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Flame retarded polymer systems based on the sol-gel approach: recent advances and future perspectives

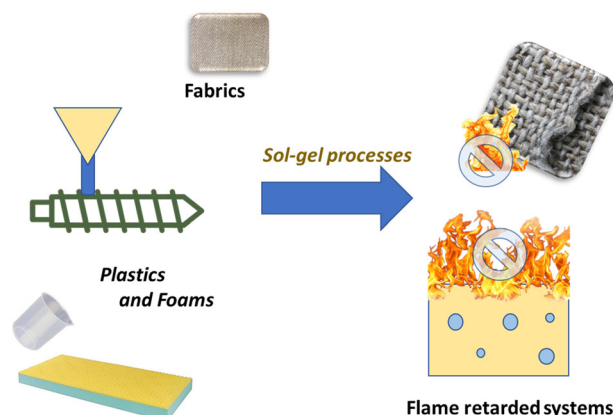
Aurelio Bifulco¹ · Claudio Imparato¹ · Antonio Aronne¹ · Giulio Malucelli^{1,2}

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Abstract

The ease of flammability of polymers represents a key issue that limits their applications in different advanced sectors. In this context, a reliable and effective solution regards the use of flame retardants, i.e., additives that are able to slow down (or even stop) the flame propagation and to enhance the resistance to an irradiative heat flux. Among the different flame retardants designed, synthesized, and applied up-to-now, the utilization of inorganic particles, inorganic and hybrid organic-inorganic coatings has gathered a great interest from either the academic and industrial community, as these structures can provide remarkable flame retardant features to different polymer systems, in which they are embedded or applied onto. In particular, the in situ generation (through sol-gel processes, i.e. hydrolysis and condensation reactions from tailored alkoxide precursors) of ceramic phases, either in the form of particles or as surface coatings, has clearly demonstrated its effectiveness in creating a physical barrier that limits the degradation of the polymer when subjected to the application of a flame or an irradiative heat flux. It also lowers the heat and mass transfer from the degrading polymer to the surroundings and vice versa, hence providing an overall enhancement of heat and fire resistance. This review work seeks to provide an up-to-date overview of the most recent advances in the use of sol-gel methods for conferring flame retardant features to bulk polymers, cellulosic textiles (cotton), and polymer foams. In addition, the current limitations and the potential progresses of these approaches are discussed.

Graphical abstract



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✉ Giulio Malucelli
giulio.malucelli@polito.it

¹ Department of Chemical, Materials and Industrial Production Engineering (DICMaPI), University of Naples Federico II,

Piazzale Tecchio 80, 80125 Napoli, Italy

² Department of Applied Science and Technology, Politecnico di Torino, and local INSTM Unit, Viale Teresa Michel 5, 15121 Alessandria, Italy

Keywords Sol-gel technique · Ceramic phases · Flame retardance · Epoxy systems · Cotton · Foams

Highlights

- Sol-gel chemistry can be successfully exploited for conferring flame retardant features to different polymer systems.
- Bulk polymers, fabrics and foamed materials can easily undergo sol-gel flame retardant processes.
- The combination of sol-gel derived phases with other flame retardant may induce synergistic effects.
- Sol-gel derived ceramic or hybrid phases can act in condensed or gas phase.

List of abbreviations

AM	ammonium polyphosphate/montmorillonite	MOS	magnesium oxysulfate
APP	ammonium polyphosphate	NiPS	nickel phyllosilicate
APTES	(3-aminopropyl)triethoxysilane	NMR	nuclear magnetic resonance
APTMS	(3-aminopropyl)trimethoxysilane	NPs	nanoparticles
ATH	aluminum trihydroxide	O-SEBS	oil-extended styrene–ethylene–butadiene–styrene
CNT	carbon nanotube	PBZ	polybenzoxazine
CoCuP	cobalt-copper bimetallic phosphide	PBZ-PSO	branched benzoxazine-containing polysiloxanes
CTAB	cetyltrimethylammonium bromide	PDMS	polydimethyl siloxane
DA	3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) propenamide	P-FRs	phosphorus-based flame retardants
DCC	N,N'-dicyclohexylcarbodiimide	P-HBPSi	hyperbranched polysiloxane
DDM	4,4'-diaminodiphenylmethane	pkHRR	peak of heat release rate
DGEBA	Bisphenol A diglycidyl ether	POSS	polyhedral oligomeric silsesquioxane
DOPO	9,10-dihydro-9-oxo-10-phosphaphenanthrene- 10-oxide	PP	polypropylene
DOPO-rGO	reduced graphene oxide functionalized with DOPO	PPDC	phenylphosphonic dichloride
DMAP	4-dimethylaminopyridine	PU	polyurethane
DP	6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido- 2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl) methoxy]-, 6-oxide	PVMDM-S	polyvinylmethyldimethoxysilane
DPHK	phosphorus-nitrogen-silicon flame retardant	PZS	polyphosphazenes
EDA	ethylenediamine	SA	nano-porous silica aerogel
FR	flame retardant	SEH	silica-epoxy hybrids
FTIR	Fourier-transform infrared spectroscopy	SEM	scanning electron microscopy
EO	epoxy resin	SFCNT	silica-grafted carbon nanotubes
GO	graphene oxide	SNEH	silica-novolac-epoxy hybrids
GOFA	sol-gel functionalized GO with furfuryl alcohol	SSA	solid super acid
GPTMS	3-glycidoxypropyltrimethoxysilane	STCA	silicon/titanium flame-retardant
HA	humic acid	TDP	2,4,6-tris(dimethylaminomethyl)phenol
H-PMAP-S	organic-inorganic hyperbranched polysiloxane	TEM	transmission electron microscopy
HP	phosphoric acid	TEOS	tetraethoxysilane
IDA	isophorone diamine	TES	triethoxysilane
IPTS	3-isocyanatopropyltriethoxysilane	THR	total heat release
LOI	limiting oxygen index	Ti-POSSbis-	N,N'-bis(methylene)-bis(dibenz[C,E][1,2]-oxa- phosphorin6-oxide)-propylisobutyl-amino-tita- nium-polyhedral oligomeric silsesquioxane
MCC	microcone calorimetry	DOPO	
MCS	metal-containing species	TPU	thermoplastic polyurethane
MER	silane-modified epoxy resin	TSR	total smoke release
MNA	methyl nadic anhydride	UPR	unsaturated polyester resin
MNR	Silane-modified novolac resin	VTES	vinyltriethoxysilane
MPTMS	3-mercaptopropyltrimethoxysilane		
M-SiO₂	mesoporous silica		

1 Introduction

Fire has been and is still a big issue for most of the applications of polymeric materials: in fact, the latter, when

exposed to an irradiative heat flux or to a flame, easily burn and may generate toxic smokes [1]. To limit this severe and stringent problem, specific additives, called flame retardants (FRs), have been designed, synthesized, and applied to different polymeric materials (i.e., bulk polymers, fibers and fabrics, and foams), starting from the early 1950s. Upon the application of a flame or an irradiative heat flux, according to their chemical structure and composition, they are able to favor the formation of a stable carbonaceous residue (i.e., the so-called char) in the condensed phase and/or to act in the gas phase, entrapping the H^{\bullet} and $\bullet OH$ radicals that are responsible for the propagation of the combustion reactions [2–5]. These phenomena are well depicted by the so-called “Emman’s fire triangle” (Fig. 1), i.e., a self-sustaining flaming combustion. In brief, any flaming combustion is the result of an oxidation, which takes place in the gas phase and involves the oxygen (or air) provided by the atmosphere that surrounds the burning polymer, as well as the gaseous products originating from the decomposition of the polymer itself. The inherent exothermicity of the reaction self-sustains the flaming combustion [6].

So far, several different types of FRs have been conceived, synthesized, and applied to different polymer systems. Regardless of the final use (i.e., for scientific/academic and/or for commercial purposes), all FRs contain specific key elements in their chemical structure such as halogens (mainly chlorine and bromine), metals, phosphorus, nitrogen, or boron, alone or even in combination, as occurs in FR formulations containing nitrogen and phosphorus [7, 8]. Different approaches can be employed for preparing flame retardant polymer systems, namely: physical incorporation of the FR into the polymer matrix (either thermoplastic or thermosetting); melt compounding (in particular spinning, when synthetic flame retarded fibers/fabrics are involved); and grafting or copolymerization reactions (which can be successfully exploited for

establishing covalent linkages between the macromolecular chains and the flame retardant, hence providing more stability and durability).

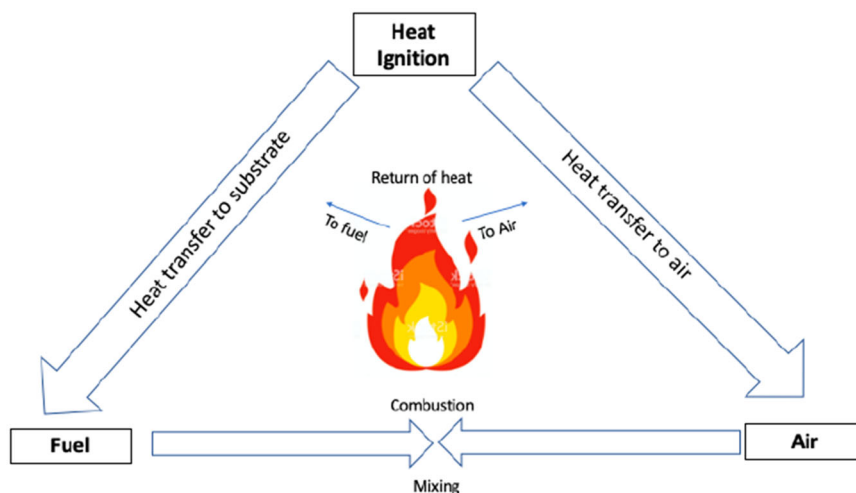
Around 15 years ago, the formation of full inorganic or hybrid organic-inorganic ceramic phases by sol-gel in situ synthetic routes started to be explored as an effective flame retardant strategy for different polymer systems (bulk thermoplastic or thermosetting polymers, fibers and fabrics, foams) [9, 10]. It has clearly been demonstrated that the formation of sol-gel derived phases within a polymer matrix causes both the enhancement of the mechanical and thermal behavior and the improvement of the resistance to a flame spread or to the exposure to an irradiative heat flux. Indeed, the obtained ceramic or hybrid moieties are able to protect the underlying material, slowing down the heat, oxygen and mass transfer phenomena between the degrading material to the surroundings or vice versa. In particular, they usually work in the condensed phase, providing a thermal shielding effect to the polymer matrix, favoring, at the same time, the formation of a stable carbonaceous residue (i.e., the so-called char) [11, 12].

The present work will review the most recent advances in the use of sol-gel processes for conferring flame retardant features to bulk polymers (either thermoplastics or thermosets), textiles (particularly regarding cotton fibers and fabrics) and foams. In addition, the current limitations and potential new developments of these approaches will be summarized.

2 Assessment of flame retardance through flammability and forced-combustion tests

Consistent test methods are now available that allow the behavior of polymer systems in relation to fire risk to be evaluated, which typically involve the evaluation of such

Fig. 1 Emman’s fire triangle. Reprinted from [7] under the Creative Commons Attribution (CC BY) license



important parameters as ease of ignition, flame propagation rate, heat release rate, generation of toxic and darkening smokes, among others. These tests must be performed under rigorously defined conditions, to provide a comparative classification of the behavior of different polymeric materials. This section will briefly summarize the most important tests that allow the flame retardance of polymer systems to be assessed.

2.1 Flammability tests

UL94 and Limiting Oxygen Index (LOI) measurements are the most common tests carried out to evaluate the flammability of any polymeric material.

UL94 is a flame spread test designed by the Underwriters Laboratories (also described in the ISO EN 11925-2 standard), which assesses the ability of the polymeric material to self-extinguish after flaming. The flame can propagate through the specimen according to the adopted configuration of the specimen, i.e., whether the latter is vertically or horizontally positioned. A rating is made according to the test results that comprise the burning time and rate, the time required for extinction, the possible dripping phenomena (i.e., dripping of incandescent drops that may propagate the flame to other ignitable materials), and the duration of afterglow. Undoubtedly, the rating in UL94 tests is strictly correlated with the wall thickness of the specimens.

In LOI measurements (standardized in ASTM D2863), a bar specimen is vertically positioned in a glass cylindrical tube and burns from the top to the bottom (i.e., according to a candle-like burning) within an ascending flow of a N_2/O_2 mixture. First, the bar specimen is ignited by a flame that is then removed; by varying the composition of the gas mixture, the minimum oxygen volume percentage, at which self-sustained combustion occurs for 3 min corresponds to the LOI of the polymer system. Usually, though it is not a strict general rule, polymers are considered flame retarded when the LOI exceeds 25%.

2.2 Forced-combustion tests

Forced-combustion tests refer to cone calorimetry measurements that take advantage of the empirical observation that the heat released by burning polymer systems is directly related to the amount of oxygen consumed during the combustion process. In this approach, described in the ISO 5660 standard, a square specimen (usually $10 \times 10 \text{ cm}^2$) is placed on a balance and exposed to the irradiative heat flux provided by a conical heater; an electrical spark is employed for igniting the flammable degradation gases that are produced by the degradation of the specimen under the heat flux. The combustion products (i.e., the smokes) are then collected, where the concentrations of the unconsumed oxygen and of

the evolved gases (namely, CO and CO_2) are measured. An optical system also assesses the obscuring power of the evolved smokes. This apparatus delivers a detailed overview of the combustion process as a function of time, by assessing the time to ignition, the heat release (estimated on the basis of the oxygen consumption), the sample weight loss, as well as opacity and composition of the produced smokes.

In addition, according to the ASTM 7309 standard, there exists a pyrolysis-combustion flow calorimetry test, known as micro-scale combustion calorimetry (MCC), able to measure the heat release rate and other related parameters using samples of a few milligrams. In MCC tests, the sample is first quickly heated up to a controlled pyrolysis state under an inert atmosphere; the gaseous pyrolyzed products that are formed during this stage are then rapidly oxidized at high temperature in excess oxygen, hence simulating a combustion process. Heat release rate vs. time curves are then plotted, which can be exploited for comparing the behavior of different polymeric systems.

3 Sol-gel derived systems for bulk polymers

3.1 Sol-gel chemistry and phosphorus-based compounds as flame retardant strategy

Phosphorus-based flame retardants (P-FRs) have been largely used to replace halogen-containing additives, due to their lower toxicity and high effectiveness. The decomposition of phosphorus-based flame retardants releases phosphoric anhydrides and acidic compounds, which mainly work as charring promoters in the condensed phase [13, 14]. The generation of phosphorus-nitrogen-silicon containing species in organic-inorganic composites is highly desirable because it results in a hybrid flame retardant activity in the gas and condensed phases. The production of nitrogen during the decomposition process can lead to the formation of phosphaphenanthrene groups in the gas phase through the reaction with acidic phosphorus compounds lying in the boundary phase. Also, phosphaphenanthrene and silicon groups can promote char formation in the condensed phase and exert a thermal shielding effect during the combustion. Luo et al. [15] synthesized a phosphorus-nitrogen-silicon flame retardant (DPHK) via a Kabachnik-Fields reaction and sol-gel method. DGEBA composites cured with 4,4'-diaminodiphenylmethane (DDM) containing 3 wt.% of DPHK achieved a V-0 rating in vertical flame spread tests (UL94) and LOI value of 29%, together with a strong suppression of released toxic fuel (carbon monoxide, CO), due to the production of a continuous and protective char promoting a decrease of both peak of Heat Release Rate, $pkHRR$, (by about 36%) and total heat release, THR, (by about 30%).

