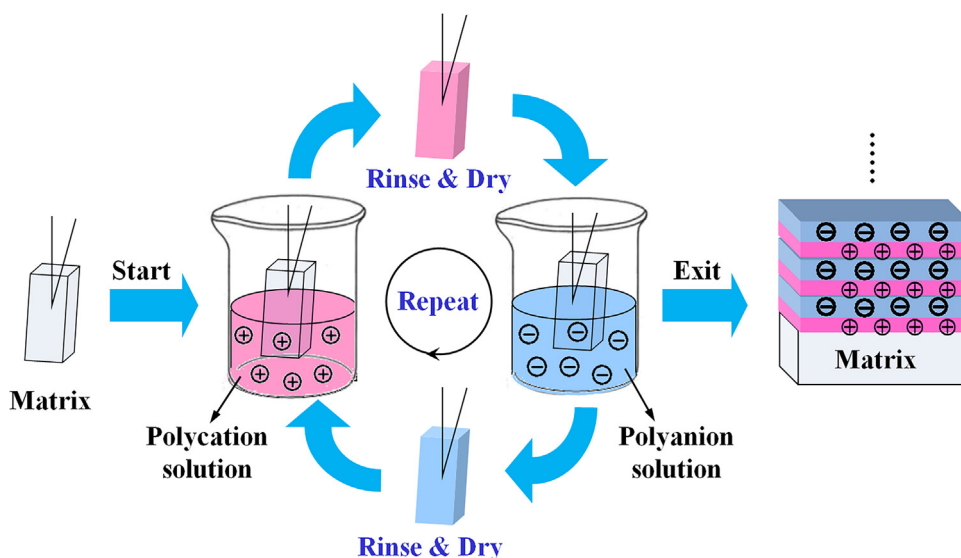
CNT/polymer nanocomposites exhibit low flammability in terms of heat release rate but it fails to other burning measure-

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 multilayered 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

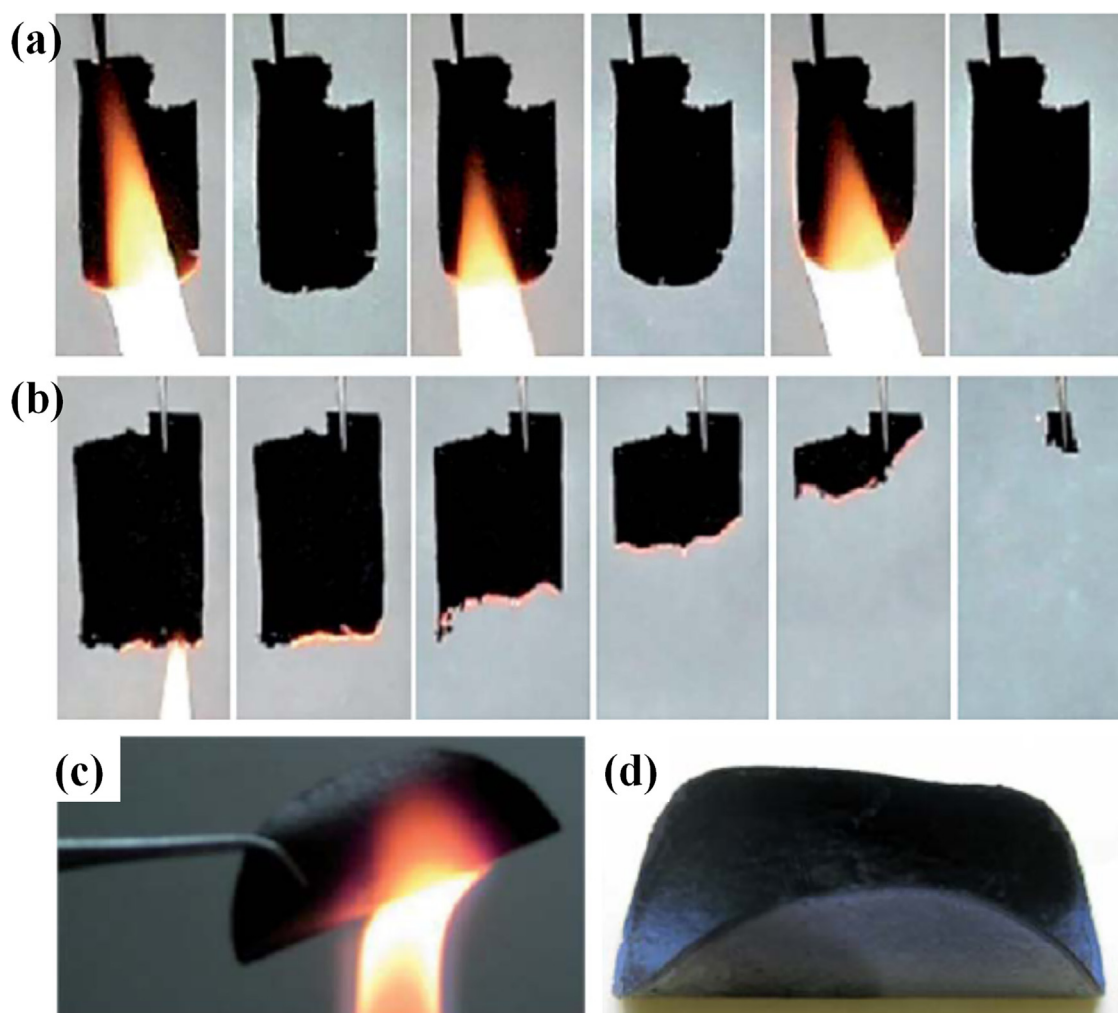


Fig. 12. (a) Snapshots showing flame treatments on reduced graphene oxide film with intervals of 3–4 s. The film was first exposed to a natural gas flame for a few seconds. The burned part turned red hot but didn't propagate, and was quenched after the flame was removed; (b) Snapshots showing flame treatment 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.)

Reproduced with permission from the Royal Society of Chemistry.

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 intumescent 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 SnO₂/graphene-epoxy and Co₃O₄/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-

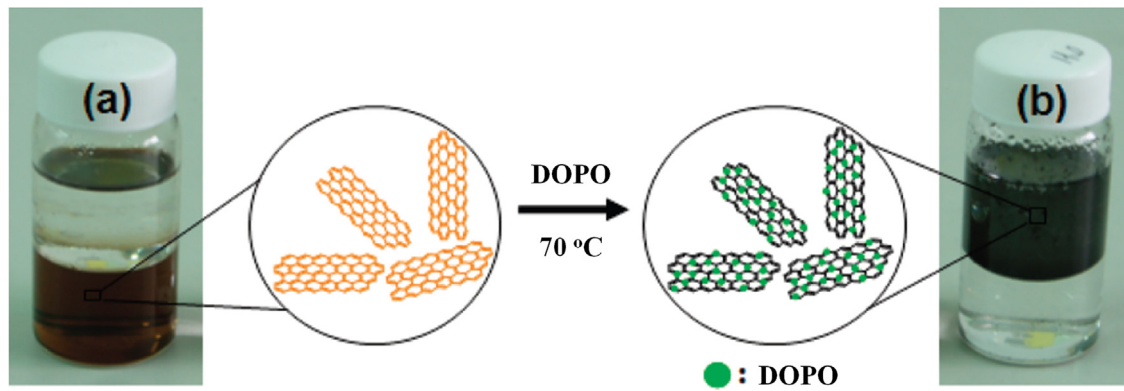
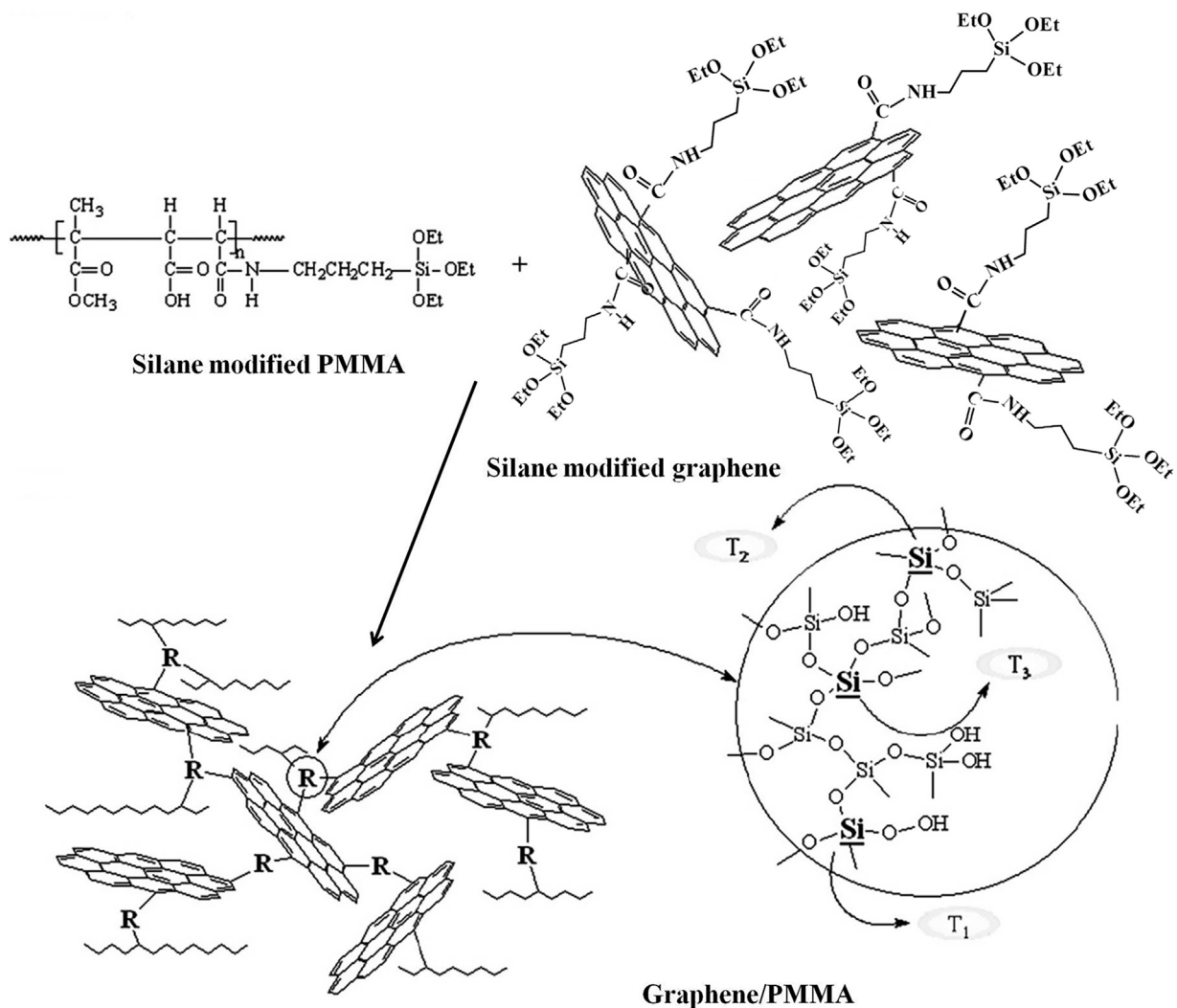


