



Flame-Retardant Polymer Materials Developed by Reactive Extrusion: Present Status and Future Perspectives

Henri Vahabi, Fouad Laoutid, Krzysztof Formela, Mohammad Reza Saeb & Philippe Dubois

To cite this article: Henri Vahabi, Fouad Laoutid, Krzysztof Formela, Mohammad Reza Saeb & Philippe Dubois (2022): Flame-Retardant Polymer Materials Developed by Reactive Extrusion: Present Status and Future Perspectives, Polymer Reviews, DOI: [10.1080/15583724.2022.2052897](https://doi.org/10.1080/15583724.2022.2052897)

To link to this article: <https://doi.org/10.1080/15583724.2022.2052897>



Published online: 18 Mar 2022.



Submit your article to this journal [↗](#)



View related articles [↗](#)



View Crossmark data [↗](#)

REVIEW



Flame-Retardant Polymer Materials Developed by Reactive Extrusion: Present Status and Future Perspectives

Henri Vahabi^a, Fouad Laoutid^b, Krzysztof Formela^c, Mohammad Reza Saeb^a, and Philippe Dubois^d

^aUniversité de Lorraine, CentraleSupélec, LMOPS, Metz, France; ^bLaboratory of Polymeric & Composite Materials, Materia Nova Research Center, Mons, Belgium; ^cDepartment of Polymer Technology, Faculty of Chemistry, Gdańsk University of Technology, Gdańsk, Poland; ^dLaboratory of Polymeric and Composite Materials (LPCM), Materia Nova/University of Mons, Mons, Belgium

ABSTRACT

The development of flame retardant polymer materials has two roots, one in materials design, and the other in materials processing. Over recent decades, different types and classes of flame retardant polymer materials have been commercialized to meet safety requirements in the construction, automotive, and coatings industries. In the vast majority of cases, the design and fabrication of new materials presenting low fire hazards could be obtained through the incorporation of one, two or more flame retardants with similar or different natures into polymers. Nevertheless, the presence of these new phases, often used at high loading levels, usually impact the polymer's other functional properties, such as mechanical, aging and transparency. These limitations could be partially or totally overcome using reactive extrusion, which is a promising process for developing new polymers or modifying the chemical structure of existing ones. Amongst other possibilities, reactive extrusion can be used for enhancing the fire behavior of existing polymers or for the synthesis of new ones presenting inherent flame retardant properties. In recent years, several new flame retardant polymers have been developed by reactive extrusion, but these developments have not been systematically described with regard to their technical circumstances, properties, and commercial potential. This short review attempts to overview and classify the available reports on the development of flame-retardant polymeric materials through reactive extrusion processes.

ARTICLE HISTORY

Received 8 July 2021
Accepted 24 February 2022

KEYWORDS

Reactive extrusion; flame retardant; fire behavior; reactive processing; polymer materials; structure-property relationships

1. Introduction

The flammability of many polymers is one of the major reasons limiting their use in many applications with high safety requirements. Global fire-safety concerns are evidently reflected in the massive volumes of flame retardant polymer materials being commercialized over the last two decades [1, 2]. In this sense, a huge amount of effort has been undertaken for the synthesis, characterization and commercialization of a broad variety of flame retardants [3]. From a material-engineering point of view, several