9,10-dihydro-9-oxo-10-phosphaphenanthrene-10-oxide (DOPO) is one of the most used P-FRs in combination with the sol-gel approach. DOPO is characterized by a single reactive hydrogen functionality, therefore it can react with polymer (e.g., epoxy resin) or other functional groups present on the surface of materials. The reaction of DOPO with oxirane rings of epoxy may reduce the glass transition temperatures and consequently the mechanical performances of the composite material. This problem can be overcome by its derivatization to unreactive compounds [16–18]. However, the decomposition of DOPO produces a huge number of phosphorous radicals acting as flame inhibitors in the gas phase. This peculiar flame retardant mechanism can be combined with a sol-gel strategy to prepare polymer-based composites with enhanced flame retardance and good mechanical behavior. More specifically, the sol-gel strategy allows for the synthesis of silica nanoparticles using mild operative conditions and the use of several precursors (e.g., tetraethoxysilane - TEOS -, sodium metasilicate, etc). The sol-gel in situ generation of silica nanoparticles in the epoxy resin can improve the fire behavior of the latter, especially in combination with phosphorus-based flame retardants. Recently, Bifulco et al. [19–21] synthesized in situ sol-gel silica nanoparticles (NPs) in a DGEBA resin cured with isophorone diamine (IDA) as cycloaliphatic hardener. The presence of silica NPs at a very low loading (2 wt.%) prevented the occurrence of dripping phenomena during vertical flame spread tests [22]. An analogous sol-gel based methodology was applied to flame retard 2,5-bis[(oxyran-2-ylmethoxy)methyl]furan (BOMF) resin cured with methyl nadic anhydride (MNA) [23]. The generation of silica NPs conferred a high char-forming character and prevented dripping phenomena as well as decreasing the heat release rate up to 35%; this value is much higher than that (25%) obtained for DGEBA-based systems cured with an aliphatic polyamine. This flame retardant strategy was used by the same research group in DGEBA systems cured with IDA to achieve V-0 rating in UL94 tests by exploiting, together with melamine, 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl) propenamide (DA) and 6H-dibenz[c,e][1,2]oxaphosphorin,6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]oct-4-yl)methoxy]-, 6-oxide (DP) as flame retardants at 2 wt.% of P-loading [24]. No dripping self-extinguishing composites were obtained with the addition of 17.3 wt.% of DP and 11.5 wt.% of melamine, even using an aliphatic hardener for the curing process. Conversely, Zhang et al. [25] prepared epoxy composites showing V-0 rating in UL94 tests only with the use of DDM and 9.1 wt.% of DP. The combined presence of DA and in situ silica NPs guaranteed V-0 rating in UL 94 tests in the presence of just 2 wt.% of P. DA and DP also allowed for the formation of an abundant char during the combustion, playing an active role both in

condensed and gas phase starting from the early stage of decomposition process [24, 26].

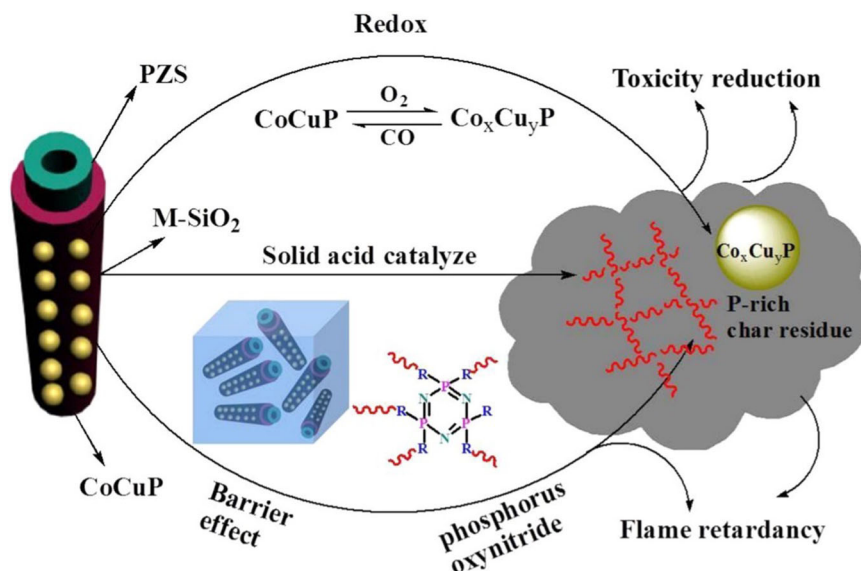
The same phosphaphenanthrene derivative (DOPO-HQ) was adopted by Shen et al. [27], who synthesized a hyper-branched organic-inorganic hybrid material containing Si, N and P, aimed at improving the flame retardancy of a polyol-based polyurethane. The sol-gel procedure employed DOPO-HQ and 3-isocyanatopropyltriethoxysilane (IPTS) through two polycondensation steps, the second following the addition of triglycidyl isocyanurate (TGIC). The hybrid flame retardant appeared uniformly dispersed in the polyurethane matrix, however the best classification achieved in the UL-94 test was V-2, at 40 wt.% loading of the FR. The chemical analysis of char showed that the siloxane and phosphide species produced during burning formed a protective layer improving the oxidation resistance of the polymer.

Ammonium polyphosphate (APP), a widely applied flame retardant, has been coupled with silicon-containing phases in the search for synergistic effects. Its micro-encapsulation in a silica gel shell by hydrolytic sol-gel has been proposed. However, the substantial hydroxylation of silica surface makes the modified APP highly hydrophilic and poorly compatible with polymers such as polyurethane.

The introduction of a siloxane component was therefore explored, for example by reacting APP with polydimethyl siloxane (PDMS), alkylphenol polyoxyethylene and then with TEOS, in the presence of ammonia [28]. The so-obtained APP microcapsules with hybrid silicone-organic shells were added to a thermoplastic polyurethane. Compared with simple APP-silica, 10 wt.% of this hybrid additive offered a greater improvement in the fire behavior of the composites, with 31.4% decrease of THR, though both allowed a V-0 rating in vertical flame spread tests. Moreover, it slightly reduced the negative impact of the filler on the tensile strength and elongation at break.

Zeng et al. [29] adopted a bottom-up sol-gel approach with the same aim. In particular, two different silanes, TEOS and vinyltriethoxysilane (VTES), were added sequentially to APP, controlling the pH (from acid to basic) and temperature to promote their hydrolysis and condensation. The resulting APP particles, wrapped by a silica gel-polysiloxane hybrid layer which provided hydrophobicity and reduced water solubility, were successfully applied to improve the fire resistance of polyurethane. The composite containing 20 wt.% of modified APP showed a LOI of 30% (+54% compared to pure polyurethane) and reached V-0 rating in vertical burning tests, showing no melt dripping, while the use of bare APP afforded only a V-2 rating and did not avoid dripping. Moreover, the smoke density upon combustion decreased by about 29%. Studying the flame retardant mechanism, the authors proposed that SiO₂ and silicon pyrophosphate produced by the

Fig. 2 Schematic illustration of flame retardancy mechanism of polyurethane composites with PZS@M-SiO₂@CoCuP. Reprinted with permission from [30]. Copyright (2017) American Chemical Society



thermal degradation of the hybrid additive enhanced the density and uniformity of the char layer, and eventually its thermal stability, preventing the heat transfer and diffusion. A different strategy to reduce the fire hazard of thermoplastic polyurethane was explored by Qiu et al. [30], who developed a novel ternary nanostructure containing P, N, Si and transition metals. It was based on polyphosphazenes (PZS), hybrid polymers with a P-N-P-N backbone. PZS nanotubes were prepared, covered with a mesoporous silica (M-SiO₂) layer and decorated with cobalt-copper bimetallic phosphide (CoCuP) nanocrystals (Fig. 2). In detail, polystyrene sulfonate and cetyltrimethylammonium bromide (CTAB) were anchored on the PZS nanotubes through layer-by-layer assembly, then M-SiO₂ was deposited by adding TEOS in basic solution, and finally the CoCuP crystalline phase was obtained by hydrothermal treatment. The incorporation of 3 wt.% nanostructured PZS@M-SiO₂@CoCuP into polyurethane led to a significant decrease in pkHRR (−58.2%) and THR (−19.4%), lowering the generation of toxic HCN and CO during combustion, as well as promoting the formation of a stable char. The enhanced fire behavior was attributed to the cooperative action of the components, i.e., the catalytic activity of the CoCuP/C system, combined with the charring effect of M-SiO₂ and barrier effect of well-distributed PZS-based network.

A further example of the introduction of P and N together with Si by linking specifically designed organic molecules with silane compounds was reported by Satdive et al. [31], who designed an amine curing agent obtained by reaction of ethylenediamine (EDA) with phenylphosphonic dichloride (PPDC), followed by reaction with 3-glycidoxypropyltrimethoxysilane (GPTMS), and final hydrolysis and self-condensation in acidic solution.

The product was used in different proportions with a commercial polyamide hardener for the deposition of epoxy resin coatings. The P- and Si-containing curing agent allowed self-extinction to be achieved in vertical flame spread tests already at 20 wt.% loading, while LOI values increased from 20 to 29% in the sample containing 40 wt.% of FR.

The most significant recent results on flame retardant systems based on sol-gel chemistry discussed in these sections are reported in Table 1.

3.2 Sol-gel chemistry and polysiloxane molecules as flame retardant strategy

Silicon-based compounds has been widely used for preparing several functional materials with enhanced thermal and fire resistance. Silicon-containing molecules can be found as precursors and/or coupling agents both for the sol-gel synthesis of inorganic nanoparticles and hybrid organic-inorganic materials. Such element can work in synergism with phosphorus and nitrogen to modify the chemical structure of polymer matrices and inorganic fillers, resulting in composites showing improved overall performances, as described in some abovementioned reports (Section 3.1). Silicon-based materials are potential flame retardants as they produce a char able to act as thermal shield and oxygen barrier during a fire, slowing down the heat release rate. Indeed, silicon oxide can be considered inherently a flame retardant material as, when exposed to heat and flames, it generates ceramics/glasses. Small amounts of silicon-containing species/moieties in certain organic polymer systems (e.g., polydimethylsiloxane-type) have been reported to improve their LOI and UL94 performance. In this Section, the role of polysiloxanes is discussed, while in the following Sections several examples of

Table 1 Recent outcomes in sol-gel flame retardant treatments applied to bulk polymer matrices

Flame Retardant (FR)	Polymer matrix	Hardener	FR content (wt%)	P content (wt%)	Fire performances	Ref.
P-HBPSi@GO hybrids	TPU	*NA	2	NA	<ul style="list-style-type: none"> • -63.5% of pkHRR • -58.3% of pSPR 	[42]
PBz-PSO	PBz-PSO reactive polymer	NA	5	NA	<ul style="list-style-type: none"> • V-0 rating in UL94 tests 	[35]
Silica xerogel from groundnut hull ash	DGEBA epoxy	MNA and TDP	2	NA	<ul style="list-style-type: none"> • Char residue increase from 15.3 to 18.0% • UL 94-V-0 	[43]
DPHK	DGEBA epoxy	DDM	3	NA	<ul style="list-style-type: none"> • V-0 rating in UL94 tests • LOI value of 29% 	[15]
Al(OH) ₃ and SA	Unsaturated polyester resin	Double bonds acting as a hardener	15	NA	<ul style="list-style-type: none"> • V-0 rating in UL94 tests • Minimal smoke production, decrease of flame propagation rate 	[44]
SiO ₂ -GO-FA	Novolac resin	DCC and DMAP	8	NA	<ul style="list-style-type: none"> • Huge amount of char residue, 65.4% higher than pristine resin 	[45]
SFCNT, MNR and ENR	DGEBA epoxy and novolac resin	EDA	4	NA	<ul style="list-style-type: none"> • Increase of char yield and degradation temperature 	[46]
GO-GPTMS, GO-APTMS-FA	Epoxy and novolac resin	EDA	1	NA	<ul style="list-style-type: none"> • Increase of char yield and degradation temperature 	[47, 48]
SSA	Unsaturated polyester resin	Phthalate solution of cobalt naphthenate and cobalt isooctanoate	10	NA	<ul style="list-style-type: none"> • Increase of LOI up to 27.2% 	[49]
Core-shell silica nanoparticles (HP/AM)	Polyurethane	NA	25	NA	<ul style="list-style-type: none"> • LOI value of 34.8% • V-0 rating in UL94 tests 	[50]
Core-shell silica nanoparticles (Si(H))	DGEBA epoxy	DDM	1.5	NA	<ul style="list-style-type: none"> • V-1 rating in UL94 tests • Increased LOI value of 30.3% 	[51]
MOS	Polypropylene	NA	30	NA	<ul style="list-style-type: none"> • Increase of LOI from 18 to 19.5%. 	[52]
SiO ₂ @UiO-66-2	DGEBA epoxy	DDM	2	NA	<ul style="list-style-type: none"> • -16% of TSP • -31% of pkHRR • -23% of THR 	[53]
H-PMAPS	RC-T/PMAPS	Thermal curing	NA	NA	<ul style="list-style-type: none"> • Dielectric stability from 10 Hz to 10⁶ Hz and lower dielectric loss 	[37]
DOPO-GO	DGEBA epoxy	DDM	3.75	NA	<ul style="list-style-type: none"> • Increase of LOI value up to 39% • -45% of pkHRR • -41% of THR 	[54]
In situ silica nanoparticles	DGEBA epoxy	IDA	2	NA	<ul style="list-style-type: none"> • -50% of HRR 	[19]

Table 1 (continued)

Flame Retardant (FR)	Polymer matrix	Hardener	FR content (wt%)	P content (wt%)	Fire performances	Ref.
DOPO-PEPA (DP)	DGEBA epoxy	DDM	9.1	2	• V-0 rating in UL94 tests	[24]
DP	DGEBA epoxy	IDA	17.3	2	• V-0 rating in UL94 tests	[25]
DOPO-AAM (DA)	DGEBA epoxy	IDA	NA	2	• V-0 rating in UL94 tests	[26]
HA and APP	DGEBA epoxy	IDA	HA (6), APP (1)	1	• V-0 rating in UL94 tests	[55]
STCA	DGEBA epoxy	STCA	4	NA	• Increased char yield of 52.7% • V-0 rating in UL94 tests	[56]
DOPO-rGO	EO	Mesogenic resin	15	NA	• V-0 rating in UL94 tests	[57]
CCD	DGEBA epoxy	DDM	10	NA	• LOI value 7.6% higher than pristine epoxy • V-0 rating in UL94 tests	[58]
MWCNT-(DOPO-HQ) nanotubes and AlPi	DGEBA epoxy	DDM	1	NA	• LOI value of 39.5% • V-0 rating in UL94 tests	[59]
DOPO-POSS	DGEBA epoxy	m-PDA	2.5	NA	• V-0 rating in UL94 tests	[38, 39]
POSS-bisDOPO	DGEBA epoxy	DDM	20	NA	• LOI value of 34.5%	[40]
Ti-POSSbisDOPO	DGEBA epoxy	DDM	3	NA	• LOI value up to 50% • V-0 rating in UL94 tests	[41]
(DOPO-HQ)-silane	Polyol polyurethane	NA	40	1.3	• V-2 rating in UL94 tests	[27]
APP-PDMS-PEO-TEOS	Polyurethane	NA	10	NA	• V-0 rating in UL94 tests • -31.4% of THR	[28]
APP-TEOS-VTES	Polyurethane	NA	20	~4	• V-0 rating in UL94 tests • 29% decrease of smoke density	[29]
Polyphosphazene-SiO ₂ -CoCuP	Polyurethane	NA	3	NA	• -19.4% of THR • -58.2% of pkHRR	[30]
PPDC-EDA-GPTMS	Epoxy resin	polyether amine	20	NA	• V-0 rating in UL94 tests	[31]
SiO ₂ nanoparticles	carbazole PBZ	NA	10	NA	• LOI from 32 to 36%	[60]
Nickel phyllosilicate-DOPO	Epoxy resin	DDM	5	NA	• V-0 rating in UL94 tests • -62.5% of pkHRR • -23.7% of THR	[61]
Mg(OH) ₂ -TES-silicone rubber	oil-styrene-ethylene-butadiene	NA	70	NA	• V-0 rating in UL94 tests • LOI from 17 to 36–38%	[62]

*NA = not available

functionalization of fillers and polymers with silane compounds are reported, along with the use of different silica-based nanostructures in flame retardance (Section 3.4).