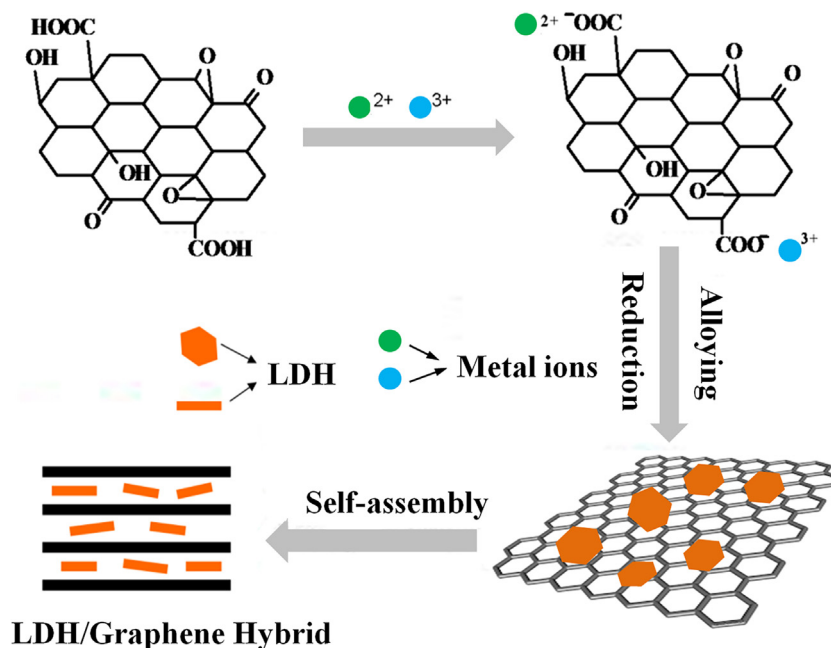
Fig. 13. Photographs of (a) GO and (b) DOPO-reduced GO dispersions in water (bottom) and toluene (top) for 1 month. [97]. Copyright 2012. Reproduced with permission from the American Chemical Society.



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 Co_3O_4 /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 ₃ O ₄ /graphene, SnO ₂ /graphene	29% and 27% reduction in PHRR of Co ₃ O 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 ₃ O ₄ /graphene, NiO/graphene	11% and 23% reduction in PHRR of Co ₃ O ₄ /graphene-PA-6 and NiO/graphene-PA-6 composites, respectively.	[110]
PBS, PLA	Co ₃ O ₄ /graphene	31% and 40% reduction in PHRR of PBS and PLA composites, respectively; the addition of Co ₃ O 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 ₂ O 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]

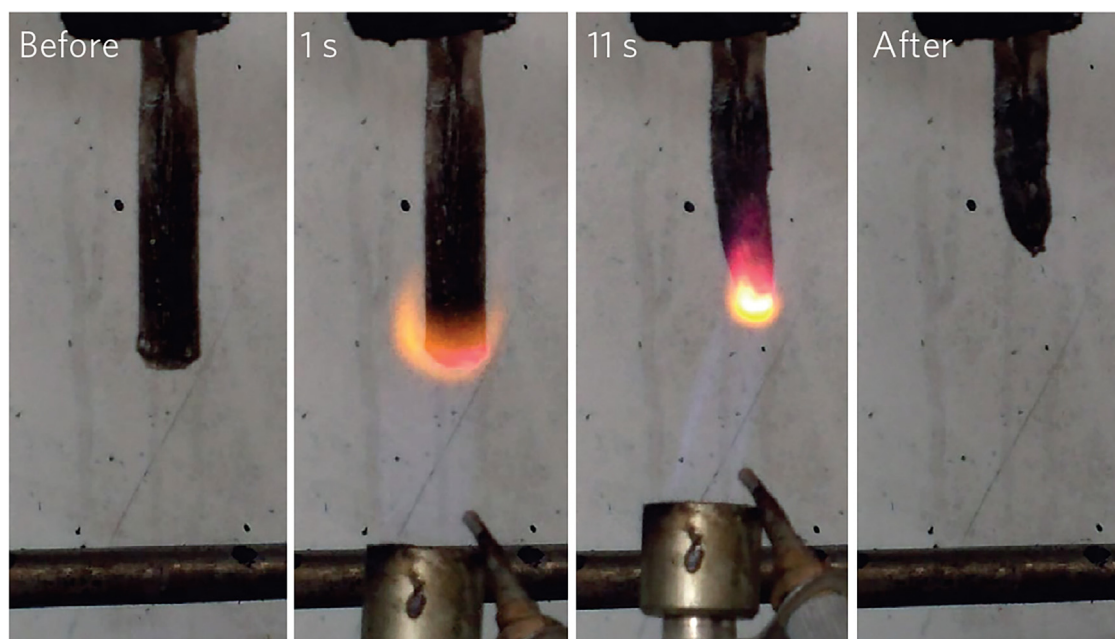


Fig. 14. Vertical burning test (UL94) of a nanocomposite foam containing 77% CNF, 10% graphene oxide, 10% SEP and 3% boric acid (in wt%). The panel shows the foam before the test, after 11 s of application of a methane flame, and the foam after the test, showing high fire retardancy. [125], Copyright 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 intumescent flame retardant polyurethane with 0.5–2.0 wt% of graphene [121].

3.3.5. Flame retardant mechanism of graphene

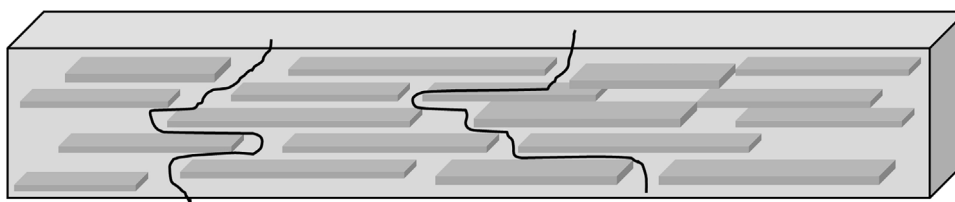
The flame retardant action of graphene is mainly focused on its influence on the structure and yield of the char formed. The 2-D fillers like nano-clays with good barrier properties have been already reported for some time [126,127]. Since GO or graphene possesses platelet morphology, it has potential 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).