Polyhedral oligomeric silsesquioxane (POSS) molecules are nanosized polyhedral or cage-type structures and can be

synthesized through sol-gel methodologies [32]. These structures are used as nanofillers in many polymer matrices and positively affect the overall performances of the resulting composites. The literature clearly demonstrates that POSS molecules can hinder dripping phenomena and

boost the fire resistance of polymers [33]. Song et al. proved that the use of POSS structures led to the occurrence of a blowing-out effect during combustion, which involved the formation of some char able to trap flammable gases in the condensed phase [34]. This effect strongly reduces the flammability of epoxy composites. The synergistic activity of silicon-nitrogen significantly affects the flammability and pyrolysis process of hybrid nanocomposites and of high-performance polymers, enhancing their flame retardance. Hsieh et al. [35] synthesized branched benzoxazine-containing polysiloxane (PBz-PSO) polymers showing a high reactivity due to the presence of benzoxazine groups that could crosslink by thermal treatment. PBz-PSO samples showed high thermal stability and LOI values (>45%); furthermore, the addition of 5 wt.% of polysiloxane-based additive into a commercial benzoxazine resin allowed it to achieve V-0 rating in vertical flame spread tests and to increase its glass transition temperature up to ~41%. Therefore, the combined use of FR elements such as silicon and nitrogen and the flexibility of sol-gel routes can facilitate the synthesis of hybrid structures containing well dispersed inorganic phases, which could replace halogen-based flame retardants.

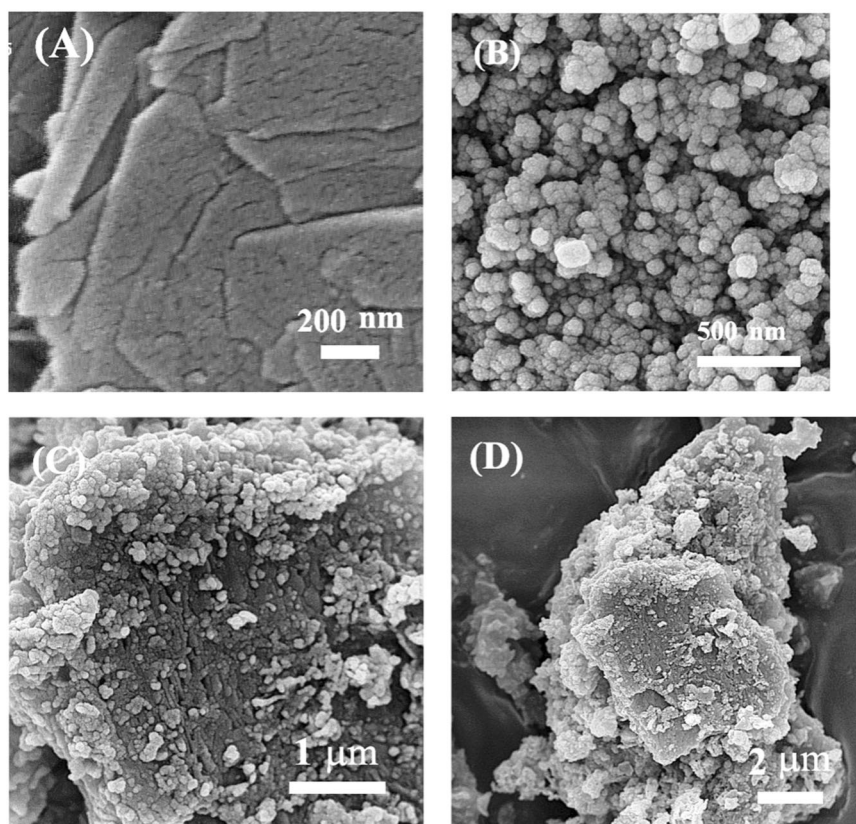
It is well known that silicone resins are widely used in industry because of their high thermal resistance and chemical stability. These materials are polymers formed by branched or cage-like oligosiloxanes and are mainly applied as silicone rubbers, coatings and additives [36]. Several sol-gel strategies have been developed to prepare silicone resins cured via traditional processes aimed at avoiding large-scale shrinkages and the formation of holes, which have a detrimental impact on the properties of the final product. Chen et al. [37] developed a sol-gel technology coupled with γ -radiation curing to overcome such limitations. The research group synthesized an organic-inorganic hyperbranched polysiloxane (H-PMAPS) through the fine control of the hydrolysis of 3-methacryloxypropyltrimethoxysilane. The thermally cured hybrid product, RC-T/PMAPS, was characterized by a riverlike morphology, optical transparency, and high thermal stability. Further, it exhibited dielectric stability from 10 Hz to 10^6 Hz and low dielectric loss at higher frequencies; therefore, this high-performance material is very promising for cutting-edge industries. Cage-like oligosiloxanes can be also functionalized with DOPO and several approaches were developed, employing sol-gel chemistry as a useful tool to achieve well-tailored interphases and generate multifunctional additives. Zhang et al. [38, 39] used DOPO-modified POSS (DOPO-POSS) molecules as flame retardant in a DGEBA resin cured with *m*-phenylenediamine (*m*-PDA), where the blowing-out effect in combination with the flame inhibition mechanism of DOPO lowered the concentration of pyrolytic gases in the flame zone, leading to V-2 rating during

vertical flame spread tests, even with a low concentration (2.5 wt.%) of additive. To enhance the flame retardance of epoxy composites containing DOPO-modified POSS molecules, Liu et al. [40] functionalized POSS structures with two DOPO moieties (POSS-bisDOPO) by using aminopropyl substituent groups. POSS-bisDOPO showed the capability to self-assemble into nanoparticles and exhibited a very good dispersion in epoxy matrix. POSS-bisDOPO was used as flame retardant in DGEBA resin cured with DDM, and 20 wt.% loading of this DOPO derivative allowed a LOI value of 34.5% to be achieved. Wu et al. [41] prepared a titanium-POSS compound, namely *N,N'*-bis(methylene)-bis(dibenz[C,E][1,2]-oxaphosphorin6-oxide)-propylisobutyl-amino-titanium-polyhedral oligomeric silsesquioxanes (Ti-POSSbisDOPO), to combine the catalytic effect of metal (i.e. titanium) on the charring process with the flame retardant mechanism of POSS-bisDOPO. Ti-POSSbisDOPO could still self-assemble and was used to flame retard a DGEBA resin cured with DDM hardener. Conversely to POSS-bisDOPO, the incorporation of 3.0 wt.% of titanium-modified DOPO derivative in the epoxy matrix allowed self-extinction to be achieved and the LOI value to be increased up to 50%. The addition of Ti-POSSbisDOPO into the resin reduced *pk*HRR and THR values, compared to the pristine sample, and led to the formation of a residual char with honeycomb-like multilayer structure, acting as a barrier for heat and oxygen diffusion. The presence of Ti in Ti-POSSbisDOPO cages catalysed the charring process and promoted the production of stable TiO_2 in a ceramic layer on the char surface. In addition, the DOPO moieties in the additive were responsible for the release of flame inhibitors PO_2^* and HPO_2^* radicals in the gas phase.

3.3 Sol-gel functionalized graphene oxide as flame retardant

Flame retardants with silicon-char forming capability can be obtained by adding graphene oxide (GO) to silica-containing systems. This char shows high thermal stability and can exert enhanced thermal shielding effects in the condensed phase because of its low thermal conductivity. To improve the mechanical properties of these polymer-based composites, their surface may be tailored by suitable coupling agents (Table 1). Thus, Mousavi et al. [45] prepared sol-gel functionalized GO with furfuryl alcohol (GOFA) and silica nanoparticles (SGOFA) by using (3-aminopropyl)triethoxysilane (APTES) as coupling agent. SGOFA was added to a novolac resin matrix cured with *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP); the composites containing 8 wt.% of SGOFA showed a substantial amount of char residue, which was about 65.4% higher than that of pristine resin. The presence of silica nanoparticles increased

Fig. 3 SEM images of (A) graphene oxide (GO), (B) silica nanoparticles and (C and D) sol-gel functionalized graphene oxide with furfuryl alcohol and silica nanoparticles (SGOFA) at different magnifications. Reprinted with permission from [45], Copyright 2018 Elsevier



the thermal degradation temperature of novolac resin, as the silica-based filler was very well dispersed in the matrix and grafted on the graphene layers' surface (Fig. 3).

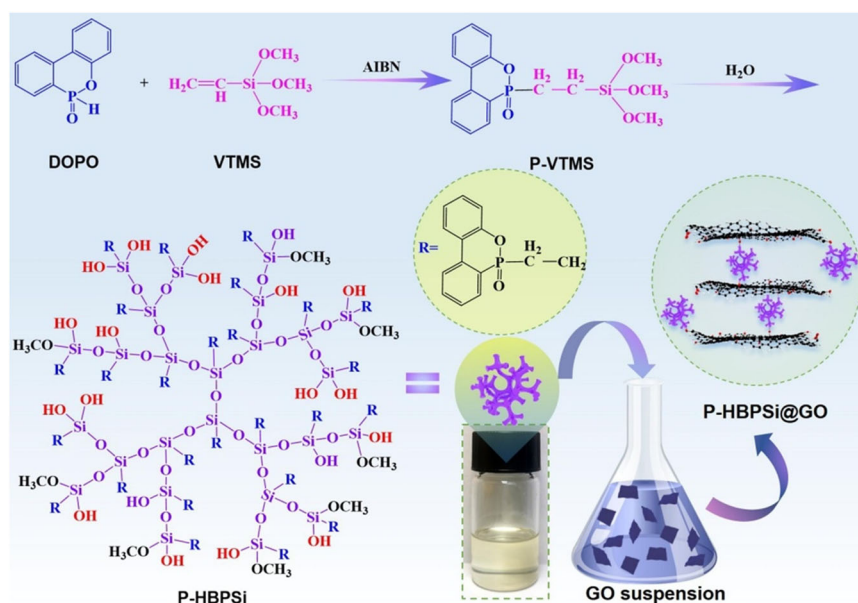
Along this research line, Ebrahimi et al. prepared silane-modified GO by grafting either furfuryl alcohol and (3-aminopropyl)trimethoxysilane (APTMS) [48] or (3-glycidyloxypropyl) trimethoxysilane (GPTMS) [47], and incorporated these hybrid fillers in composites of typical epoxy and novolac resins. In the first case, different samples were obtained by mixing epoxidized novolac, silane-modified novolac or epoxy resin, and functionalized GO. Another composite material was prepared from two silane-modified components of GO and DGEBA, cured with novolac resin in the presence of triphenylphosphine (TPP). Comparable results on the thermal properties were obtained for the two types of filler: for example, 1 wt.% of GPTMS-modified GO in the epoxy/novolac composite gave an increase of char residue from 26.7 to 34.3% and a slightly raised decomposition temperature (T_{\max} shifted from 417 to 422 °C). On the other hand, the authors did not perform a deep investigation of the fire behavior of the composites.

Also, Huang et al. [42] functionalized graphene oxide through sol-gel methodology via modification with a hyperbranched polysiloxane (P-HBPSi) (Fig. 4). The P-HBPSi@GO hybrids were used as flame retardants for thermoplastic polyurethane (TPU) by melt compounding.

SEM measurements revealed a good dispersion of the additives with well-tailored interphases in the TPU matrix. The presence of P-HBPSi in the TPU nanocomposites led to a strong decrease of pkHRR (−63.5%) and peak of smoke production rate (pSPR, −58.3%), even at a very low loading of 2 wt.%. The decomposition of P-HBPSi released trapping phosphorous radicals (e.g. PO^*) in the gas phase and formed a silicon-rich char through a catalytic charring effect of GO sheets in the condensed phase.

As reported above, the flame retardant ability of DOPO is mainly related to a gas phase mechanism, therefore the coupling with a charring agent may result in an improved thermal stability together with a strong inhibition effect. Zhi et al. [54] grafted DOPO on the surface of graphene oxide (GO) by a sol-gel route, then the so-obtained nanofiller was incorporated into a DGEBA resin cured with DDM hardener. Epoxy composite with a DOPO-GO loading of 3.75 wt.% showed an increase of LOI value up to 39% and a remarkable reduction of pkHRR (−45%) as well as of THR (−41%) compared to the pristine sample. The thermal degradation can involve both the formation a highly graphitized silica-rich char (i.e. Si–O–Si bridged structures) acting as heat barrier, and the partial decomposition of DOPO in the gas phase by a flame inhibition mechanism [63]. Luo et al. [57] functionalized reduced graphene oxide (DOPO-rGO) to be used as flame retardant for mesogenic

Fig. 4 Synthesis route of P-HBPSi@GO hybrid by sol-gel methodology. Reprinted with permission from [42], Copyright 2021 Elsevier



epoxy resin (EO). The addition of 15 wt.% of DOPO-rGO to EO (DOPO-rGO/EO-15) increased the Young's modulus by around 26.7% compared to pristine resin, which supported a reinforcing effect of the filler on the polymer matrix. DOPO-rGO/EO-15 composites exhibited higher thermal stability and char yield with respect to the unmodified resin, together with a decrease of THR value up to ~19%. Finally, DOPO-rGO/EO-15 was V-0 ranked in vertical flame spread tests.