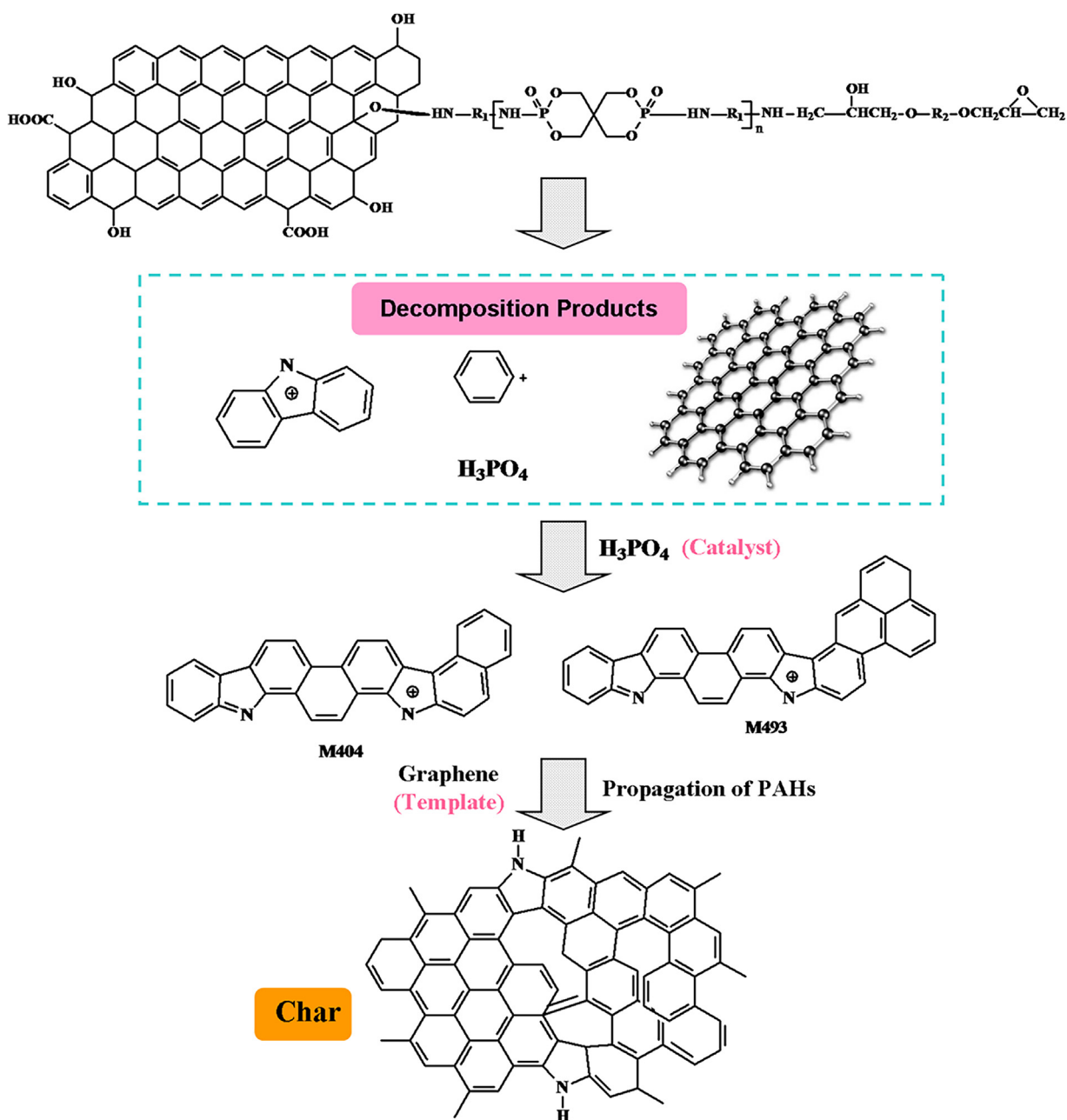
3.4. Graphite

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 nanoplatelet modification of polymer composites

Fig. 15. Permeation path imposed by graphene nanoplatelet 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.

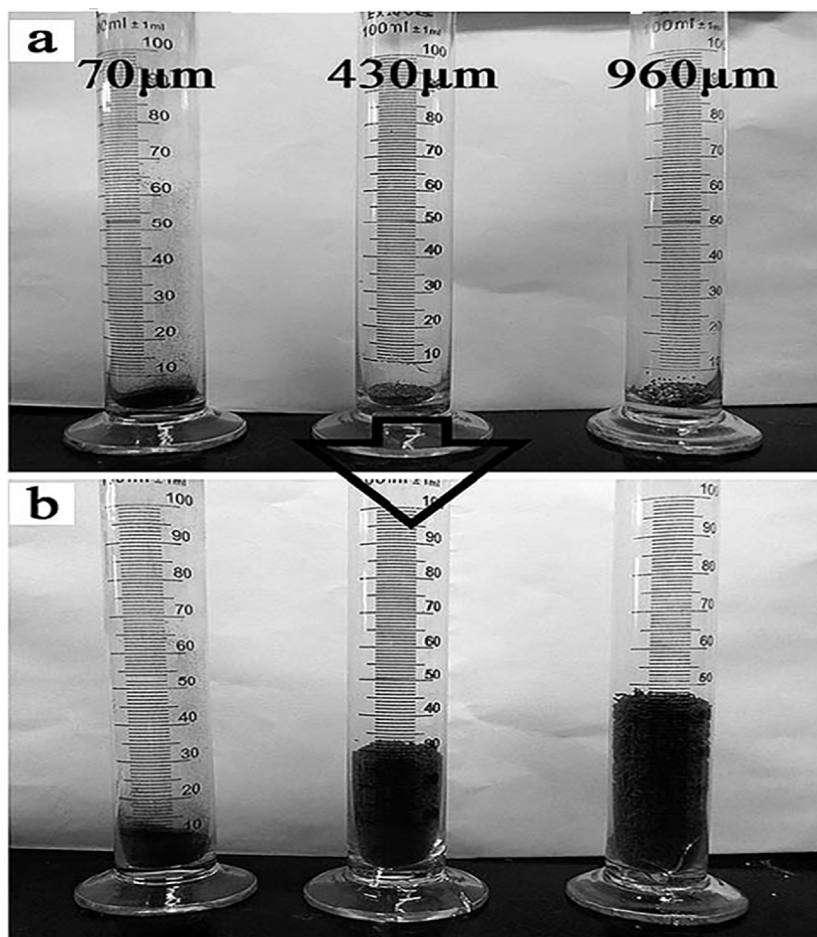


Fig. 16. Digital photos of three kinds of EG particles: (a) original and (b) after heat treatment. Lower size EG particles display lower volume expansion ratio. [140], Copyright 2014.

Reproduced with permission from the Royal Society of Chemistry.

3.4.1. Utilization of EG or modified EG

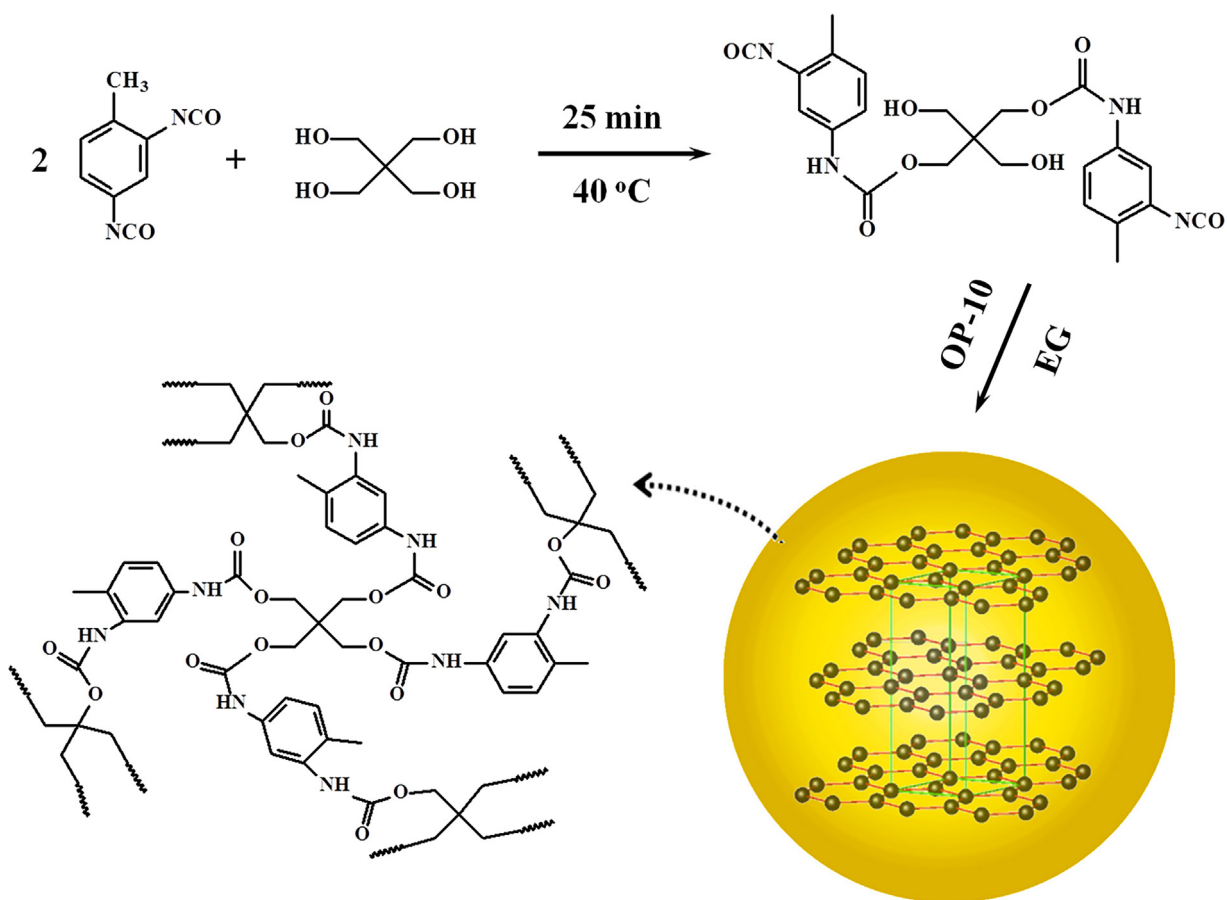
As a type of graphite intercalation compound, EG is in general prepared by exposing flake graphite to concentrated sulphuric acid in combination with strong oxidizers such hydrogen peroxide or potassium permanganate [131–137].

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 SPFs; however, EG-70 μm shows almost no

effect on the improvement in flame retardant properties of SPFs. 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 $^{\circ}\text{C}$ 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 intumescent flame retardant system for polymers where an intumescent 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 intumescent/blowing effect ('chemical' action) in the condensed phase. When exposed to heat, EG, expands hun-

ded 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 (Reofos 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]

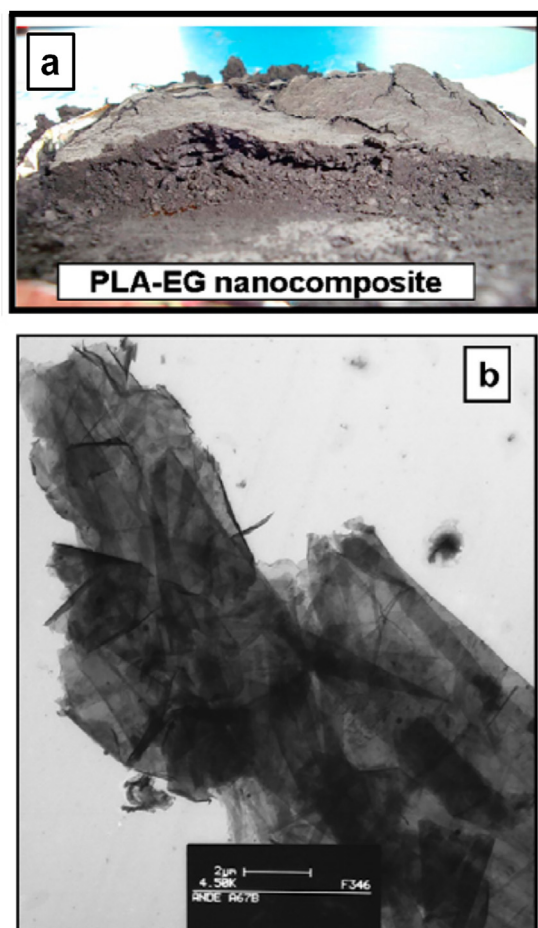


Fig. 17. (a) Illustration of the char formed in PLA-EG composite during cone calorimeter testing and (b) TEM image realized on the char of PLA-EG composite. [174], Copyright 2010.

Reproduced with permission from Elsevier Ltd.

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.

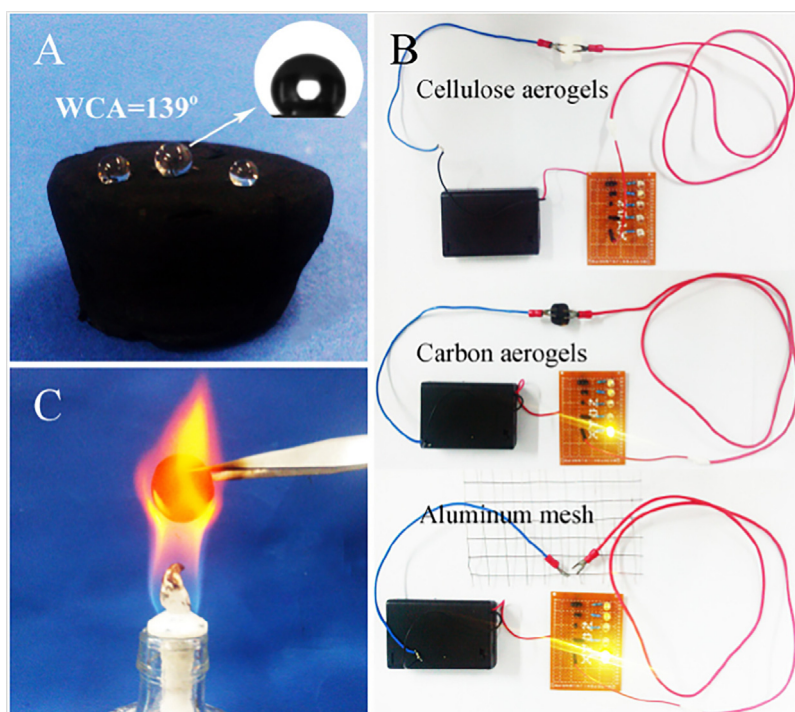


Fig. 18. (A) Hydrophobic carbon aerogel with several water drops on the surface, and the inset shows the water contact angle measurement. (B) Snapshots of electrical tests of the cellulose aerogel, the carbon aerogel and the aluminum mesh in a circuit. (C) Digital photograph of the carbon aerogel in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

Reproduced with permission from Elsevier Ltd.

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

The authors are grateful to thank partly support by the European Commission under the 7th Framework Programme (Marie Curie Career Integration Grant), Ramón y Cajal grant (RYC-2012-10737) and the COST Action CM1302 “European Network on Smart Inorganic Polymers” (SIPs).

References

- [1] Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C_{60} : buckminsterfullerene. *Nature* 1985;318:162–3.
- [2] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354:56–8.
- [3] Novoselov KS, Geim AK, Morozov S, Jiang D, Zhang Y, Dubonos S, et al. Electric field effect in atomically thin carbon films. *Science* 2004;306:666–9.
- [4] Geim AK, Novoselov KS. The rise of graphene. *Nat Mater* 2007;6:183–91.
- [5] Dasari A, Yu ZZ, Cai GP, Mai YW. Recent developments in the fire retardancy of polymeric materials. *Prog Polym Sci* 2013;38:1357–87.
- [6] Laoutid F, Bonnaud L, Alexandre M, Lopez-Cuesta JM, Dubois Ph. New prospects in flame retardant polymer materials: from fundamentals to nanocomposites. *Mater Sci Eng R* 2009;63:100–25.
- [7] Jimenez M, Duquesne S, Bourbigot S. Intumescent fire protective coating: toward a better understanding of their mechanism of action. *Thermochim Acta* 2006;449, 16–16.
- [8] Wang X, Song L, Pornwannchai W, Hu Y, Kandola B. The effect of graphene presence in flame retarded epoxy resin matrix on the mechanical and flammability properties of glass fiber-reinforced composites. *Composites Part A* 2013;53:88–96.
- [9] Wang X, Song L, Yang HY, Xing WY, Kandola B, Hu Y. Simultaneous reduction and surface functionalization of graphene oxide with POSS for reducing fire hazards in epoxy composites. *J Mater Chem* 2012;22:22037–43.
- [10] Zhu W, Weil ED, Mukhopadhyay S. Intumescent flame-retardant system of phosphates and 5, 5', 5'', 5''', 5''''-hexamethyltris (1, 3, 2-dioxaphosphorinanemethan) amine 2, 2', 2''-trioxide for polyolefins. *J Appl Polym Sci* 1996;62:2267–80.
- [11] Bourbigot S, Le Bras M, Delobel R, Gengembre L. XPS study of an intumescent coating: II. Application to the ammonium polyphosphate/pentaerythritol/ethylene terpolymer fire retardant system with and without synergistic agent. *Appl Surf Sci* 1997;120:15–29.
- [12] Wang X, Yang HY, Song L, Hu Y, Xing WY, Lu HD. Morphology, mechanical and thermal properties of graphene-reinforced poly (butylene succinate) nanocomposites. *Compos Sci Technol* 2011;72:1–6.
- [13] Feng XM, Wang X, Xing WY, Yu B, Song L, Hu Y. Simultaneous reduction and surface functionalization of graphene oxide by chitosan and their synergistic reinforcing effects in PVA films. *Ind Eng Chem Res* 2013;52:12906–14.
- [14] Loutfy RO, Wexler EM. Ablative and flame-retardant properties of fullerenes. In: Osawa E, editor. *Perspectives of Fullerene Nanotechnology*. Dordrecht: Springer Science + Business Media B.V.; 2002. p. 275–80.
- [15] Song PA, Zhu Y, Tong L, Fang Z. C_{60} reduces the flammability of polypropylene nanocomposites by in situ forming a gelled-ball network. *Nanotechnology* 2008;19(225707):1–10.
- [16] Krusic P, Wasserman E, Keizer P, Morton J, Preston K. Radical reactions of C_{60} . *Science* 1991;254:1183–5.
- [17] Troitskii B, Troitskaya L, Dmitriev A, Yakhnov A. Inhibition of thermo-oxidative degradation of poly (methyl methacrylate) and polystyrene by C_{60} . *Eur Polym J* 2000;36:1073–84.
- [18] Song PA, Liu H, Shen Y, Du B, Fang ZP, Wu Y. Fabrication of dendrimer-like fullerene (C_{60})-decorated oligomeric intumescent flame retardant for reducing the thermal oxidation and flammability of polypropylene nanocomposites. *J Mater Chem* 2009;19:1305–13.
- [19] Song PA, Shen Y, Du B, Guo Z, Fang ZP. Fabrication of fullerene-decorated carbon nanotubes and their application in flame-retarding polypropylene. *Nanoscale* 2009;1:118–21.
- [20] Demczyk B, Wang Y, Cumings J, Hetman M, Han W, Zettl A, et al. Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes. *Mater Sci Eng A* 2002;334:173–8.
- [21] Kashiwagi T, Grulke E, Hilding J, Groth K, Harris R, Butler K, et al. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. *Polymer* 2004;45:4227–39.