3.4 Metal hydroxides, oxides, and sol-gel architectures as flame retardants

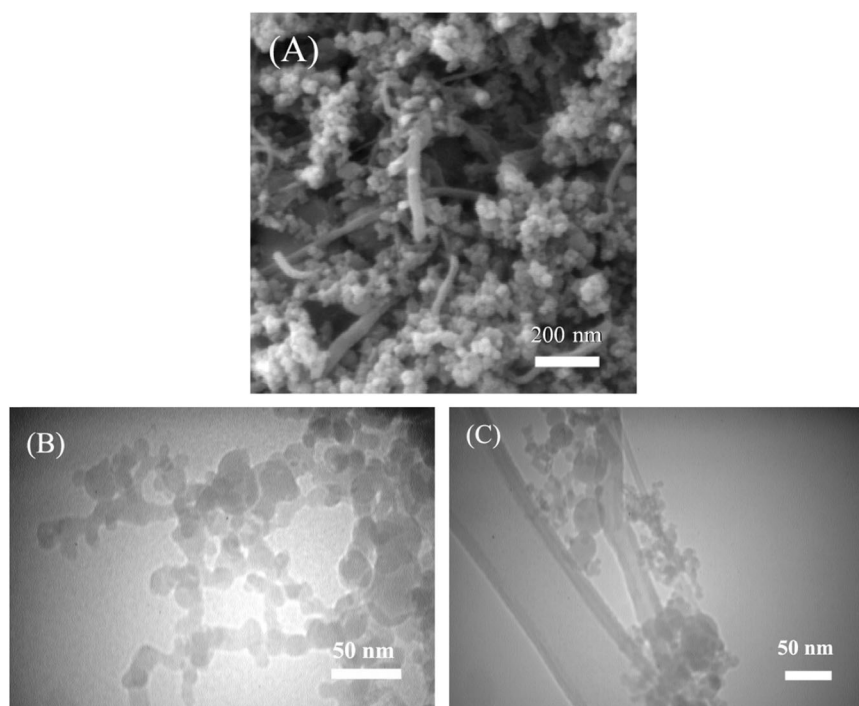
Metal hydroxides are considered green flame retardants because of their low toxicity and high effectiveness. Their flame retardant mechanism is based on the release of water diluting the flame zone and the formation of refractive oxides exerting thermal shielding and oxygen barrier effects. This mechanism is known in the literature as the "sink effect" and shows eco-friendly and low-cost characteristics. Metal hydroxides such as aluminum hydroxide and magnesium hydroxide are widely used for enhancing the fire protection and thermal stability of polymer-based composites.

Silicon-based structures act as versatile grafting agents, allowing for excellent interphases and tailored hybrid phases; moreover, they can play a relevant role in flame retardance by themselves. Silica has been incorporated in polymer matrices by either in situ synthesis or separately prepared nanoparticles, as summarized in Table 1. The former approach, relying on sol-gel reactions of different silane precursors, offers a vast range of possibilities.

Epoxy and novolac resins conjugated with silane compounds were synthesized by Abdollahi et al. [46, 64]

through sol-gel processing, using TEOS, APTES, and (3-glycidyloxypropyl) trimethoxysilane (GPTMS). Specifically, silane-modified epoxy resin (MER) was prepared by grafting TEOS oligomers onto the hydroxyl groups of epoxy resin, forming silica-epoxy hybrids (SEH). Silane-modified novolac resin (MNR) was obtained with GPTMS through a ring-opening reaction, then it was mixed with MER to form silica-novolac-epoxy hybrids (SNEH). Both samples were prepared with 4 and 8 wt.% of SiO₂. Moreover, hybrids with epoxidized novolac resin (ENR) were studied. The composites were cured with ethylenediamine in 4 steps, within 90 and 160 °C. The hydrolysis and condensation processes led to the growth of spherical silica nanoparticles anchored in the polymer matrix. Thermal analysis evidenced a char yield of about 22% in the silica-epoxy resin composite, and much larger values in the presence of novolac components (around 50–60%), confirming the significant thermal stability of novolac resins and the role of the SiO₂ phase in its enhancement. In a further research effort [46], in addition to TEOS-modified epoxy resin (MER), GPTMS-modified novolac resin (MNR) and epoxidized novolac resin (ENR), silica-grafted carbon nanotubes (SFCNT) were synthesized and used to obtain the hybrid systems. Carbon nanotubes (CNT) were functionalized with APTES-modified hydroxylated silica nanoparticles. The formulation containing 4 wt.% of SFCNT, MNR, and ENR showed the highest char yield (58.4%), while that containing 4 wt.% of SFCNT and MER exhibited the highest degradation temperature (443 °C). The combined presence of 4 wt.% of SFCNT, MER, and MNR guaranteed a degradation temperature of 439 °C and char yield as high as 47.2%. Microscopy analysis and X-ray diffraction revealed that the silica nanoparticles were finely

Fig. 5 A SEM image of SFCNT and TEM images of (B) SiO₂ and (C) SFCNT. Reprinted with permission from [46], Copyright 2018 Elsevier



distributed on the surface of CNTs by chemical bonding (Fig. 5). The use of functionalized carbon-based nanostructures can be highly effective in boosting the char formation, and a strong decrease of flammability can be obtained by a synergistic effect with nitrogen or phosphorus. Carbon-based nanostructures can promote the charring process, thus giving a predominant role in the condensed phase during the combustion.

In situ methodology allows for a variety of self-extinguishing strategies, including the production of organic-inorganic hybrid composites. Among these materials, aerogels made of polymer-ceramic networks, characterized by very low density and thermal conductivity, attract large interest in thermal insulation and fire protection [65]. It is well known that the low thermal conductivity of silica aerogels, due to the presence of air entrapped in their structure, positively affects the endothermic processes during the combustion by slowing down the heat transfer. In view of the above, phenol-formaldehyde resin/silica aerogels were prepared by co-polymerization and nanoscale phase separation, starting from TEOS, phenol and formaldehyde, via hydrothermal treatment and supercritical CO₂ drying [66]. Homogeneous interconnected networks with domain sizes below 20 nm were obtained. The composites showed good mechanical features and the minimum thermal conductivity value (i.e., 24 mW/(m·K)), lower than commercial expanded polystyrene or glass wool. The aerogel with 70% silica content resisted a high-temperature flame (about 1300 °C) without disintegration and prevented the temperature increase on the non-exposed side above

350 °C, suggesting efficient protection against fire-induced collapse of reinforced concrete structures. Also, hybrid aerogels composed of polyvinylmethyldimethoxysilane (PVMDMS) and polybenzoxazine (PBZ), in molar ratios between 1 and 3, were prepared by a sol-gel method and ambient pressure drying [67]. During the synthesis in acidic environment, the ring-opening polymerization of the benzoxazine monomer occurred simultaneously with the hydrolysis and condensation of methoxy groups in PVMDMS to form polysiloxanes. The result was a three-dimensional network structure with specific surface area of 51–57 m²/g, pore size distribution of 30–300 nm, density as low as 0.11 g/cm³, and low thermal conductivity (43.2 mW/(m·K)). With the highest PVMDMS content, the density and thermal conductivity decreased, compressive modulus and strength notably increased, and the flame retardance improved, as suggested by the decrease of pkHRR compared to PBZ aerogel (91.7 W/g, –26.6%).

Furthermore, Halim et al. [44] combined the use of aluminum hydroxide with nano-porous silica aerogel (SA) to prepare a hybrid flame retarded unsaturated polyester resin (UPR). The SA was extracted through a sol-gel route from renewable rice husk, and can therefore be considered as a suitable bio-waste flame retardant for such polymer matrices. Halim et al. doped aluminum trihydroxide (ATH) with SA and the SA-ATH hybrid additive was incorporated into the UPR to improve the thermal stability of the final composite via a synergistic effect exerted by the hydroxide and silica aerogel. In particular, the styrene monomer contains carbon double bonds acting as a hardener by bridging

adjacent polymer molecules at their unsaturation points [68]. The SA-ATH hybrid flame retardant increased the tensile strength of UPR by 18% and conferred self-extinguishing characteristics to the polymer. 15 wt.% of ATH could allow for V-0 rank in vertical flame spread tests, although the combination of ATH (15 wt.%) and SA (15 wt.%) was necessary to obtain negligible smoke production and a significant decrease of flame propagation rate.

Another example of polymer-silica hybrid composite was reported by Devaraju et al. [69], who developed a novel bio-based polybenzoxazine (PBZ) using eugenol and furfurylamine through a Mannich reaction. 3-mercaptopropyltrimethoxysilane (MPTMS) was introduced as coupling agent by a thiol-ene click reaction between the -SH group and the allyl group of eugenol and then a PBZ-silica network was obtained using TEOS in variable concentration, up to 1:1 weight ratio with the biopolymer. The composites showed a T_g as high as 175 °C, char yield reaching 67.5% and considerable LOI increase, from 34.0 to 44.5%. It was proposed that the abundant silica phase acts as a protective passive layer on the surface of the composite, preventing further oxidation of the inner part of the PBZ.

The addition of acidic compounds into polymer systems can promote char formation during combustion. For example, the degradation of phosphorus-based flame retardants can release acidic phosphorous species, exerting their flame retardant effect in the condensed phase [70]. Also, the presence of metal-containing species (MCS) in combination with carbon sources can catalyze the char production, where MCS are active in the condensed phase by dehydrating the polymer matrix. Chen et al. [49] prepared five $SO_4^{2-}/TiO_2-M_xO_y$ solid super acids (SSA: Cu@Ti:SSA, Zr@Ti:SSA, Fe@Ti:SSA, Mn@Ti:SSA, Mo@Ti:SSA) through sol-gel methods and incorporated them together with ammonium polyphosphate/montmorillonite (AM) into an unsaturated polyester resin cured with a phthalate solution of cobalt naphthenate and cobalt isooctanoate to boost its flame retardance. The incorporation of SSA in the resin resulted in an enhanced thermal stability and a lower smoke production rate, due to the formation of a continuous and compact char showing high density and barrier effect toward flammable gases and heat. In addition, SSA additives exerted a strong catalytic effect on esterification and dehydration processes, leading to an increase of LOI up to 27.2% and thus a lower flammability.

The sol-gel methodology allows for the developments of several type of nanostructures. The use of core-shell nanoparticles in the improvement of flame retardance of polymer nanocomposites can be promising in the exploitation of different flame retardant effects. In addition, the design of such nanoparticles can be modulated to obtain flame retardant additives able to act at different stages of the

combustion process. Phosphorus-containing compounds can exert a strong flame inhibition by releasing PO^* and PO_2^* radicals, which can terminate oxygen radicals in the flame, leading to self-extinguishing behavior. Also, the combined use of silica nanoparticles and nitrogen-based flame retardant, such as melamine, can promote the formation of a silicon-rich and intumescent char in the condensed phase. This char can work as a physical barrier limiting the oxygen diffusion toward the polymer bulk, also reducing the thermal conductivity during the pyrolysis. To combine all these effects and enhance the flame retardance of polyurethane foams, Liu et al. [50] synthesized core-shell nanoparticles by encapsulation of silica in a shell consisting of phosphoric acid (HP) and ammonium molybdate. These nanoparticles were used as flame retardant; polyurethane samples containing 25 wt.% of SiO_2 microcapsules achieved a LOI value of 34.8% and V-0 ranking in vertical flame spread tests, without any detrimental impact on the mechanical properties of the composites. Qu et al. [51] investigated the use of a microencapsulated flame retardant to improve the fire behavior of a DGEBA epoxy resin cured with DDM. In this case, silica was selected as shell phase and the core was hexaphenoxycyclotriphosphazene (HPCTP, Fig. 6). The hybrid system (Si(H)) was designed to exploit the synergistic flame retardant action of phosphorus–nitrogen–silicon combinations and prevent the use of a significant amount of additive to achieve good performances. Epoxy composites containing Si(H) were manufactured by using KH-550 or KH-560 as coupling agents to promote interactions. Si(H)/EP composites containing 1.5 wt.% of additive showed good tensile properties and V-1 rating in the vertical flame spread tests, with an increased LOI value of 30.3%. Due to its composition, the flame retardant could exert a flame inhibition mechanism on oxygen radicals and dilute the gas phase by releasing

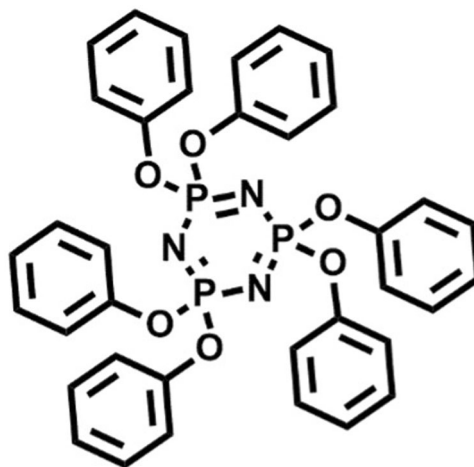
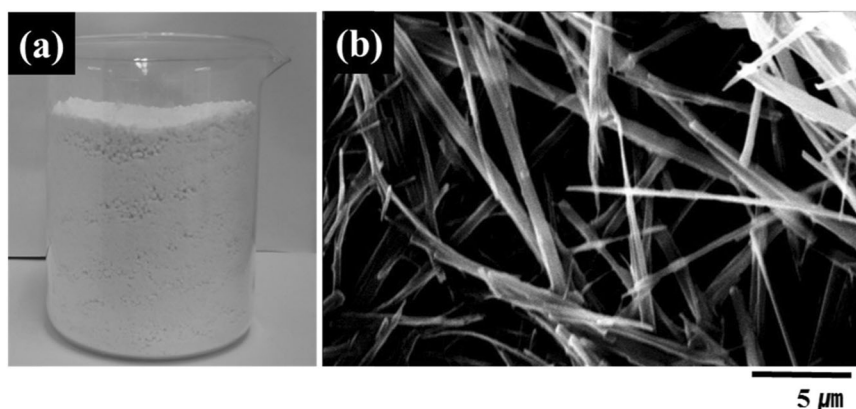


Fig. 6 Chemical structure of hexaphenoxycyclotriphosphazene (HPCTP) flame retardant [51]

Fig. 7 Images of MOS: (a) MOS powder, and (b) SEM morphology of MOS. Reprinted with permission from [52], Copyright 2018 Elsevier



nitrogen. On the other hand, the generation of acidic phosphorous compounds boosted the charring effect and, in the presence of silica, the formation of a protective silica-rich char in the condensed phase.

The sol-gel technique allows for a flexible chemistry and for the preparation of several architectures, as for example whisker nanoparticles. Kim et al. [52] prepared magnesium oxysulfate (MOS) whiskers (Fig. 7) to be used as flame retardants for polypropylene composites. Polypropylene is widely employed as a commodity and it is fundamental for the manufacturing of several products, for which good thermal stability and fire behavior are required. Polypropylene is a thermoplastic and non-charring polymer; therefore, the combination of sol-gel chemistry and inorganic-based additives could increase the melt viscosity of the burning system, promoting a thermal shielding effect in the condensed phase during combustion. MOS whiskers with high aspect ratio were treated with 3-methacryloyloxypropyl-trimethoxy silane via sol-gel reactions to improve the interphase of the final composites. The incorporation of 30 wt.% of MOS into polypropylene increased the tensile strength at yield and modulus by 50.8% and 362%, respectively, compared to the pristine system. The research group demonstrated that MOS could exert a notable endothermic effect by releasing water molecules through a two-step weight-loss, which reduces the flammability and increases the LOI from 18 to 19.5%.

In the development of new flame retardant systems for polymer-based composites, smoke suppression is a priority target, as it is one of the most dangerous hazards during a fire scenario. The literature reports that metallic oxides are effective smoke suppressants because of their ability to increase the content of post-combustion char residue and reduce the production of benzene [71]. Sol-gel methodology can help to combine this property of metal oxides with beneficial aspects of silicon-containing species, as a synergistic activity could boost the flame retardance of burning polymers in the condensed phase. Indeed, sol-gel processing offers great flexibility in the production of multi-component oxides containing silicon, phosphorus and

metals, with homogeneously cross-linked structures and fine dispersion of each phase [72]. Silicon and/or metal-containing particles synthesized by sol-gel approaches have often been tested as flame retardant fillers. The addition of silica nanoparticles is generally less effective in the improvement of flame retardance compared to silica aerogel and in situ generated silica. However, the assembly of a backbone of nanoscale SiO_2 obtained by the Stöber method in polymer fiber networks through electrospinning showed the ability to induce fire resistance in polyvinylpyrrolidone blankets [73, 74].