- [22] Kashiwagi T, Grulke E, Hilding J, Harris R, Awad W, Douglas J. Thermal degradation and flammability properties of poly (propylene)/carbon nanotube composites. *Macromol Rapid Commun* 2002;23:761–5.
- [23] Costache MC, Heidecker MJ, Manias E, Camino G, Frache A, Beyer G, et al. The influence of carbon nanotubes, organically modified montmorillonites and layered double hydroxides on the thermal degradation and fire retardancy of polyethylene, ethylene-vinyl acetate copolymer and polystyrene. *Polymer* 2007;48:6532–45.
- [24] Hapuarachchi TD, Peijs T. Multiwalled carbon nanotubes and sepiolite nanoclays as flame retardants for poly lactide and its natural fibre reinforced composites. *Composites Part A* 2010;41:954–63.
- [25] Kashiwagi T, Du F, Douglas JF, Winey KI, Harris RH, Shields JR. Nanoparticle networks reduce the flammability of polymer nanocomposites. *Nat Mater* 2005;4:928–33.
- [26] Kashiwagi T, Mu M, Winey K, Cipriano B, Raghavan S, Pack S, et al. Relation between the viscoelastic and flammability properties of polymer nanocomposites. *Polymer* 2008;49:4358–68.
- [27] Kashiwagi T, Fagan J, Douglas JF, Yamamoto K, Heckert AN, Leigh SD, et al. Relationship between dispersion metric and properties of PMMA/SWNT nanocomposites. *Polymer* 2007;48:4855–66.
- [28] Scharrel B, Pötschke P, Knoll U, Abdel-Goad M. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. *Eur Polym J* 2005;41:1061–70.
- [29] Scharrel B, Braun U, Knoll U, Bartholmai M, Goering H, Neubert D, et al. Mechanical, thermal, and fire behavior of bisphenol A polycarbonate/multiwall carbon nanotube nanocomposites. *Polym Eng Sci* 2008;48:149–58.
- [30] Patel P, Stec AA, Hull TR, Naffakh M, Diez-Pascual AM, Ellis G, et al. Flammability properties of PEEK and carbon nanotube composites. *Polym Degrad Stabil* 2012;97:2492–502.
- [31] Zúñiga C, Bonnaud L, Lligadas G, Ronda JC, Galà M, Cádiz V, et al. Convenient and solventless preparation of pure carbon nanotube/polybenzoxazine nanocomposites with low percolation threshold and improved thermal and fire properties. *J Mater Chem A* 2014;2:6814–22.
- [32] Rahatekar SS, Zammarano M, Matko S, Koziol KK, Windle AH, Nyden M, et al. Effect of carbon nanotubes and montmorillonite on the flammability of epoxy nanocomposites. *Polym Degrad Stabil* 2010;95:870–9.
- [33] Kashiwagi T, Du F, Winey KI, Groth KM, Shields JR, Bellayer SP, Kim H, Douglas JF. Flammability properties of polymer nanocomposites with single-walled carbon nanotubes: effects of nanotube dispersion and concentration. *Polymer* 2005;46:471–81.
- [34] Peeterbroeck S, Laoutid F, Swoboda B, Lopez-Cuesta JM, Moreau N, Nagy JB, et al. How carbon nanotube crushing can improve flame retardant behaviour in polymer nanocomposites. *Macromol Rapid Commun* 2007;28:260–4.
- [35] Bourbigot S, Fontaine G, Gallos A, Bellayer S. Reactive extrusion of PLA and of PLA/carbon nanotubes nanocomposite: processing, characterization and flame retardancy. *Polym Adv Technol* 2011;22:30–7.
- [36] Verdejo R, Barroso-Bujans F, Rodriguez-Perez MA, Antonio de Saja J, Arroyo M, Lopez-Manchado MA. Carbon nanotubes provide self-extinguishing grade to silicone-based foams. *J Mater Chem* 2008;18:3933–9.
- [37] Anderson RE, Guan J, Ricard M, Dubev G, Su J, Lopinski G, et al. Multifunctional single-walled carbon nanotube–cellulose composite paper. *J Mater Chem* 2010;20:2400–7.
- [38] Wu Q, Zhang C, Liang R, Wang B. Fire retardancy of a buckypaper membrane. *Carbon* 2008;46:1164–5.
- [39] Wu Q, Zhu W, Zhang C, Liang Z, Wang B. Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites. *Carbon* 2010;48:1799–806.
- [40] Fu X, Zhang C, Liu T, Liang R, Wang B. Carbon nanotube buckypaper to improve fire retardancy of high-temperature/high-performance polymer composites. *Nanotechnology* 2010;21(235701):1–8.
- [41] Wu Q, Bao J, Zhang C, Liang R, Wang B. The effect of thermal stability of carbon nanotubes on the flame retardancy of epoxy and bismaleimide/carbon fiber/buckypaper composites. *J Therm Anal Calorim* 2011;103:237–42.
- [42] He Q, Yuan T, Yan X, Ding D, Wang Q, Luo Z, et al. Flame-retardant polypropylene/multiwall carbon nanotube nanocomposites: effects of surface functionalization and surfactant molecular weight. *Macromol Chem Phys* 2014;215:327–40.
- [43] Kuan CF, Chen WJ, Li YL, Chen CH, Kuan HC, Chiang CL. Flame retardance and thermal stability of carbon nanotube epoxy composite prepared from sol-gel method. *J Phys Chem Solids* 2010;71:539–43.
- [44] Wang L, Jiang PK. Thermal and flame retardant properties of ethylene-vinyl acetate copolymer/modified multiwalled carbon nanotube composites. *J Appl Polym Sci* 2011;119:2974–83.
- [45] Ebadi M, Mirdamadian Z, Ghanbari D, Moradi L. The effect of aminated carbon nanotube and phosphorus pentoxide on the thermal stability and flame retardant properties of the acrylonitrile–butadiene–styrene. *J Clust Sci* 2014;25:541–8.
- [46] Gashti MP, Almasian A. UV radiation induced flame retardant cellulose fiber by using polyvinylphosphonic acid/carbon nanotube composite coating. *Composites Part B* 2013;45:282–9.
- [47] Liu Y, Wang X, Qi K, Xin J. Functionalization of cotton with carbon nanotubes. *J Mater Chem* 2008;18:3454–60.
- [48] Song PA, Xu L, Guo Z, Zhang Y, Fang ZP. Flame-retardant-wrapped carbon nanotubes for simultaneously improving the flame retardancy and mechanical properties of polypropylene. *J Mater Chem* 2008;18:5083–91.