Sol-gel SiO_2 nanoparticles were added in small percentages to typical phenol-formaldehyde resins, which were further processed as foams with the aid of Tween 80 surfactant, n-pentane and a curing agent [75]. An increase in the initial decomposition temperature was observed, though the lack of data hindered an insight into the effect of nanosilica on the behavior of the composites. Silica nanoparticles (2–10 wt.%) were added also to a carbazole terminal benzoxazine monomer, synthesized using p-phenylene core diimines with N-(4-aminophenyl) carbazole through a Mannich reaction [60]. Nanosilica condensed with the monomer during polymerization and thermal curing. As a consequence, some shift of the degradation onset temperature and an increase of LOI from about 32–36% was observed.

The functionalization of sol-gel silica is a viable way toward the enhancement of their performances. Guo et al. [53] developed core-shell microspheres of SiO_2 with a Zr-based metal organic framework (Universitetet i Oslo-66, UiO-66) by covalent linkages between amine groups in UiO-66- NH_2 and epoxy groups on the functionalized surface of silica. The so-prepared microspheres ($\text{SiO}_2@$ UiO-66-2) exhibited very good dispersion in a DGEBA matrix cured with DDM, compared to systems containing either SiO_2 or UiO-66- NH_2 only, resulting in a slight increase of glass transition temperature and modulus. Hybrid epoxy composites containing 3 wt.% of $\text{SiO}_2@$ UiO-66-2 showed a strong decrease of total smoke

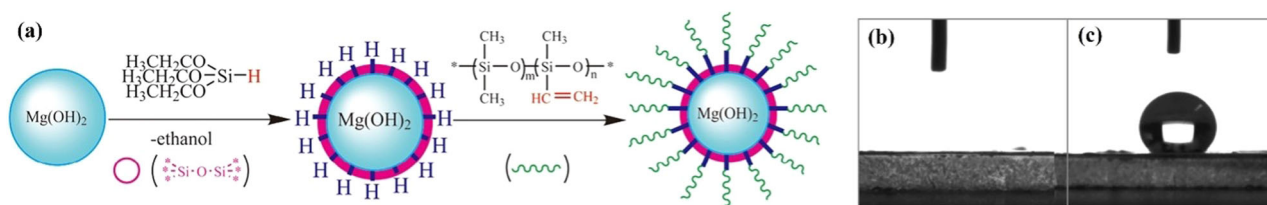


Fig. 8 Preparation of magnesium hydroxide modified with TEOS and polymethyl–vinyl silicone rubber (a); photographs of a water droplet on bare (b) and modified $\text{Mg}(\text{OH})_2$ (c). Reprinted with permission from [62], Copyright (2019) Wiley

production (by ~16%), pkHRR (~31%) and THR (~23%). The enhancement in the flame retardance was attributed to the presence of the silicon- and zirconium-containing complexes in the additive and to the formation of a continuous and compact char during the combustion, acting as barrier for oxygen and heat.

Phosphorus-containing silica was prepared by acid hydrolysis and condensation of sodium silicate using three different phosphorus precursors (namely, H_3PO_4 , H_3PO_2 and Na_2HPO_4) [76]. The obtained particles, about 1 μm in size, incorporating 2–5 wt.% of P, were used as fillers in an epoxy resin cured with an alkylamine. Beside a shift of the degradation onset temperature and a slight increase of LOI (from 23 to 24%), only qualitative observations on the effect of the fillers were reported.

Nickel phyllosilicate (NiPS) particles characterized by layered structures were added to an epoxy resin, studying their effect on the fire behavior and mechanical properties [61]. The bare NiPS was ineffective in improving the flame retardance of the composites, whereas its decoration with Fe elements enabled it to pass the UL-94 test with V-1 rating. In a further effort by the same research group, NiPS particles were functionalized by DOPO during the sol-gel synthesis, adding DOPO grafted on GPTMS to $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, followed by hydrolysis and condensation in alkaline medium. The presence of 5 wt.% of the obtained phosphorus-modified filler (P-NiPS) increased the LOI from 23.8 to 29.2% while the burning time dropped down to 7 s, achieving the V-0 rating in vertical flame spread tests. The pkHRR and THR considerably decreased compared to pure epoxy (–62.5% and –23.7%, respectively) and the final residual mass was tripled. Moreover, smoke and CO productions were also suppressed significantly, whereas the mechanical properties underwent only limited variations [61].

Finally, in order to reduce its hydrophilicity and improve its compatibility with the polymer, magnesium hydroxide was modified with triethoxysilane (TES) and polymethyl–vinyl silicone rubber and added to composites of oil-extended styrene–ethylene–butadiene–styrene (O-SEBS) with polypropylene, useful in the manufacture of cables and wires (Fig. 8) [62]. Both bare and modified $\text{Mg}(\text{OH})_2$ allowed a V-0 rating in vertical flame spread tests to be achieved

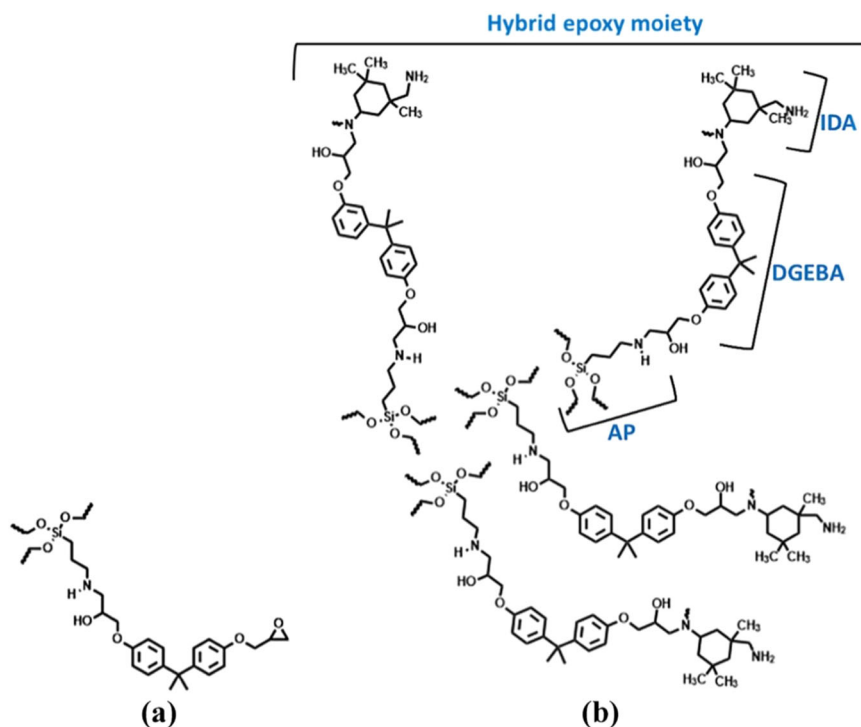
without melt dripping when the filler loading was increased up to 70% or beyond, with corresponding LOI about 38–36%, more than double the initial value of the O-SEBS-PP polymer (LOI = 17%). In addition, the functionalization and encapsulation of $\text{Mg}(\text{OH})_2$ resulted in a reduction of total smoke production and improvement of the mechanical properties (tensile strength and elongation at break) and water resistance of the composites.

3.5 Sol-gel chemistry and biowaste materials for the development of greener flame retardant strategies

The exploration of new greener methodologies to flame retard polymer-based composites is gaining attention. To reduce the environmental issues related to the growing pollution, the use of sol-gel strategies involving biowastes as flame retardant additives is considered highly promising. Traditional methodologies are based on the exploitation of halogen-based compounds to improve the fire behavior, although these species are responsible for the release of toxic gases, especially during the disposal of composites. In this context, Venezia et al. [55] investigated the use of humic acid (HA) as a biowaste flame retardant in epoxy resins. Among the bio-wastes, HA is one of the most interesting being explored as a flame retardant. Humic matter is the result of a chemical extraction from the soil organic matter and represents the humic molecules distributed in the soil or water. From a chemical point of view, it is composed of a mixture of many different acids containing carboxyl and phenolate groups [77]. To effectively use humic acid as a bio-waste flame retardant, the authors modified a DGEBA resin, cured with IDA, with APTES to obtain hybrid moieties with more polar groups (Fig. 9). This procedure allowed for a good dispersion of humic acid throughout the APTES-modified epoxy matrix and thus the final composites showed uniform composition and properties.

HA was used alone and in combination with urea and ammonium polyphosphate to flame retard DGEBA resin. Silicon-modified epoxy chains improved the dispersion of HA, which alone prevented melt dripping during combustion. Epoxy composites containing 6 wt.% of HA and 1

Fig. 9 **(a)** Silanized epoxy species; **(b)** hybrid polymer moiety (reprinted with permission from [55]). Copyright (2021) American Chemical Society



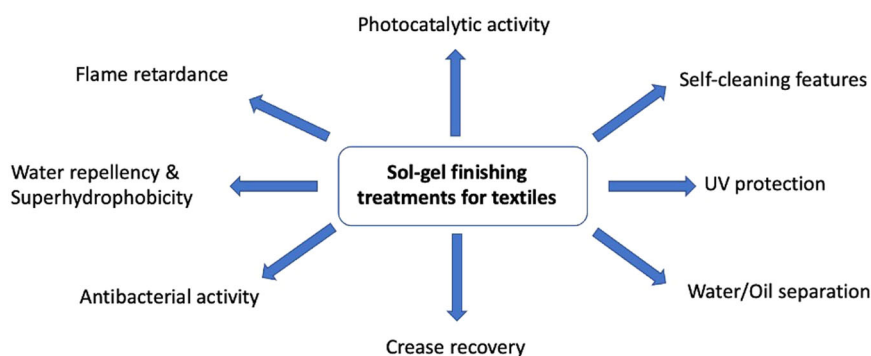
wt.% of APP achieved V-0 rating in vertical flame spread tests. Furthermore, the combination of HA with APP and urea was found to reduce the pkHRR up to 52% and increase the time to flashover up to 1.8 min, without any negative effect on the mechanical properties. The self-extinguishing capability of the hybrid epoxy resin was explained through microscopy and gas evolution analysis. HA was responsible for a strong condensed phase activity. The synergism of HA with urea and APP could produce N–P–O–Si chain containing intumescent char, acting as protective barrier for heat and oxygen, whereas ammonium polyphosphate mainly exerted a gas phase activity by a flame inhibition mechanism.

However, the conversion of bio-waste into flame retardant additives for polymers is allowing for a reduction of primary sources depletion (e.g., phosphorus) and the development of new products through a waste-to-wealth approach. Kaya et al. [43] prepared a silica xerogel from groundnut hull ash, which was sol-gel functionalized with tetrabutylammonium bromide to improve its dispersion in DGEBA epoxy. In addition, methyl nadic anhydride (MNA) and 2,4,6-tris(dimethylaminomethyl)phenol (TDP) were used as accelerator and curing agent, respectively. Amorphous silica xerogel was characterized by low thermal conductivity and high thermal stability and the incorporation of 2 wt.% of this additive into the resin resulted in an increase of char residue from 15.3 to 18.0% and self-extinguishing capability (UL 94-V-0 rating). In a context of green chemistry, the use of tetrabutylammonium bromide should be avoided, as it contains halogen species, although

the sol-gel methodology allows for mild operative conditions and thus cost and energy saving.

Concerning thermosetting polymers, epoxy resins are widely used in several industrial applications and it is well known that these polymers can be cured by using aromatic or aliphatic hardeners. Indeed, the chemistry of curing agents strongly influences the final properties of epoxy-based composites. Though the use of aromatic hardeners guarantees higher mechanical performances and thermal stability, the aliphatic alternatives are preferred because of their lower environmental impact. At variance, these latter compounds are also highly flammable and require longer curing processes [78]. In light of this, the sol-gel methodology can also be applied to modify curing agents of epoxy-based materials, allowing for the production of more sustainable hardeners. The introduction of metals or phosphorus groups in the chemical structure of amino curing agents can improve the fire behavior without any addition of additive in the polymer matrix. This strategy is usually exploited to avoid any negative effect on the glass transition temperature and mechanical properties. In such perspectives, Cheng et al. [56] synthesized an amino curing agent composed of silicon/titanium flame-retardant elements (STCA) and based on APTES and tetrabutyl titanate. The incorporation of 4 wt.% of STCA into DGEBA resin led to composites showing high strength and glass transition temperature, with relatively good toughness. Besides, the composites containing 4 wt.% of STCA exhibited V-0 rating in vertical flammability tests and increased char yield (+52.7%) compared to the pristine system. The presence of

Fig. 10 Main uses of sol-gel finishing treatments for textile materials



silicon/titanium species (i.e., Si–O–Ti, Ti–O–Ti bonds) in the amino curing agent promoted the formation of a compact and intumescent char layer during the degradation process, slowing down the diffusion of heat and oxygen into the interior polymer structure.

4 Sol-gel flame retarded cotton textiles: recent advances

The exploitation of sol-gel treatments for conferring flame retardance to textiles is nowadays well consolidated; however, the main disadvantage of this approach is the reduced thickness of the fibers and fabrics, as these latter can be only partially protected by the in situ created ceramic or hybrid coating. Therefore, to solve this issue, usually the sol-gel treatments are carried out in the presence of other flame retardant systems, hence giving rise to synergistic or at least combined effects that allow good fire performances to be achieved. This finding further justifies the use of sol-gel treatments in combination with phosphorus- or phosphorus/nitrogen- containing additives.

Apart from the very pioneering works that appeared in the mid-2000s [79–81], the research on the use of sol-gel derived systems for conferring high flame retardant properties to different textile materials has grown substantially in recent years. In addition, the recent advances in this topic are focused on providing not only flame retardance to the treated substrates, but also multifunctional features, as shown in Fig. 10.

Hereafter, the most recent advances will be summarized and discussed, specifically referring to cotton, which represents the purest source of cellulose and the most important natural fiber, on which sol-gel treatments have been performed. The economic importance of cotton fibers and fabrics in the worldwide market is witnessed by their dominant share (beyond 50%) among the fibers employed for clothing and textile goods [82]. Despite all of its interesting features (such as dyeability, hydrophilicity, wearability, comfort, and breathability, among others) cotton fabrics easily burn when exposed to an irradiative

heat flux or to a direct flame application, leaving a negligible residue and producing harmful smokes. Also taking advantage of the structure of cellulose, which bears several “reactive” hydroxyl groups, cotton fibers and fabrics have been the focus of several successful academic and industrial research studies, aiming at providing effective flame retardant features. Many of the proposed approaches deal with the design of tailored sol-gel treatments; the most recent ones are summarized in Table 2 and discussed in the following Sections.

One of the recent approaches focuses on the use of sol-gel precursors bearing P and N elements in their molecules, i.e., an “all in one” FR recipe; this way, its application to the cellulosic substrate is quite simplified and does not require successive steps.

A first example comes from our group [83], who exploited the sol-gel approach for synthesizing a P- and N- ceramic FR intumescent coating starting from 3-glycidyloxypropyl triethoxysilane modified N-(phosphonomethyl) iminodiacetic acid, hydrolyzed and condensed with tetraethoxysilane. The cotton fabrics treated with the synthesized flame retardant (25.2% add-on) achieved self-extinction in vertical flame spread tests; in addition, an increase of the residue (+26%) and a decrease of THR (–41%) and pkHRR (–12%) with respect to untreated fabric was found during forced combustion tests under an irradiative heat flux of 35 kW/m². The flame retardant mechanism was also identified; in particular, the sol-gel derived coating catalyzed the formation of a char layer that confines the heat and mass transfer, thus reducing the formation of flammable volatile species. Meanwhile, the concurrent presence of the created silica phase synergistically acted with the formed char, with the latter being more stable and preventing the fire spread.