- [49] Ma HY, Tong LF, Xu ZB, Fang ZP. Functionalizing carbon nanotubes by grafting on intumescent flame retardant: nanocomposite synthesis, morphology, rheology, and flammability. *Adv Funct Mater* 2008;18:414–21.
- [50] Peeterbroeck S, Laoutid F, Taulemesse JM, Monteverde F, Lopez-Cuesta JM, Nagy JB, et al. Mechanical properties and flame-retardant behavior of ethylene vinyl acetate/high-density polyethylene coated carbon nanotube nanocomposites. *Adv Funct Mater* 2007;17:2787–91.
- [51] Xu G, Cheng J, Wu H, Lin Z, Zhang Y, Wang H. Functionalized carbon nanotubes with oligomeric intumescent flame retardant for reducing the agglomeration and flammability of poly (ethylene vinyl acetate) nanocomposites. *Polym Compos* 2013;34:109–21.
- [52] Wang L, Yu J, Tang Z, Jiang P. Synthesis, characteristic, and flammability of modified carbon nanotube/poly(ethylene-co-vinyl acetate) nanocomposites containing phosphorus and silicon. *J Mater Sci* 2010;45:6668–76.
- [53] Wang M, Li B, Wang J, Bai P. Preparation and properties of polysiloxane grafting multi-walled carbon nanotubes/polycarbonate nanocomposites. *Polym Adv Technol* 2011;22:1738–46.
- [54] Yu H, Liu J, Wen X, Jiang Z, Wang Y, Wang L, et al. Charing polymer wrapped carbon nanotubes for simultaneously improving the flame retardancy and mechanical properties of epoxy resin. *Polymer* 2011;52:4891–8.
- [55] Zhang Z, Yuan L, Liang G, Gu A, Qiang Z, Yang C, et al. Unique hybridized carbon nanotubes and their high performance flame retarding composites with high smoke suppression, good toughness and low curing temperature. *J Mater Chem A* 2014;2:4975–88.
- [56] Zhang T, Du Z, Zou W, Li H, Zhang C. Hydroxyl-phosphazene-wrapped carbon nanotubes and its application in ethylene-vinyl acetate copolymer. *J Appl Polym Sci* 2013;130:4245–54.
- [57] Ma HY, Zhao L, Liu J, Wang J, Xu J. Functionalizing carbon nanotubes by grafting cyclotriphosphazene derivative to improve both mechanical strength and flame retardancy. *Polym Compos* 2014;35:2187–93.
- [58] Tang Y, Gou J, Hu Y. Covalent functionalization of carbon nanotubes with polyhedral oligomeric silsesquioxane for superhydrophobicity and flame retardancy. *Polym Eng Sci* 2013;53:1021–30.
- [59] Du B, Fang Z. The preparation of layered double hydroxide wrapped carbon nanotubes and their application as a flame retardant for polypropylene. *Nanotechnology* 2010;21(315603):1–6.
- [60] Zhang T, Du Z, Zou W, Li H, Zhang C. The flame retardancy of blob-like multi-walled carbon nanotubes/silica nanospheres hybrids in poly (methyl methacrylate). *Polym Degrad Stabil* 2012;97:1716–23.
- [61] Pal K, Kang DJ, Zhang ZX, Kim JK. Synergistic effects of zirconia-coated carbon nanotube on crystalline structure of polyvinylidene fluoride nanocomposites: electrical properties and flame-retardant behavior. *Langmuir* 2009;26:3609–14.
- [62] Mi YN, Liang G, Gu A, Zhao F, Yuan L. Thermally conductive aluminum nitride/multiwalled carbon nanotube/cyanate ester composites with high flame retardancy and low dielectric loss. *Ind Eng Chem Res* 2013;52:3342–53.
- [63] Ran S, Guo Z, Chen C, Zhao L, Fang Z. Carbon nanotube bridged cerium phenylphosphonate hybrids, fabrication and their effects on the thermal stability and flame retardancy of the HDPE/BFR composite. *J Mater Chem A* 2014;2:2999–3007.
- [64] Yu H, Liu J, Wang Z, Jiang Z, Tang T. Combination of carbon nanotubes with Ni₂O₃ for simultaneously improving the flame retardancy and mechanical properties of polyethylene. *J Phys Chem C* 2009;113:13092–7.
- [65] Du B, Fang Z. Effects of carbon nanotubes on the thermal stability and flame retardancy of intumescent flame-retarded polypropylene. *Polym Degrad Stabil* 2011;96:1725–31.
- [66] Shahvazian M, Ghaffari M, Azimi H, Jahanmardi R. Effects of multi-walled carbon nanotubes on flame retardation and thermal stabilization performance of phosphorus-containing flame retardants in polypropylene. *Int Nano Lett* 2012;2(27):1–7.
- [67] Yu H, Zhang Z, Wang Z, Jiang Z, Liu J, Wang L, et al. Double functions of chlorinated carbon nanotubes in its combination with Ni₂O₃ for reducing flammability of polypropylene. *J Phys Chem C* 2010;114:13226–33.
- [68] Lu H, Wilkie CA. Synergistic effect of carbon nanotubes and decabromodiphenyl oxide/Sb₂O₃ in improving the flame retardancy of polystyrene. *Polym Degrad Stabil* 2010;95:564–71.
- [69] Wu Z, Xue M, Wang H, Tian X, Ding X, Zheng K, et al. Electrical and flame-retardant properties of carbon nanotube/poly (ethylene terephthalate) composites containing bisphenol A bis (diphenyl phosphate). *Polymer* 2013;54:3334–40.
- [70] Yang W, Yang B, Lu HD, Song L, Hu Y. Effect of modified carbon nanotube on the thermal behavior, flame retardancy and mechanical properties of poly(1,4-butylene terephthalate)/aluminum phosphinate composites. *Ind Eng Chem Res* 2014;53:18489–96.
- [71] Isitman NA, Kaynak C. Nanoclay and carbon nanotubes as potential synergists of an organophosphorus flame-retardant in poly (methyl methacrylate). *Polym Degrad Stabil* 2010;95:1523–32.
- [72] Pack S, Kashiwagi T, Stemp D, Koo J, Si M, Sokolov JC, et al. Segregation of carbon nanotubes/organoclays rendering polymer blends self-extinguishing. *Macromolecules* 2009;42:6698–709.
- [73] Ye L, Wu Q, Qu B. Synergistic effects and mechanism of multiwalled carbon nanotubes with magnesium hydroxide in halogen-free flame retardant EVA/MH/MWNT nanocomposites. *Polym Degrad Stabil* 2009;94:751–6.
- [74] Wu Z, Wang H, Tian X, Ding X, Xue M, Zhou H, et al. Mechanical and flame-retardant properties of styrene-ethylene-butylene-styrene/carbon nanotube composites containing bisphenol A bis (diphenyl phosphate). *Compos Sci Technol* 2013;82:8–14.
- [75] Li C, Kang NJ, Labrandero SD, Wan J, González C, Wang DY. Synergistic effect of carbon nanotube and polyethersulfone on flame retardancy of carbon fiber reinforced epoxy composites. *Ind Eng Chem Res* 2013;53:1040–7.
- [76] Ma HY, Tong L, Xu Z, Fang ZP. Synergistic effect of carbon nanotube and clay for improving the flame retardancy of ABS resin. *Nanotechnology* 2007;18(375602):1–8.
- [77] Beyer G. Short communication: carbon nanotubes as flame retardants for polymers. *Fire Mater* 2002;26:291–3.
- [78] Kim YS, Davis R. Multi-walled carbon nanotube layer-by-layer coatings with a trilayer structure to reduce foam flammability. *Thin Solid Films* 2014;550:184–9.
- [79] Pan HF, Pan Y, Wang W, Song L, Hu Y, Liew KM. Synergistic effect of layer-by-layer assembled thin films based on clay and carbon nanotubes to reduce the flammability of flexible polyurethane foam. *Ind Eng Chem Res* 2014;53:14315–21.
- [80] Zhang T, Yan H, Peng M, Wang L, Ding H, Fang Z. Construction of flame retardant nanocoating on ramie fabric via layer-by-layer assembly of carbon nanotube and ammonium polyphosphate. *Nanoscale* 2013;5:3013–21.
- [81] Gao F, Beyer G, Yuan Q. A mechanistic study of fire retardancy of carbon nanotube/ethylene vinyl acetate copolymers and their clay composites. *Polym Degrad Stabil* 2005;89:559–64.
- [82] Stoller MD, Park S, Zhu Y, An J, Ruoff RS. Graphene-based ultracapacitors. *Nano Lett* 2008;8:3498–502.
- [83] Lee C, Wei X, Kysar JW, Hone J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* 2008;321:385–8.
- [84] Bolotin KI, Sikes K, Jiang Z, Klima M, Fudenberg G, Hone J, et al. Ultrahigh electron mobility in suspended graphene. *Solid State Commun* 2008;146:351–5.
- [85] Balandin AA, Ghosh S, Bao W, Calizo I, Teweldebrhan D, Miao F, et al. Superior thermal conductivity of single-layer graphene. *Nano Lett* 2008;8:902–7.
- [86] Zhang Y, Tan YW, Stormer HL, Kim P. Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* 2005;438:201–4.
- [87] Kim F, Luo JY, Cruz-Silva R, Cote LJ, Sohn K, Huang JX. Self-propagating domino-like reactions in oxidized graphite. *Adv Funct Mater* 2010;20:2867–73.
- [88] Zhang C, Tjiu WW, Fan W, Yang Z, Huang S, Liu T. Aqueous stabilization of graphene sheets using exfoliated montmorillonite nanoplatelets for multifunctional free-standing hybrid films via vacuum-assisted self-assembly. *J Mater Chem* 2011;21:18011–7.
- [89] Kim MJ, Jeon IY, Seo JM, Dai L, Baek JB. Graphene phosphonic acid as an efficient flame retardant. *ACS Nano* 2014;8:2820–5.
- [90] Hofmann D, Wartig KA, Thomann R, Ditttrich B, Schartel B, Mülhaupt R. Functionalized graphene and carbon materials as additives for melt-extruded flame retardant polypropylene. *Macromol Mater Eng* 2013;298:1322–34.
- [91] Hu J, Zhang F. Self-assembled fabrication and flame-retardant properties of reduced graphene oxide/waterborne polyurethane nanocomposites. *J Therm Anal Calorim* 2014;118:1561–8.
- [92] Lee YR, Kim SC, Lee HI, Jeong HM, Raghu AV, Reddy KR, et al. Graphite oxides as effective fire retardants of epoxy resin. *Macromol Res* 2011;19:66–71.
- [93] Han Y, Wu Y, Shen M, Huang X, Zhu J, Zhang X. Preparation and properties of polystyrene nanocomposites with graphite oxide and graphene as flame retardants. *J Mater Sci* 2013;48:4214–22.
- [94] Liu S, Yan H, Fang Z, Wang H. Effect of graphene nanosheets on morphology, thermal stability and flame retardancy of epoxy resin. *Compos Sci Technol* 2014;90:40–7.
- [95] Xu G, Shi T, Wang Q, Liu J, Yi Y. A facile way to prepare two novel DOPO-containing liquid benzoxazines and their graphene oxide composites. *J Appl Polym Sci* 2015;132(11), <http://dx.doi.org/10.1002/app.41634>, 11 pp.
- [96] Stankovich S, Piner RD, Nguyen ST, Ruoff RS. Synthesis and exfoliation of isocyanate-treated graphene oxide nanoplatelets. *Carbon* 2006;44:3342–7.
- [97] Liao SH, Liu PL, Hsiao MC, Teng CC, Wang CA, Ger MD, et al. One-step reduction and functionalization of graphene oxide with phosphorus-based compound to produce flame-retardant epoxy nanocomposite. *Ind Eng Chem Res* 2012;51:4573–81.
- [98] Li KY, Kuan CF, Kuan HC, Chen CH, Shen MY, Yang JM, et al. Preparation and properties of novel epoxy/graphene oxide nanosheets (GON) composites functionalized with flame retardant containing phosphorus and silicon. *Mater Chem Phys* 2014;146:354–62.
- [99] Hu WZ, Zhan J, Wang X, Hong NN, Wang BB, Song L, et al. Effect of functionalized graphene oxide with hyper-branched flame retardant on flammability and thermal stability of cross-linked polyethylene. *Ind Eng Chem Res* 2014;53:3073–83.
- [100] Yu B, Wang X, Qian XD, Xing WY, Yang H, Ma LY, et al. Functionalized graphene oxide/phosphoramidate oligomer hybrids flame retardant prepared via in situ polymerization for improving the fire safety of polypropylene. *RSC Adv* 2014;4:31782–94.
- [101] Wang X, Xing WY, Feng XM, Yu B, Song L, Hu Y. Functionalization of graphene with grafted polyphosphamide for flame retardant epoxy composites: synthesis, flammability and mechanism. *Polym Chem* 2014;5:1145–54.
- [102] Huang GB, Chen S, Tang S, Gao J. A novel intumescent flame retardant-functionalized graphene: nanocomposite synthesis,

- characterization, and flammability properties. *Mater Chem Phys* 2012;135:938–47.
- [103] Wang Z, Wei P, Qian Y, Liu J. The synthesis of a novel graphene-based inorganic–organic hybrid flame retardant and its application in epoxy resin. *Composites Part B* 2014;60:341–9.
- [104] Qian XD, Song L, Yu B, Wang BB, Yuan BH, Shi YQ, et al. Novel organic–inorganic flame retardants containing exfoliated graphene: preparation and their performance on the flame retardancy of epoxy resins. *J Mater Chem A* 2013;1:6822–30.
- [105] Qian XD, Yu B, Bao CL, Song L, Wang BB, Xing WY, et al. Yuen RK. Silicon nanoparticle decorated graphene composites: preparation and their reinforcement on the fire safety and mechanical properties of polyurea. *J Mater Chem A* 2013;1:9827–36.
- [106] Jiang SD, Bai ZM, Tang G, Hu Y, Song L. Fabrication and characterization of graphene oxide-reinforced poly (vinyl alcohol)-based hybrid composites by the sol–gel method. *Compos Sci Technol* 2014;102:51–8.
- [107] Li YL, Kuan CF, Chen CH, Kuan HC, Yip MC, Chiu SL, et al. L. Preparation, thermal stability and electrical properties of PMMA/functionalized graphene oxide nanosheets composites. *Mater Chem Phys* 2012;134:677–85.
- [108] Wang X, Xing WY, Feng XM, Yu B, Lu HD, Song L, et al. The effect of metal oxide decorated graphene hybrids on the improved thermal stability and the reduced smoke toxicity in epoxy resins. *Chem Eng J* 2014;250:214–21.
- [109] Hong NN, Song L, Wang BB, Stec AA, Hull TR, Zhan J, et al. Co-precipitation synthesis of reduced graphene oxide/NiAl-layered double hydroxide hybrid and its application in flame retarding poly (methyl methacrylate). *Mater Res Bull* 2014;49:657–64.
- [110] Hong NN, Song L, Hull TR, Stec AA, Wang BB, Pan Y, et al. Facile preparation of graphene supported Co_3O_4 and NiO for reducing fire hazards of polyamide 6 composites. *Mater Chem Phys* 2013;142:531–8.
- [111] Wang X, Song L, Yang HY, Xing WY, Lu HD, Hu Y. Cobalt oxide/graphene composite for highly efficient CO oxidation and its application in reducing the fire hazards of aliphatic polyesters. *J Mater Chem* 2012;22:3426–31.
- [112] Wang D, Zhou KQ, Yang W, Xing WY, Hu Y, Gong XL. Surface modification of graphene with layered molybdenum disulfide and their synergistic reinforcement on reducing fire hazards of epoxy resins. *Ind Eng Chem Res* 2013;52:17882–90.
- [113] Wang X, Zhou S, Xing WY, Yu B, Feng XM, Song L, et al. Self-assembly of Ni–Fe layered double hydroxide/graphene hybrids for reducing fire hazard in epoxy composites. *J Mater Chem A* 2013;1:4383–90.
- [114] Wang D, Zhang QJ, Zhou KQ, Yang W, Hu Y, Gong XL. The influence of manganese–cobalt oxide/graphene on reducing fire hazards of poly (butylene terephthalate). *J Hazard Mater* 2014;278:391–400.
- [115] Jiang SD, Bai ZM, Tang G, Hu Y, Song L. Synthesis of ZnS decorated graphene sheets for reducing fire hazards of epoxy composites. *Ind Eng Chem Res* 2014;53:6708–17.
- [116] Jiang SD, Bai ZM, Tang G, Song L, Stec AA, Hull TR, et al. Fabrication of Ce-doped MnO_2 decorated graphene sheets for fire safety applications of epoxy composites: flame retardancy, smoke suppression and mechanism. *J Mater Chem A* 2014;2:17341–51.
- [117] Dong YY, Gui Z, Hu Y, Wu Y, Jiang SH. The influence of titanate nanotube on the improved thermal properties and the smoke suppression in poly (methyl methacrylate). *J Hazard Mater* 2012;209:34–9.
- [118] Song PA, Liu L, Fu S, Yu Y, Jin C, Wu Q, et al. Striking multiple synergies created by combining reduced graphene oxides and carbon nanotubes for polymer nanocomposites. *Nanotechnology* 2013;24(125704):1–8.
- [119] Hong NN, Zhan J, Wang X, Stec AA, Hull TR, Ge H, et al. Enhanced mechanical, thermal and flame retardant properties by combining graphene nanosheets and metal hydroxide nanorods for Acrylonitrile–Butadiene–Styrene copolymer composite. *Composites Part A* 2014;64:203–10.
- [120] Han Z, Wang Y, Dong W, Wang P. Enhanced fire retardancy of polyethylene/alumina trihydrate composites by graphene nanoplatelets. *Mater Lett* 2014;128:275–8.
- [121] Gavani JN, Adelinia H, Gudarzi MM. Intumescent flame retardant polyurethane/reduced graphene oxide composites with improved mechanical, thermal, and barrier properties. *J Mater Sci* 2014;49:243–54.
- [122] Wang X, Song L, Yang HY, Lu HD, Hu Y. Synergistic effect of graphene on antidripping and fire resistance of intumescent flame retardant poly (butylene succinate) composites. *Ind Eng Chem Res* 2011;50:5376–83.
- [123] Huang GB, Chen S, Song P, Lu P, Wu C, Liang H. Combination effects of graphene and layered double hydroxides on intumescent flame-retardant poly (methyl methacrylate) nanocomposites. *Appl Clay Sci* 2014;88:78–85.
- [124] Huang GB, Wang S, Song Pa Wu C, Chen S, Wang X. Combination effect of carbon nanotubes with graphene on intumescent flame-retardant polypropylene nanocomposites. *Composites Part A* 2014;59:18–25.
- [125] Wicklein B, Kocjan A, Salazar-Alvarez G, Carosio F, Camino G, Antonietti M, et al. Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. *Nat Nanotechnol* 2015;10:277–83.
- [126] Messersmith PB, Giannelis EP. Synthesis and barrier properties of poly (ϵ -caprolactone)-layered silicate nanocomposites. *J Polym Sci Part A Polym Chem* 1995;33:1047–57.
- [127] Yano K, Usuki A, Okada A, Kurauchi T, Kamigaito O. Synthesis and properties of polyimide–clay hybrid. *J Polym Sci Part A Polym Chem* 1993;31:2493–8.
- [128] Bunch JS, Verbridge SS, Alden JS, van der Zande AM, Parpia JM, Craighead HG, et al. Impermeable atomic membranes from graphene sheets. *Nano Lett* 2008;8:2458–62.
- [129] Paul D, Robeson L. Polymer nanotechnology: nanocomposites. *Polymer* 2008;49:3187–204.
- [130] Huang GB, Gao J, Wang X, Liang H, Ge C. How can graphene reduce the flammability of polymer nanocomposites. *Mater Lett* 2012;66:187–9.
- [131] Hummers WS, Offeman RE. Preparation of graphitic oxide. *J Am Chem Soc* 1958;80:1339.
- [132] Kang F, Zhang TY, Leng Y. Influences of H_2O_2 on synthesis of H_2SO_4 -GICs. *J Phys Chem Solids* 1996;57:889–92.
- [133] Kang F, Leng Y, Zhang TY. Electrochemical synthesis of sulfate graphite intercalation compounds with different electrolyte concentrations. *J Phys Chem Solids* 1996;57:883–8.
- [134] Kang F, Zhang TY, Leng Y. Electrochemical behavior of graphite in electrolyte of sulfuric and acetic acid. *Carbon* 1997;35:1167–73.
- [135] Zabel H, Solin SA. Graphite Intercalation Compounds I. Berlin: Springer-Verlag; 1990. p. 1–3.
- [136] Ebert LB. Intercalation compounds of graphite. *Annu Rev Mater Sci* 1976;6:181–211.
- [137] Selig H, Ebert LB. Graphite intercalation compounds. *Adv Inorg Chem Radiochem* 1980;23:281–327.
- [138] Dasari A, Yu ZZ, Mai YW, Cai G, Song H. Roles of graphite oxide, clay and POSS during the combustion of polyamide 6. *Polymer* 2009;50:1577–87.
- [139] Tsai KC, Kuan HC, Chou HW, Kuan CF, Chen CH, Chiang CL. Preparation of expandable graphite using a hydrothermal method and flame-retardant properties of its halogen-free flame-retardant HDPE composites. *J Polym Res* 2011;18:483–8.
- [140] Luo W, Li Y, Zou H, Liang M. Study of different-sized sulfur-free expandable graphite on morphology and properties of water-blown semi-rigid polyurethane foams. *RSC Adv* 2014;4:37302–10.
- [141] Thirumal M, Khashtgir D, Singha NK, Manjunath B, Naik Y. Effect of expandable graphite on the properties of intumescent flame-retardant polyurethane foam. *J Appl Polym Sci* 2008;110:2586–94.
- [142] Chiang CL, Hsu SW. Novel epoxy/expandable graphite halogen-free flame retardant composites—preparation, characterization, and properties. *J Polym Res* 2010;17:315–23.
- [143] Chen CH, Yen WH, Kuan HC, Kuan CF, Chiang CL. Preparation, characterization, and thermal stability of novel PMMA/expandable graphite halogen-free flame retardant composites. *Polym Compos* 2010;31:18–24.
- [144] Kuan CF, Yen WH, Chen CH, Yuen SM, Kuan HC, Chiang CL. Synthesis, characterization, flame retardance and thermal properties of halogen-free expandable graphite/PMMA composites prepared from sol–gel method. *Polym Degrad Stabil* 2008;93:1357–63.
- [145] Wang BB, Hu S, Zhao KM, Lu HD, Song L, Hu Y. Preparation of polyurethane microencapsulated expandable graphite, and its application in ethylene vinyl acetate copolymer containing silica–gel microencapsulated ammonium polyphosphate. *Ind Eng Chem Res* 2011;50:11476–84.
- [146] Zhang XG, Ge LL, Zhang WQ, Tang JH, Ye L, Li ZM. Expandable graphite–methyl methacrylate–acrylic acid copolymer composite particles as a flame retardant of rigid polyurethane foam. *J Appl Polym Sci* 2011;122:932–41.
- [147] Duan HJ, Kang HQ, Zhang WQ, Ji X, Li ZM, Tang JH. Core-shell structure design of pulverized expandable graphite particles and their application in flame-retardant rigid polyurethane foams. *Polym Int* 2014;63:72–83.
- [148] Qian L, Feng F, Tang S. Bi-phase flame-retardant effect of hexa-phenoxy-cyclotriphosphazene on rigid polyurethane foams containing expandable graphite. *Polymer* 2014;55:95–101.
- [149] Zhang L, Zhang M, Zhou Y, Hu L. The study of mechanical behavior and flame retardancy of castor oil phosphate-based rigid polyurethane foam composites containing expanded graphite and triethyl phosphate. *Polym Degrad Stabil* 2013;98:2784–94.
- [150] Feng F, Qian L. The flame retardant behaviors and synergistic effect of expandable graphite and dimethyl methylphosphonate in rigid polyurethane foams. *Polym Compos* 2014;35:301–9.
- [151] Wolska A, Goździkiewicz M, Ryszkowska J. Thermal and mechanical behaviour of flexible polyurethane foams modified with graphite and phosphorous fillers. *J Mater Sci* 2012;47:5627–34.
- [152] Wang CQ, Ge FY, Sun J, Cai ZS. Effects of expandable graphite and dimethyl methylphosphonate on mechanical, thermal, and flame-retardant properties of flexible polyurethane foams. *J Appl Polym Sci* 2013;130:916–26.
- [153] Bian XC, Tang JH, Li ZM. Flame retardancy of whisker silicon oxide/rigid polyurethane foam composites with expandable graphite. *J Appl Polym Sci* 2008;110:3871–9.
- [154] Fukushima K, Murariu M, Camino G, Dubois P. Effect of expanded graphite/layered-silicate clay on thermal, mechanical and fire retardant properties of poly (lactic acid). *Polym Degrad Stabil* 2010;95:1063–76.
- [155] Zhu H, Zhu Q, Li J, Tao K, Xue L, Yan Q. Synergistic effect between expandable graphite and ammonium polyphosphate on flame retarded polylactide. *Polym Degrad Stabil* 2011;96:183–9.
- [156] Tang G, Zhang R, Wang X, Wang BB, Song L, Hu Y, et al. Enhancement of flame retardant performance of bio-based polylactic acid composites with the incorporation of aluminum hypophosphite and expanded graphite. *J Macromol Sci Part A* 2013;50:255–69.
- [157] Qu BJ, Xie R. Intumescent char structures and flame-retardant mechanism of expandable graphite-based halogen-free flame-retardant linear low density polyethylene blends. *Polym Int* 2003;52:1415–22.
- [158] Zhang P, Hu Y, Song L, Ni JX, Xing WY, Wang J. Effect of expanded graphite on properties of high-density polyethylene/paraffin composite with