Pursuing this effort, Xu and co-workers [84] synthesized an α -aminodiphosphonate siloxane through a Kabachnik-field reaction, employing dimethyl phosphate as diacylphosphite, paraformaldehyde as carbonyl compound and 3-aminopropyltriethoxysilane as nitrogen source. After having confirmed its chemical structure by means of NMR and FTIR analyses, the synthesized siloxane was applied to

Table 2 Recent sol-gel FR treatments applied to cotton – main outcomes

Sol-gel system	Main outcomes of the treated fabrics	Ref.
3-Glycidyoxypropyl triethoxysilane modified N-(phosphonomethyl) iminodiacetic acid + Tetraethoxy silane	<ul style="list-style-type: none"> • V-0 classification in vertical flame spread tests • Decrease of THR (–41%) and pkHRR (–12%) in forced combustion tests 	[83]
a-aminodiphosphonate siloxane	<ul style="list-style-type: none"> • 27.5% LOI achieved • V-0 classification in vertical flame spread tests • Acceptable durability to laundry cycles 	[84]
1-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-4-(trimethoxysilylmethyl) piperazine	<ul style="list-style-type: none"> • V-0 classification in vertical flame spread tests • 27.6% LOI achieved for the highest dry add-on (i.e., 42.4%) • Decrease of THR (–30%) and pkHRR (–30%) in forced combustion tests for the highest dry add-on (i.e., 42.4%) 	[85]
di-(trimethoxysilylpropyl) spirocyclic pentaerythritol bisphosphonate	<ul style="list-style-type: none"> • V-0 classification in vertical flame spread tests • 29.5% LOI achieved for the highest dry add-on (i.e., 32.3%) • Decrease of THR (–32%) and pkHRR (–23%) in forced combustion tests for the highest dry add-on (i.e., 32.3%) • Acceptable durability to 20 laundry cycles 	[86]
P-diphenyl-N-(3-(trithoxysilyl) propyl) phosphinic amide + polydimethylsiloxane @silicon dioxide	<ul style="list-style-type: none"> • LOI values as high as 26% • Self-extinction in vertical flame spread tests • Decrease of pkHRR (by 22%) and THR (by 25%) • Super hydrophobicity (water contact angle with water >150°) and self-cleaning features • Increased abrasion resistance 	[87]
dimethyl-3-triethoxysilanepropyl phosphoramidate	<ul style="list-style-type: none"> • 30.3% LOI achieved for the highest dry add-on (i.e., 16%) • Decrease of THR (-33%) and pkHRR (-51%) in forced combustion tests for the highest dry add-on (i.e., 16%) • Washing fastness (20 laundry cycles) 	[88]
Titanium (IV) butoxide and boric acid	<ul style="list-style-type: none"> • V-0 classification in vertical flame spread tests for the fabrics treated with the highest dry add-on (i.e., 16.2%) • The titania-based treatments provided hydrophobicity to cotton • Weak durability (FR features lost after 5 laundry cycles) 	[89]
Ionic liquid-assisted in situ sol-gel metathesis reaction	For the ionic liquid made of methylimidazolium cation in combination with PF ₆ anion: <ul style="list-style-type: none"> • Increased LOI up to 24% • Decrease of THR (–38%) in MCC tests 	[90]
(3-piperazinypropyl)methyldimethoxysilane reacted with phytic acid	<ul style="list-style-type: none"> • Increased LOI up to 29% (cotton treated with 5 wt.% of FR product) • Decrease of THR (–58%) and pkHRR (–46%) for cotton treated with 5 wt.% of FR product 	[91]
Tetraethoxysilane reacted with phytic acid in the presence of sodium alginate	<ul style="list-style-type: none"> • Self-extinction in vertical flame spread tests • Decrease of THR (–80%) and pkHRR (–74%) for cotton treated with the sol-gel recipe containing the highest tetraethoxysilane loading (i.e., 0.9 mol/L) 	[92]

cotton fabrics by soaking at 70 °C for 1 h, subsequently drying at 100 °C for 5 min and finally curing at 180 °C for 5 min. The sol-gel treated fabrics showed high LOI values (achieving 27.5%) and reached V-0 classification in vertical flame spread tests. In addition, as assessed by forced combustion tests, the sol-gel treatments accounted for a decrease of both pkHRR (–51%) and THR (–33%), as well as for a remarkable increase of the final residue (up to 20.3%), hence indicating their char-forming effectiveness in the condensed

phase. Finally, the fire performances were not significantly affected by washing cycles, though self-extinction in vertical flame spread test was lost after laundry.

Another possibility to exploit sol-gel precursors containing P and N elements in their molecule has been demonstrated by Zhang and co-workers [85], who synthesized a reactive flame retardant, (namely 1-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-4-(trimethoxysilylmethyl) piperazine), which was applied to cotton through soaking, subsequent

drying (30 min at 90 °C) and final curing (10 min at 110 °C). Three treatments with different dry add-ons (namely, 25.2, 33.2 and 42.4%) were carried out on the cellulosic substrate. Irrespective of the weight gain, the treated fabrics shows increased LOI values (up to 27.6%) and V-0 classification in vertical flame spread tests. Furthermore, as revealed by forced-combustion tests performed at 35 kW/m² irradiative heat flux, the fabric treated by the sol-gel derived FR at the highest loading was able to decrease either pkHRR or THR (each by about 30%), as well as to significantly increase the final residue (+19.1%) with respect to the untreated counterpart, indicating the occurrence of a combined condensed and gas phase FR mechanism.

In a further research effort, the same research group [86] treated cotton with di-(trimethoxysilylpropyl) spirocyclic pentaerythritol bisphosphate. In particular, after soaking in the sol-gel precursor solution, the treated fabrics were dried at 90 °C for 10 min, and finally cured at 120 °C for 5 min. Regardless of the final dry add-on, all the sol-gel treated cotton was self-extinguishing as revealed by vertical flame spread tests; in addition, at the highest dry add-on (i.e., 32.3%), LOI was as high as 29.5% (vs. 18.1% for untreated fabric). Further, at this add-on, forced-combustion tests carried out at 35 kW/m² irradiative heat flux showed a remarkable decrease of pkHRR and THR (around -23 and -32%, respectively). Finally, the proposed treatment showed a very good durability, as the treated fabrics were able to withstand 20 laundry cycles without significantly losing their fire behavior. The flame retardant mechanism was explained either on the basis of the formation of a stable aromatic char in the condensed phase, or on the release of non-combustible volatile species in the gas phase.

Qi et al. [87] succeeded in providing cotton fabrics with multifunctional features (i.e., super-hydrophobicity, abrasion resistance and flame retardance) by combining P-diphenyl-N-(3-(triethoxysilyl) propyl) phosphinic amide with a hydrophobic finishing agent (namely polydimethylsiloxane@silicon dioxide) in a sol-gel process. To achieve this aim, cotton fabrics were soaked in the sol solution at room temperature for 30 min and dried in an oven at 70 °C for 5 h. As revealed by flammability tests, the treated fabrics showed LOI values as high as 26% and achieved self-extinction in vertical flame spread tests. In addition, the surface treatment accounted for a significant decrease of pkHRR and THR (around -22 and -25%, respectively), as assessed in forced-combustion tests. These findings were attributed to the high char-forming character of P-diphenyl-N-(3-(triethoxysilyl) propyl) phosphinic amide. In addition, the presence of polydimethylsiloxane@silicon dioxide was responsible for very high contact angle values with water (beyond 150°), as well as for self-cleaning features. Finally, the sol-gel recipe was able to increase the abrasion resistance of the cellulosic substrate.

Jiang and co-workers [88] exploited the Atherton-Todd reaction for synthesizing a reactive phosphoramidate siloxane, namely dimethyl-3-triethoxysilane propyl phosphoramidate; the product was applied to cotton by means of a sol-gel process. Three different final dry add-ons were achieved, namely 5, 9 and 16 wt.%. For the latter value, it was possible to reach a LOI as high as 30.3%, as well as self-extinction in vertical flame spread tests. Besides, the same FR loading was found to significantly lower both pkHRR and THR (by about 68 and 49%, respectively) with respect to the untreated cellulosic fabric, as assessed by forced-combustion tests (irradiative heat flux: 35 kW/m²). These findings were attributed to either the high char-forming character of the sol-gel derived coatings, or the release of noncombustible species in the gas phase. Finally, the proposed treatment showed a very good durability, as the treated fabrics were able to resist 20 washing cycles without significantly losing their fire retardance, with a very limited effect on the overall mechanical behavior of cotton.

The recent scientific literature also reports some excellent papers describing the exploitation of sol-gel processes for conferring flame retardant features to cotton but using different alkoxy precursors not containing Si. As an example, Bentsis et al. [89] prepared a series of sols based on titanium (IV) butoxide and boric acid (used as a functional additive in different molar ratios, namely 0.1, 0.5, 1.0, and 2.5). Cotton fabrics were treated with the obtained sols, using a pad-dry-cure process, in which the fabrics were soaked in the precursor solution at room temperature for 5 min, then padded, dried at 80 °C for 1 h and finally cured at 120 °C for 1 h. Self-extinction in vertical flammability tests was achieved by the fabrics with the highest dry add-on (i.e., 15.2%). In addition, the titania-based deposited coatings were also hydrophobic, remarkably decreasing the water uptake with respect to the untreated cotton. Unfortunately, the washing fastness of the treated fabrics was very poor, as the FR properties were lost after 5 laundry cycles.

The same research group [90] recently proposed an interesting sol-gel approach involving ionic liquids and consisting of two consecutive steps. In the first, 1-methylimidazolium chloride propyltriethoxysilane or pyridinium chloride propyltriethoxysilane were applied by sol-gel processing to cotton (soaking for 5 min at room temperature; drying at 80 °C for 1 h; curing at 120 °C for 1 h). Then, the treated fabric underwent an anion exchange with different products, namely hexafluorophosphoric acid, sodium tetrafluoroborate, sodium acetate, bis(trifluoromethane)sulfonimide lithium. The ionic liquid made of methylimidazolium cation in combination with PF₆ anion showed the best fire behavior with a LOI as high as 24% (vs. 20%, untreated cotton) and decreased THR (by about 38% with respect to the neat fabric), as assessed by microcone calorimetry (MCC) tests.

A significant part of the research on FR sol-gel derived systems has been recently addressed toward the design and application of formulations containing bio-sourced additives. Some interesting examples refer to the use of inositol hexakisphosphate acid, better known as phytic acid. This compound has a high phosphorus content (28 wt.%, distributed in 6 phosphate groups) and can be easily obtained from plant tissues, such as cereal grains, beans, and oil seeds [93]. In particular, (3-piperazinylpropyl)methyldimethoxysilane was reacted with phytic acid, and the obtained product applied to cotton fabrics using a sol-gel method [91]. The fabrics treated with 4 or 5 wt.% of FR product achieved self-extinction in vertical flame spread tests and showed high LOI values (around 26% and 29%, respectively). In addition, the fabrics treated with 5 wt.% of FR product exhibited a remarkable decrease in both pkHRR and THR by about 46 and 58%, respectively, as assessed through cone calorimetry tests (irradiative heat flux: 35 kW/m²). Again, the flame retardant mechanism was ascribed either to the formation of a stable aromatic char in the condensed phase (due to the concurrent thermal shielding effect of the sol-gel derived ceramic phase, and the presence of phosphate groups of phytic acid, which favor the dehydration of cotton), or to the release of incomustible volatile species in the gas phase.

Cheng and co-workers [92] further implemented the system, using a ternary sol-gel recipe made of tetraethoxysilane, phytic acid and sodium alginate. Cotton fabrics were soaked into sol solutions containing 0.2 mol/L of phytic acid and different tetraethoxysilane loadings (namely, 0.2, 0.4, 0.6 and 0.9 mol/L), then roll-squeezed to a 100% wet pickup, and finally dried at 80 °C and cured at 160 °C for 3 min. All the treated fabrics achieved self-extinction in vertical flame spread tests and showed remarkably decreased pkHRR and THR values (by about 74 and 80%, respectively, for the sol-gel system containing the highest tetraethoxysilane content), as assessed by MCC tests. In addition, a significant lowering of the smoke density (−73% with respect to the untreated fabric) was observed. These findings were ascribed to the formation of a stable and protective char, with an important FR mechanism in the condensed phase.

5 Sol-gel flame retarded foams: recent advances

The scientific literature reports few papers dealing with the use of sol-gel processes for conferring flame retardant features to foamed polymers. This section will summarize the most significant outcomes achieved.

Quite recently, Bellayer and co-workers [94] designed an effective sol-gel process for decreasing the flammability of flexible polyurethane foams. To achieve this aim, the latter

were soaked into a solution comprising tetraethoxysilane, methyltriethoxysilane, 3-aminopropyl triethoxysilane and diethyl phosphite. When a proper ratio among the components of the sol-gel recipe was established, the coated foams achieved self-extinction in vertical flame spread tests. In addition, as assessed by forced-combustion tests carried out under 50 kW/m² irradiative heat flux, the pkHRR decreased by about 60% with respect to the untreated counterparts. These findings were ascribed to the formation of a char layer comprising a three-dimensional silica network upon the application of the flame or the irradiative heat flux. This layer, acting in the condensed phase, was able to protect the underlying foamed substrate, as well as to lower the release of volatile combustible species, hence decreasing the smoke production [95]. Further, it is worth noting that the proposed sol-gel treatment did not affect the overall mechanical behavior of the treated foams.

Shi et al. [96] exploited a sol-gel process (starting from tetraethoxysilane, in the presence of a commercially-available polyacrylate resin, as film-former), suitable for precipitating silica nanoparticles on the surface of the fibers of a melamine-formaldehyde foam, hence giving rise to the formation of a protective layer. The adopted approach increased the LOI up to 43.7% (LOI of untreated foam: 33.8%) and to outstandingly decrease both THR (−91%) and pkHRR (−89%), as assessed by MCC tests.

Further, tetraethoxysilane was employed in a sol-gel method (Stöber process) in order to form silica nanospheres on the inside walls and fibers of open-cell polyurethane foams. Three different concentrations of the alkoxy silane precursor in the prepared sols were selected, namely 0.25, 0.50 and 1 M. All the treatments, irrespective of sol concentration, promoted self-extinction, blocking the dripping phenomena during vertical flame spread tests. In addition, as assessed by forced-combustion tests (irradiative heat flux: 50 kW/m²), the deposition of silica nanospheres starting from 1 M tetraethoxysilane sol accounted for a significant decrease of pkHRR (by about 55%) and of the smoke parameters (namely, Total Smoke Release and Specific Extinction Area, which both decreased by about 64%, with respect to the untreated foam). Finally, as assessed by cyclic compression tests, small changes in the mechanical behavior were observed for all the treated foams, except for those soaked in 1 M tetraethoxysilane sol, for which about 30% increase in engineering stress during the application of the compression cycles was observed.