- intumescent flame retardant as a shape-stabilized phase change material. *Sol Energy Mater Sol Cells* 2010;94:360–5.
- [159] Mhike W, Ferreira IV, Li J, Stoliarov SI, Focke WW. Flame retarding effect of graphite in rotationally molded polyethylene/graphite composites. *J Appl Polym Sci* 2015;132(7), <http://dx.doi.org/10.1002/app.41472>, 11 pp.
- [160] Han Z, Dong L, Li Y, Zhao H. A comparative study on the synergistic effect of expandable graphite with APP and IFR in polyethylene. *J Fire Sci* 2007;25:79–91.
- [161] Zhang P, Song L, Lu HD, Wang J, Hu Y. The influence of expanded graphite on thermal properties for paraffin/high density polyethylene/chlorinated paraffin/antimony trioxide as a flame retardant phase change material. *Energy Convers Manage* 2010;51:2733–7.
- [162] Chen X, Wu H, Luo Z, Yang B, Guo S, Yu J. Synergistic effects of expandable graphite with magnesium hydroxide on the flame retardancy and thermal properties of polypropylene. *Polym Eng Sci* 2007;47:1756–60.
- [163] Bai G, Guo C, Li L. Synergistic effect of intumescent flame retardant and expandable graphite on mechanical and flame-retardant properties of wood flour-polypropylene composites. *Constr Build Mater* 2014;50:148–53.
- [164] Alongi J, Frache A, Gioffredi E. Fire-retardant poly (ethylene terephthalate) by combination of expandable graphite and layered clays for plastics and textiles. *Fire Mater* 2011;35:383–96.
- [165] Ye L, Meng XY, Ji X, Li ZM, Tang JH. Synthesis and characterization of expandable graphite/poly (methyl methacrylate) composite particles and their application to flame retardation of rigid polyurethane foams. *Polym Degrad Stabil* 2009;94:971–9.
- [166] Focke WW, Muiambo H, Mhike W, Kruger HJ, Ofosu O. Flexible PVC flame retarded with expandable graphite. *Polym Degrad Stabil* 2014;100:63–9.
- [167] Lu Y, Zhang Y, Xu W. Flame retardancy and mechanical properties of ethylene-vinyl acetate rubber with expandable graphite/ammonium polyphosphate/dipentaerythritol system. *J Macromol Sci Part B* 2011;50:1864–72.
- [168] Zheng J, Li B, Guo C, Wu Q, Wang Y. Flame-retardant properties of acrylonitrile-butadiene-styrene/wood flour composites filled with expandable graphite and ammonium polyphosphate. *J Appl Polym Sci* 2014;131(10), <http://dx.doi.org/10.1002/app.40281>, 6 pp.
- [169] Ge LL, Duan HJ, Zhang XG, Chen C, Tang JH, Li ZM. Synergistic effect of ammonium polyphosphate and expandable graphite on flame-retardant properties of acrylonitrile-butadiene-styrene. *J Appl Polym Sci* 2012;126:1337–43.
- [170] Awad WH, Wilkie CA. Investigation of the thermal degradation of polyurea: the effect of ammonium polyphosphate and expandable graphite. *Polymer* 2010;51:2277–85.
- [171] Bahramian AR. Pyrolysis and flammability properties of novolac/graphite nanocomposites. *Fire Safety J* 2013;61:265–73.
- [172] Bian XC, Tang JH, Li ZM, Lu ZY, Lu A. Dependence of flame-retardant properties on density of expandable graphite filled rigid polyurethane foam. *J Appl Polym Sci* 2007;104:3347–55.
- [173] Camino G, Duquesne S, Delobel R, Eling B, Lindsay C, Roels T. Mechanism of expandable graphite fire retardant action in polyurethanes. *ACS Symp Ser* 2001;797:90–109.
- [174] Murariu M, Dechief AL, Bonnaud L, Paint Y, Gallos A, Fontaine G, et al. The production and properties of polylactide composites filled with expanded graphite. *Polym Degrad Stabil* 2010;95:889–900.
- [175] Wen X, Wang Y, Gong J, Liu J, Tian N, Wang Y, et al. Thermal and flammability properties of polypropylene/carbon black nanocomposites. *Polym Degrad Stabil* 2012;97:793–801.
- [176] Wen X, Gong J, Yu H, Liu Z, Wan D, Liu J, et al. Catalyzing carbonization of poly (L-lactide) by nanosized carbon black combined with Ni₂O₃ for improving flame retardancy. *J Mater Chem* 2012;22:19974–80.
- [177] Wen X, Tian N, Gong J, Chen Q, Qi Y, Liu Z, et al. Effect of nanosized carbon black on thermal stability and flame retardancy of polypropylene/carbon nanotubes nanocomposites. *Polym Adv Technol* 2013;24:971–7.
- [178] Gong J, Niu R, Liu J, Chen X, Wen X, Mijowska E, et al. Simultaneously improving the thermal stability, flame retardancy and mechanical properties of polyethylene by the combination of graphene with carbon black. *RSC Adv* 2014;4:33776–84.
- [179] Zhu J, Xiao P, Li H, Carabineiro SA. Graphitic carbon nitride: synthesis, properties, and applications in catalysis. *ACS Appl Mater Interfaces* 2014;6:16449–65.
- [180] Wang Y, Wang X, Antonietti M. Polymeric graphitic carbon nitride as a heterogeneous organocatalyst: from photochemistry to multipurpose catalysis to sustainable chemistry. *Angew Chem Int Ed* 2012;51:68–89.
- [181] Shi YQ, Jiang SH, Zhou KQ, Bao CL, Yu B, Qian XD, et al. Influence of g-C₃N₄ nanosheets on thermal stability and mechanical properties of biopolymer electrolyte nanocomposite films: a novel investigation. *ACS Appl Mater Interfaces* 2013;6:429–37.
- [182] Shi YQ, Yu B, Zhou KQ, Yuen RK, Gui Z, Hu Y, et al. Novel CuCo₂O₄/graphitic carbon nitride nanohybrids: highly effective catalysts for reducing CO generation and fire hazards of thermoplastic polyurethane nanocomposites. *J Hazard Mater* 2015;293:87–96.
- [183] Song X, Lin L, Rong M, Wang Y, Xie Z, Chen X. Mussel-inspired, ultralight, multifunctional 3D nitrogen-doped graphene aerogel. *Carbon* 2014;80:174–82.
- [184] Wan C, Lu Y, Jiao Y, Jin C, Sun Q, Li J. Fabrication of hydrophobic, electrically conductive and flame-resistant carbon aerogels by pyrolysis of regenerated cellulose aerogels. *Carbohydr Polym* 2015;118:115–8.
- [185] Wu ZY, Li C, Liang HW, Chen JF, Yu SH. Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose. *Angew Chem* 2013;125:2997–3001.
- [186] Li J, Li J, Meng H, Xie S, Zhang B, Li L, et al. Ultra-light, compressible and fire-resistant graphene aerogel as a highly efficient and recyclable absorbent for organic liquids. *J Mater Chem A* 2014;2:2934–41.
- [187] Ditttrich B, Wartig KA, Hofmann D, Mulhaupt R, Scharrel B. Flame retardancy through carbon nanomaterials: carbon black, multiwall nanotubes, expanded graphite, multi-layer graphene and graphene in polypropylene. *Polym Degrad Stabil* 2013;98:1495–505.