A different approach for conferring flame retardant properties to rigid polyurethane foams was exploited by Yang et al. [97], who embedded ammonium polyphosphate into gel-silica microcapsules by means of a sol-gel approach, using tetraethoxysilane as precursor. Then the resulting microcapsules were incorporated (30 parts per hundred of polyol) into the polyurethane reactive system and the foams

were obtained. V-0 rating was achieved in vertical flame spread tests and the compressive strength slightly decreased after the incorporation of the microcapsules.

Very recently, Bo and co-workers [98] exploited a sol-gel method for obtaining a silica aerogel that was subsequently either blended in the rigid polyurethane foam or coated onto its surface. The latter approach showed the best flame retardance, with LOI values increased up to 29.4% (untreated foam: 19.5%) and V-0 rating in vertical flame spread tests. In addition, as revealed by forced-combustion tests carried out under 50 kW/m² irradiative heat flux, the treated rigid foams showed significantly decreased values of the first and second pkHRR (about -47 and -43% with respect to the untreated counterparts), due to the formation of a dense and coherent silica-containing char, which reduced the heat conduction and the air flow.

6 Conclusions

This review paper has clearly demonstrated the feasibility and reliability of sol-gel treatments for conferring outstanding flame retardant features to different polymeric materials, namely bulk thermoplastics and thermosets, textiles, and even foams. Undoubtedly, the ease of designing and creating sol-gel derived fully inorganic or hybrid organic-inorganic phases within or on the surface of different polymeric materials justifies the remarkable and still growing development that the sol-gel approach has experienced also in the last 5 to 10 years. The so-obtained inorganic or hybrid organic-inorganic phases account for a significant overall improvement of the flame retardance of the treated polymer matrices, as they are able to favor the formation of a stable char (reaction mechanism in the condensed phase), while creating a physical barrier that behaves as an insulator, hence hindering the heat and mass transfer phenomena involved during a fire scenario. In addition, the combination of sol-gel derived phases with P- or P- and N-containing compounds represents a further added value, as the related sol-gel flame retardant recipes can be active not only in the condensed phase, but also in the gas phase, entrapping the propagating radical species, hence limiting the fire hazard.

It is noteworthy that the wide availability of sol-gel precursors and the deep knowledge about the chemistry behind the sol-gel processes enables the obtainment of high-performing flame retardant systems, suitable for different polymer matrices. Further, the accurate control of the chemical reactions that occur in situ ensures a very homogeneous distribution/incorporation of the sol-gel derived phases within the polymer bulk or on its surface, even making possible to tune their morphology.

In addition, it is worth mentioning that the liquid state and the tunable polarity of the sol-gel precursors account for their easy processing either by incorporation in bulk liquid monomers and oligomers or for their use in impregnation/exhaustion apparatus in the case of fabric treatments. Further, the in situ formation of ceramic or hybrid organic-inorganic phases as in the sol-gel processes allows for their better distribution within the thermoplastic or thermosetting polymer matrix, hence usually providing better performances with respect to those achieved through the incorporation of pre-formed ceramic phases, which often show some propensity to agglomerate. Although commercially available flame retardant additives are usually effective and reliable, they suffer from some limitations, as they are not always exploitable for every polymer system mainly because of compatibility issues. In contrast, this problem is quite easily overcome by the wide availability of sol-gel precursors. In addition, the sol-gel approach seems very promising especially for flame retarding technical fabrics, for which already existing industrial roll-to-roll plants can be adapted for carrying on flame retardant treatments on different textile substrates.

Apart from these significant advantages, the use of sol-gel methods in flame retardance still shows some drawbacks. In particular, in some cases it is not easy to combine the reactivity of the sol-gel precursors with the curing kinetics of the thermosetting polymer system; as a consequence, the FR efficiency of the resulting material is somehow lowered, as the dispersion of the sol-gel derived phases is not very homogeneous. In addition, when synergistic effects do not occur among the components of the sol-gel recipes, it may be necessary to design FR systems with quite high flame retardant loadings. In this way, the overall mechanical behavior of the flame retarded material could be worsened, as may occur in epoxy systems, for which the presence of sol-gel derived phases increases the stiffness but, at the same time, decreases the ductility and hence the overall impact resistance.

Specifically referring to textiles, two main problems have to be considered. The first regards the durability of the sol-gel flame retardant treatments, as very often fabrics have to withstand laundry cycles. The formation of covalent bonds between the sol-gel system and the underlying textile substrate usually solves this issue, although in some cases the efficacy of the FR treatment is partially lost upon washing. The second difficulty refers to the loss of fabric soft touch (i.e., the so-called “hand”), because of the sol-gel treatment. This latter issue has been partially fixed by applying hybrid organic-inorganic sol-gel coatings, tuning the flexibility of these latter by increasing the organic fraction (and the length of the alkyl chains) of the precursors.

Finally, one remaining open issue regards the cost-effectiveness of the proposed sol-gel flame retardant

treatments. Indeed, regardless of a few attempts performed at the pilot scale, most of the sol-gel treatments have been proposed at the lab scale, for which the cost of sol-gel precursors is of limited importance. However, it is likely to foresee that the scale-up of the required sol-gel precursors can be performed under cost-effective conditions, hence making these precursors suitable for future industrial applications.

Though a lot of research work has been performed so far, it is expected that sol-gel chemistry will still play a key role in flame retardance in the next years with its great potential being further exploited.

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References

- Vahabi H (2022) Analysis of Flame Retardancy in Polymer Science. Elsevier
- Horrocks AR, Price D, Price D (2001) Fire retardant materials. woodhead Publishing
- Malucelli G, Carosio F, Alongi J, Fina A, Frache A, Camino G (2014) Materials engineering for surface-confined flame retardancy. *Mater Sci Eng: R: Rep.* 84:1–20
- Morgan AB, Cusack PA, Wilkie CA (2014) Other non-halogenated flame retardant chemistries and future flame retardant solutions. *Non-Halogenated Flame Retardant Handbook*:347–403
- Hu Y, Wang X (2019) Flame Retardant Polymeric Materials: A Handbook. CRC Press
- Emmons HW, Atreya A (1982) The science of wood combustion. *Proc Indian Acad Sci Sect C: Eng Sci* 5(4):259–268
- Morgan AB (2019) The future of flame retardant polymers—met needs and likely new approaches. *Polym Rev* 59(1):25–54
- Fink JK (2020) Flame retardants. John Wiley & Sons
- Hsiue GH, Liu YL, Liao HH (2001) Flame-retardant epoxy resins: An approach from organic–inorganic hybrid nanocomposites. *J Polym Sci Part A: Polym Chem* 39(7):986–996
- Chiang CL, Ma CCM, Wu DL, Kuan HC (2003) Preparation, characterization, and properties of novolac-type phenolic/SiO₂ hybrid organic–inorganic nanocomposite materials by sol–gel method. *J Polym Sci Part A: Polym Chem* 41(7):905–913
- Shen J, Liang J, Lin X, Lin H, Yu J, Wang S (2021) The Flame-Retardant Mechanisms and Preparation of Polymer Composites and Their Potential Application in Construction Engineering. *Polymers* 14(1):82–82
- Nikolaeva M, Kärki T (2011) A review of fire retardant processes and chemistry, with discussion of the case of wood-plastic composites. *Baltic* 17(2):314–326
- Cheng Y, Li J, He Y, Wang B, Liu Y, Wang Q (2015) Acidic buffer mechanism of cyclotriphosphazene and melamine cyanurate synergism system flame retardant epoxy resin. *Polym Eng Sci* 55(5):1046–1051
- Vangrevelinghe M, Le Nouvel L, Pesenti C, Sonnier R, Ferry L, Gesta E, Lagrève C (2022) A method to quantitatively assess the modes-of-action of flame-retardants. *Polym Degrad Stab* 195:109767–109767
- Luo H, Rao W, Zhao P, Wang L, Liu Y, Yu C (2020) An efficient organic/inorganic phosphorus-nitrogen-silicon flame retardant towards low-flammability epoxy resin. *Polym Degrad Stab* 178:109195. <https://doi.org/10.1016/j.polymdegradstab.2020.109195>
- Ciesielski M, Schäfer A, Döring M (2008) Novel efficient DOPO-based flame-retardants for PWB relevant epoxy resins with high glass transition temperatures. *Polym Adv Technol* 19(6):507–515
- Salmeia KA, Gaan S (2015) An overview of some recent advances in DOPO-derivatives: Chemistry and flame retardant applications. *Polym Degrad Stab* 113:119–134
- Bifulco A, Varganici CD, Rosu L, Mustata F, Rosu D, Gaan S (2022) Recent advances in flame retardant epoxy systems containing non-reactive DOPO based phosphorus additives. *Polym Degrad Stab* 200:109962. <https://doi.org/10.1016/j.polymdegradstab.2022.109962>
- Bifulco A, Tescione F, Capasso A, Mazzei P, Piccolo A, Durante M, Lavorgna M, Malucelli G, Branda F (2018) Effects of post cure treatment in the glass transformation range on the structure and fire behavior of in situ generated silica/epoxy hybrids. *J Sol-Gel Sci Technol* 87(1):156–169
- Branda F, Passaro J, Pauer R, Gaan S, Bifulco A (2022) Solvent-Free One-Pot Synthesis of Epoxy Nanocomposites Containing Mg (OH) 2 Nanocrystal–Nanoparticle Formation Mechanism. *Langmuir* 38(5795):5802
- Branda F, Bifulco A, Jehnichen D, Parida D, Pauer R, Passaro J, Gaan S, Pospiech D, Durante M (2021) Structure and Bottom-up Formation Mechanism of Multisheet Silica-Based Nanoparticles Formed in an Epoxy Matrix through an In Situ Process. *Langmuir* 37(29):8886–8893. <https://doi.org/10.1021/acs.langmuir.1c01363>
- Matějka L, Dušek K, Pleštil J, Kříž J, Lednický F (1999) Formation and structure of the epoxy-silica hybrids. *Polymer* 40(1):171–181
- Bifulco A, Marotta A, Passaro J, Costantini A, Cerruti P, Gentile G, Ambrogi V, Malucelli G, Branda F (2020) Thermal and fire behavior of a bio-based epoxy/silica hybrid cured with methyl nadic anhydride. *Polymers* 12(8):1661–1661
- Bifulco A, Parida D, Salmeia K, Lehner S, Stämpfli R, Markus H, Malucelli G, Branda F, Gaan S (2020) Improving Flame Retardancy of in-situ Silica-Epoxy Nanocomposites cured with Aliphatic Hardener: Combined effect of DOPO-based flame-retardant and Melamine. *Compos Part C: Open Access* 2:100022. <https://doi.org/10.1016/j.jcomc.2020.100022>

25. Zhang Y, Yu B, Wang B, Liew KM, Song L, Wang C, Hu Y (2017) Highly effective P-P synergy of a novel DOPO-based flame retardant for epoxy resin. *Ind Eng Chem Res* 56(5):1245–1255
26. Bifulco A, Parida D, Salmeia KA, Nazir R, Lehner S, Stämpfli R, Markus H, Malucelli G, Branda F, Gaan S (2020) Fire and mechanical properties of DGEBA-based epoxy resin cured with a cycloaliphatic hardener: Combined action of silica, melamine and DOPO-derivative. *Mater Des* 193:108862–108862
27. Shen MY, Kuan CF, Kuan HC, Ke CY, Chiang CL (2021) Flame retardance and char analysis of an eco-friendly polyurethane hyperbranched hybrid using the sol-gel method. *Sustainability (Switz)* 13(2):1–14. <https://doi.org/10.3390/su13020486>
28. Gao W, Qian X, Wang S (2018) Preparation of hybrid silicon materials microcapsulated ammonium polyphosphate and its application in thermoplastic polyurethane. *J Appl Polym Sci* 135(4):1–8. <https://doi.org/10.1002/app.45742>
29. Zeng F, Zhao Y, Meng Y, Su J, Han J (2021) Study on sol-gel-modified ammonium polyphosphate and its application in the flame-retardant polyurethane composites. *J Sol-Gel Sci Technol* 98(3):615–626. <https://doi.org/10.1007/s10971-021-05526-w>
30. Qiu S, Shi Y, Wang B, Zhou X, Wang J, Wang C, Gangireddy CSR, Yuen RKK, Hu Y (2017) Constructing 3D Polyphosphazene Nanotube@Mesoporous Silica@Bimetallic Phosphide Ternary Nanostructures via Layer-by-Layer Method: Synthesis and Applications. *ACS Appl Mater Interfaces* 9(27):23027–23038. <https://doi.org/10.1021/acsami.7b06440>
31. Satdive A, Mestry S, Borse P, Mhaske S (2020) Phosphorus- and silicon-containing amino curing agent for epoxy resin. *Iran Polym J (Engl Ed)* 29(5):433–443. <https://doi.org/10.1007/s13726-020-00808-6>
32. Dutkiewicz M, Karasiewicz J, Rojewska M, Skrzypiec M, Dopierała K, Prochaska K, Maciejewski H (2016) Synthesis of an Open-Cage Structure POSS Containing Various Functional Groups and Their Effect on the Formation and Properties of Langmuir Monolayers. *Chem—A Eur J* 22(37):13275–13286
33. Wang X, Wang DY (2017) Fire-retardant polylactic acid-based materials: Preparation, properties, and mechanism. *Novel fire retardant polymers and composite materials*. Elsevier, pp 93–116
34. Song L, He Q, Hu Y, Chen H, Liu L (2008) Study on thermal degradation and combustion behaviors of PC/POSS hybrids. *Polym Degrad Stab* 93(3):627–639
35. Hsieh C-Y, Su W-C, Wu C-S, Lin L-K, Hsu K-Y, Liu Y-L (2013) Benzoxazine-containing branched polysiloxanes: Highly efficient reactive-type flame retardants and property enhancement agents for polymers. *Polymer* 54(12):2945–2951. <https://doi.org/10.1016/j.polymer.2013.03.060>
36. Clarson SJ, Semlyen JA (1993) In *Siloxane Polymers*; PTR Prentice Hall, Inc: Englewood Cliffs, New Jersey
37. Chen S, Zhuo D, Hu J (2018) Sol-Gel Technology Plus Radiation Curing: A Novel and Facile Technique for Preparing Thick, Large-Area Hyperbranched Polysiloxane Hybrids. *Ind Eng Chem Res* 57(31):10372–10378
38. Zhang W, Li X, Yang R (2011) Novel flame retardancy effects of DOPO-POSS on epoxy resins. *Polym Degrad Stab* 96(12):2167–2173
39. Zhang W, Fina A, Ferraro G, Yang R (2018) FTIR and GCMS analysis of epoxy resin decomposition products feeding the flame during UL 94 standard flammability test. Application to the understanding of the blowing-out effect in epoxy/polyhedral silsesquioxane formulations. *J Anal Appl pyrolysis* 135:271–280
40. Liu C, Chen T, Yuan CH, Song CF, Chang Y, Chen GR, Xu YT, Dai LZ (2016) Modification of epoxy resin through the self-assembly of a surfactant-like multi-element flame retardant. *J Mater Chem A* 4(9):3462–3470
41. Wu H, Zeng B, Chen J, Wu T, Li Y, Liu Y, Dai L (2019) An intramolecular hybrid of metal polyhedral oligomeric silsesquioxanes with special titanium-embedded cage structure and flame retardant functionality. *Chem Eng J* 374:1304–1316
42. Huang W, Huang J, Yu B, Meng Y, Cao X, Zhang Q, Wu W, Shi D, Jiang T, Li RKY (2021) Facile preparation of phosphorus containing hyperbranched polysiloxane grafted graphene oxide hybrid toward simultaneously enhanced flame retardancy and smoke suppression of thermoplastic polyurethane nanocomposites. *Compos Part A: Appl Sci Manuf* 150:106614–106614
43. Kaya GG, Deveci H (2020) Modified silica xerogel derived from groundnut hull ash by alkyl-ammonium salt for epoxy nanocomposites: Synergistic effects on thermal stability and flame retardancy. *Thermochim Acta* 689:178637–178637
44. Halim ZAA, Yajid MAM, Nurhadi FA, Ahmad N, Hamdan H (2020) Effect of silica aerogel–Aluminium trihydroxide hybrid filler on the physio-mechanical and thermal decomposition behaviour of unsaturated polyester resin composite. *Polym Degrad Stab* 182:109377–109377
45. Mousavi A, Roghani-Mamaqani H, Salami-Kalajahi M, Shahi S, Abdollahi A (2018) Grafting of silica nanoparticles at the surface of graphene for application in novolac-type phenolic resin hybrid composites. *Mater Chem Phys* 216:468–475
46. Abdollahi A, Roghani-Mamaqani H, Salami-Kalajahi M, Mousavi A, Razavi B, Shahi S (2018) Preparation of organic-inorganic hybrid nanocomposites from chemically modified epoxy and novolac resins and silica-attached carbon nanotubes by sol-gel process: Investigation of thermal degradation and stability. *Prog Org Coat* 117:154–165
47. Ebrahimi H, Roghani-Mamaqani H, Salami-Kalajahi M, Shahi S, Abdollahi A (2020) Chemical incorporation of epoxy-modified graphene oxide into epoxy/novolac matrix for the improvement of thermal characteristics. *Carbon Lett* 30(1):13–22. <https://doi.org/10.1007/s42823-019-00065-5>
48. Ebrahimi H, Roghani-Mamaqani H, Salami-Kalajahi M (2018) Incorporation of graphene oxide nanolayers into thermally stable hybrid composites of thermosetting resins by combination of curing and sol-gel reactions. *Polym Bull* 75(11):4859–4880. <https://doi.org/10.1007/s00289-018-2307-0>
49. Chen X, Wan M, Gao M, Wang Y, Yi D (2020) Improved flame resistance properties of unsaturated polyester resin with TiO₂-MXOY solid superacid. *Chin J Chem Eng* 28(9):2474–2482
50. Liu H, Zhang B, Han J (2018) Improving the flame retardancy and smoke suppression properties of polyurethane foams with SiO₂ microcapsule and its flame-retardant mechanism. *Polym-Plast Technol Eng* 57(11):1139–1149
51. Qu L, Sui Y, Zhang C, Dai X, Li P, Sun G, Xu B, Fang D (2020) Improved flame retardancy of epoxy resin composites modified with a low additive content of silica-microencapsulated phosphazene flame retardant. *React Funct Polym* 148:104485–104485
52. Kim E-S, Kim YC, Park J, Kim Y, Kim S-H, Kim KJ, Suhr J, Lee Y, Lee SH, Kim D-S (2018) Mechanical properties and flame retardancy of surface modified magnesium oxysulfate (5Mg(OH)2·MgSO4·3H2O) whisker for polypropylene composites. *J Materomics* 4(2):149–156
53. Guo W, Nie S, Kalali EN, Wang X, Wang W, Cai W, Song L, Hu Y (2019) Construction of SiO₂@ UiO-66 core-shell microarchitectures through covalent linkage as flame retardant and smoke suppressant for epoxy resins. *Compos Part B: Eng* 176:107261–107261
54. Zhi M, Liu Q, Chen H, Chen X, Feng S, He Y (2019) Thermal stability and flame retardancy properties of epoxy resin modified with functionalized graphene oxide containing phosphorus and silicon elements. *ACS Omega* 4(6):10975–10984. <https://doi.org/10.1021/acsomega.9b00852>
55. Venezia V, Matta S, Lehner S, Vitiello G, Costantini A, Gaan S, Malucelli G, Branda F, Luciani G, Bifulco A (2021) Detailed thermal, fire, and mechanical study of silicon-modified epoxy

- resin containing humic acid and other additives. *ACS Appl Polym Mater* 3(11):5969–5981
56. Cheng Z, Fang M, Chen X, Zhang Y, Wang Y, Li H, Qian J (2020) Thermal stability and flame retardancy of a cured tri-functional epoxy resin with the synergistic effects of silicon/titanium. *ACS omega* 5(8):4200–4212
 57. Luo F, Wu K, Guo H, Zhao Q, Lu M (2017) Simultaneous reduction and surface functionalization of graphene oxide for enhancing flame retardancy and thermal conductivity of mesogenic epoxy composites. *Polym Int* 66(1):98–107
 58. Chen R, Luo Z, Yu X, Tang H, Zhou Y, Zhou H (2020) Synthesis of chitosan-based flame retardant and its fire resistance in epoxy resin. *Carbohydr Polym* 245:116530. <https://doi.org/10.1016/j.carbpol.2020.116530>
 59. Gu L, Qiu C, Qiu J, Yao Y, Sakai E, Yang L (2020) Preparation and Characterization of DOPO-Functionalized MWCNT and Its High Flame-Retardant Performance in Epoxy Nanocomposites. *Polymers* 12:613. <https://doi.org/10.3390/polym12030613>
 60. Arivalagan V, Stephen LD, Meera M, Gunasekaran SG (2021) Carbazole terminal phenylene core imine skeletal nanosilica reinforced polybenzoxazine (nSi O₂ /PBZ) hybrid nanocomposites. *J Polymer Res* 28 (10). <https://doi.org/10.1007/s10965-021-02756-y>
 61. Xu Yx NieSb, Dai G1 YangJn, Dong X, Feng XS (2022) Effect of phosphorus-modified nickel phyllosilicates on the thermal stability, flame retardancy and mechanical property of epoxy composites. *J Polym Res* 29(1):1–15. <https://doi.org/10.1007/s10965-021-02843-0>
 62. Liu L, Xu M, Hu Y, Xu Y, Zhang Z, Li B (2019) Surface modification of magnesium hydroxide and its application in flame-retardant oil-extended styrene–ethylene–butadiene–styrene/polypropylene composites. *J Appl Polym Sci* 136(9):1–11. <https://doi.org/10.1002/app.47129>
 63. Ran S, Ye R, Cai Y, Shen H, He Y, Fang Z, Guo Z (2019) Synergistic flame retardant mechanism of lanthanum phenylphosphonate and decabromodiphenyl oxide in polycarbonate. *Polym Compos* 40(3):986–999
 64. Abdollahi A, Roghani-Mamaqani H, Salami-Kalajahi M, Razavi B, Mousavi A, Shahi S (2018) Preparation of hybrid composites based on epoxy, novolac, and epoxidized novolac resins and silica nanoparticles with high char residue by sol-gel method. *Polym Compos* 39:E2316–E2323. <https://doi.org/10.1002/pc.24631>
 65. Liu Q, Yan K, Chen J, Xia M, Li M, Liu K, Wang D, Wu C, Xie Y (2021) Recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation. *Aggregate* 2(2):1–27. <https://doi.org/10.1002/agt2.30>
 66. Yu ZL, Yang N, Apostolopoulou-Kalkavoura V, Qin B, Ma ZY, Xing WY, Qiao C, Bergström L, Antonietti M, Yu SH (2018) Fire-retardant and thermally insulating phenolic-silica aerogels. *Angew Chem Int Ed* 57(17):4538–4542
 67. Li L, Xiao Y, Zhang S, Feng J, Jiang Y, Feng J (2021) Lightweight, strong and thermally insulating polymethylsilsequioxane-polybenzoxazine aerogels by ambient pressure drying. *Journal of Sol-Gel Science and Technology*. <https://doi.org/10.1007/s10971-021-05619-6>
 68. Chirayil CJ, Mathew L, Hassan PA, Mozetic M, Thomas S (2014) Rheological behaviour of nanocellulose reinforced unsaturated polyester nanocomposites. *Int J Biol macromolecules* 69:274–281
 69. Devaraju S, Krishnadevi K, Naveena E, Alagar M (2021) Eco-friendly fully bio-based polybenzoxazine-silica hybrid materials by sol-gel approach. *Polym Bull* 78(8):4251–4260. <https://doi.org/10.1007/s00289-020-03309-x>
 70. Scharfel B (2010) Phosphorus-based flame retardancy mechanisms—old hat or a starting point for future development? *Materials* 3(10):4710–4745
 71. Rodolfo Jr A, Innocentini Mei LH (2010) Metallic oxides as fire retardants and smoke suppressants in flexible poly (vinyl chloride). *J Appl Polym Sci* 118(5):2613–2623
 72. Clayden NJ, Imperato C, Avolio R, Ferraro G, Errico ME, Vergara A, Busca G, Gervasini A, Aronne A, Silvestri B (2020) Chloride-free hydrolytic sol-gel synthesis of Nb-P-Si oxides: An approach to solid acid materials. *Green Chem* 22(20):7140–7151. <https://doi.org/10.1039/d0gc02519d>
 73. Passaro J, Imperato C, Parida D, Bifulco A, Branda F, Aronne A (2022) Electrospinning of PVP-based ternary composites containing SiO₂ nanoparticles and hybrid TiO₂ microparticles with adsorbed superoxide radicals. *Compos Part B: Eng* 238:109874
 74. Passaro J, Russo P, Bifulco A, De Martino MT, Granata V, Vitolo B, Iannace G, Vecchione A, Marulo F, Branda F (2019) Water resistant self-extinguishing low frequency soundproofing polyvinylpyrrolidone based electrospun blankets. *Polymers* 11(7):1205
 75. Guo Y, Hu L, Jia P, Zhang B, Zhou Y (2018) Enhancement of thermal stability and chemical reactivity of phenolic resin ameliorated by nanoSiO₂. *Korean J Chem Eng* 35(1):298–302. <https://doi.org/10.1007/s11814-017-0240-9>
 76. Shree V, Sen AK (2018) Study of thermal and flame behavior of phosphorus-based silica for epoxy composites. *J Sol-Gel Sci Technol* 85(2):269–279. <https://doi.org/10.1007/s10971-017-4546-1>
 77. Piccolo A (2016) In memoriam Prof. FJ Stevenson and the Question of humic substances in soil. vol 3. SpringerOpen
 78. Guadagno L, Raimondo M, Vittoria V, Vertuccio L, Naddeo C, Russo S, De Vivo B, Lamberti P, Spinelli G, Tucci V (2014) Development of epoxy mixtures for application in aeronautics and aerospace. *RSC Adv* 4(30):15474–15488
 79. Cireli A, Onar N, Ebeoglugil MF, Kayatekin I, Kutlu B, Culha O, Celik E (2007) Development of flame retardancy properties of new halogen-free phosphorous doped SiO₂ thin films on fabrics. *J Appl Polym Sci* 105(6):3748–3756
 80. Mahltig B, Haufe H, Böttcher H (2005) Functionalisation of textiles by inorganic sol-gel coatings. *J Mater Chem* 15(41):4385–4398
 81. Alongi J, Ciobanu M, Tata J, Carosio F, Malucelli G (2011) Thermal stability and flame retardancy of polyester, cotton, and relative blend textile fabrics subjected to sol-gel treatments. *J Appl Polym Sci* 119(4):1961–1969
 82. Gordon S, Hsieh Y-L (2006) Cotton: Science and technology. Woodhead Publishing.
 83. Castellano A, Colleoni C, Iacono G, Mezzi A, Plutino MR, Malucelli G, Rosace G (2019) Synthesis and characterization of a phosphorous/nitrogen based sol-gel coating as a novel halogen- and formaldehyde-free flame retardant finishing for cotton fabric. *Polym Degrad Stab* 162:148–159
 84. Xu D, Gao Z, Xu B, Ren H, Zhao X, Zhang Y, Wang S, Jiang Z, Zhu P (2020) A facile and effective flame-retardant coating for cotton fabric with α -aminodiphosphonate siloxane. *Polym Degrad Stab* 180:109312–109312
 85. Zhang Z, Dong C, Liu J, Kong D, Sun L, Lu Z (2020) Preparation of a synergistic reactive flame retardant based on silicon, phosphorus and nitrogen and its application to cotton fabrics. *Cellulose* 27(3):1799–1815
 86. Liu J, Dong C, Zhang Z, Sun H, Kong D, Lu Z (2020) Durable flame retardant cotton fabrics modified with a novel silicon-phosphorus-nitrogen synergistic flame retardant. *Cellulose* 27(15):9027–9043
 87. Qi L, Qiu S, Xi J, Yu B, Hu Y, Xing W (2022) Construction of super-hydrophobic, highly effective flame retardant coating for cotton fabric with superior washability and abrasion resistance. *J Colloid Interface Sci* 607:2019–2028
 88. Jiang Z, Xu D, Ma X, Liu J, Zhu P (2019) Facile synthesis of novel reactive phosphoramidate siloxane and application to flame retardant cellulose fabrics. *Cellulose* 26(9):5783–5796

89. Bentis A, Boukhriss A, Gmouh S (2020) Flame-retardant and water-repellent coating on cotton fabric by titania–boron sol–gel method. *J Sol-Gel Sci Technol* 94(3):719–730
90. Bentis A, Boukhriss A, Grancaric AM, El Bouchti M, El Achaby M, Gmouh S (2019) Flammability and combustion behavior of cotton fabrics treated by the sol gel method using ionic liquids combined with different anions. *Cellulose* 26(3):2139–2153
91. Li P, Wang B, Xu Y-J, Jiang Z, Dong C, Liu Y, Zhu P (2019) Ecofriendly flame-retardant cotton fabrics: preparation, flame retardancy, thermal degradation properties, and mechanism. *ACS Sustain Chem Eng* 7(23):19246–19256
92. Cheng X-W, Tang R-C, Guan J-P, Zhou S-Q (2020) An eco-friendly and effective flame retardant coating for cotton fabric based on phytic acid doped silica sol approach. *Prog Org Coat* 141:105539–105539
93. Costes L, Laoutid F, Brohez S, Dubois P (2017) Bio-based flame retardants: When nature meets fire protection. *Mater Sci Eng: R: Rep.* 117:1–25
94. Bellayer S, Jimenez M, Barrau S, Bourbigot S (2016) Fire retardant sol–gel coatings for flexible polyurethane foams. *RSC Adv* 6(34):28543–28554
95. Bellayer S, Jimenez M, Prieur B, Dewailly B, Ramgobin A, Sarazin J, Revel B, Tricot G, Bourbigot S (2018) Fire retardant sol-gel coated polyurethane foam: Mechanism of action. *Polym Degrad Stab* 147:159–167
96. Shi Y, Wang N, Liu L, Liu Y (2018) Surface sedimentation and adherence of Nano-SiO₂ to improve thermal stability and flame resistance of melamine-formaldehyde foam via sol-gel method. *Fire Mater* 42(2):183–189
97. Yang Y, Chen W, Liu M, Zhu Q, Liu X, Zhang B, Chen D, Liu X, Zhang K, Tang G (2021) Flame retarded rigid polyurethane foam composites based on gel-silica microencapsulated ammonium polyphosphate. *J Sol-Gel Sci Technol* 98(1):212–223
98. Bo G, Xu X, Tian X, Wu J, He X, Xu L, Yan Y (2021) Enhancing the flame retardancy for castor oil-based rigid polyurethane foams via silica aerogel. *J Non-Crystalline Solids* 562:120783–120783