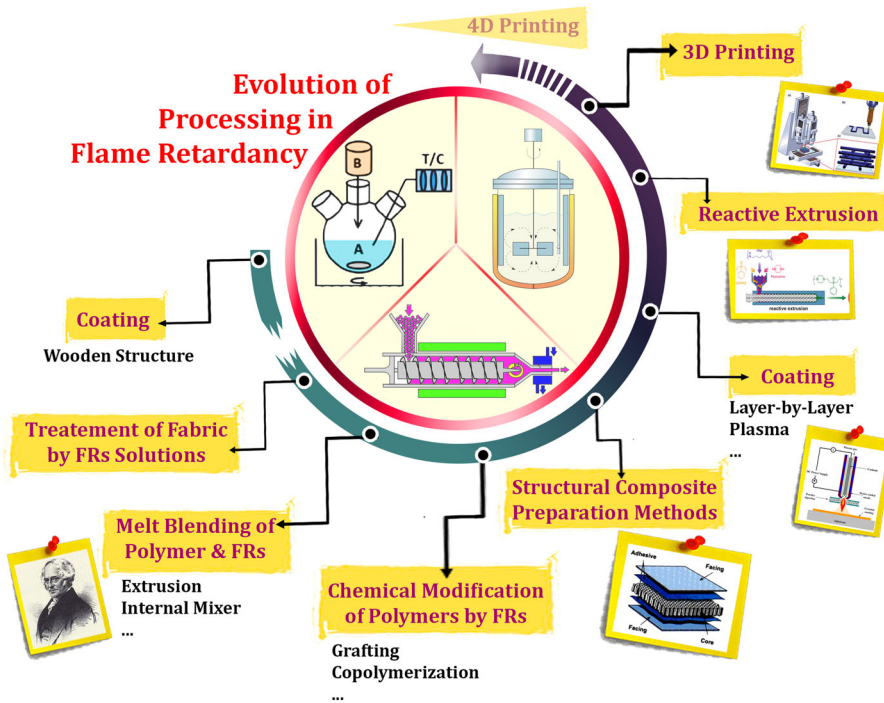


Figure 1. An overview of evolution in developments occurred in manufacturing flame retardant materials. In the past people used to apply natural coatings to their wooden structures, and also cotton. Later, human beings learned to use alum solutions to protect wooden battleships against fire. Nowadays, a wide range of additives are used to systematically incorporate flame retardants into polymers. In this sense, various processing methods are used to improve the dispersion of flame retardants throughout the polymer matrix at high loadings. Today both the bulk and the surface of polymer materials are armed with flame retardants to protect them against fire. The main technologies being used are melt extrusion, functionalization of polymers, layer-by-layer and plasma coating, reactive extrusion, electrospinning and 3D/4D printing. Reactive extrusion accelerated the development of flame-retardant polymers. In this process, the extruder acts as a continuous reactor supporting efficient distributive and dispersive mixing. It also makes it possible to sequentially incorporate ingredients for surface functionalization and cross-linking of polymers with flame retardants. The ability to control the processing temperature is another beneficial feature of developing flame retardant polymer materials by using the reactive extrusion strategy [5]. Reproduced/Adapted with permission from [5]. Copyright (2021, Elsevier).

kinds of flame retardant additives and formulations are examined to acquire the required level of fire safety. Although the development of new classes of flame retardants through hybridization and/or modification of both conventional and novel additives has been the main route for protecting polymers against fire, major steps have simultaneously been taken to make use of efficient processing/manufacturing methods to improve the performance of flame retardants [4]. The history of using flame-retardants goes back many years, when Ancient Egyptians used to protect wooden structures by applying natural resins. Now, after thousands of years, advanced processing methods like electrospinning, reactive extrusion, and 3D printing are used to improve the performance of flame retardant polymer materials, as shown in Fig. 1.

There are three different ways to protect materials against fire. The first, classical strategy consists in applying a flame retardant coating as a top layer on the surface, which can be conducted by layer-by-layer assembly, simple water- or solvent-based paints, a sol-gel process, and plasma technology [6]. The second strategy consists in incorporating flame retardants as additives into the bulk of a polymeric matrix via melt or solvent blending. Reactive extrusion is the third way, able to homogeneously disperse flame-retardant promoters at molecular level [7]. Reactive extrusion gives rise to the *in situ* development of flame retardant polymer materials through which sequences of flame-retardant molecules are covalently positioned along the backbone of polymer chains [8, 9]. The covalent bonds formed between flame retardant and polymer chains provides the major advantage of flame retardant molecules being unable to migrate instead of performing their function. Moreover, the low release of flame retardants into the environment is also a promising result [9, 10]. The resulting polymers have acceptable mechanical and thermal properties in addition to flame-retardant characteristics, as a result of the formation of chemically bonded and homogeneously dispersed flame retardants.

Chemical modification of polymers is a method to synthesize flame retardant thermoset materials and polyurethane foams [11]. Phosphorus-based molecules are widely used as comonomers or curing agents [12], or sometimes polyols are used [13]. There are also examples of bio-based epoxy systems chemically modified with flame retardants [14, 15]. Although chemical modification/functionalization of polymers is a robust process, it is known to be expensive. Reactive extrusion makes it possible to prepare intrinsic flame retardant thermoplastics through *in situ* incorporation of reactive flame retardants into polymers at a relatively low cost compared with traditional polymerization and chemical modification techniques [16, 17]. This approach makes it possible to prepare flame-retardant polymers through well-controlled dispersive and distributive mixing in a reactive pathway, i.e., typical of reactive extrusion [18]. The chemical or reactive modification of polymers in the reactive extrusion processing is based on the chemical structure of the polymer matrix. Reactive extrusion has been extensively used in recent years to develop polymer compounds.

In the present work, we first overview the principles of reactive extrusion as an advanced processing technique for ensuring chemical modification of a polymer backbone. We also present both the advantages and disadvantages of this method, and summarize works dealing with the development of flame-retardant polymeric materials by reactive extrusion. Some beneficial aspects of reactive extrusion for manufacturing flame-retardant materials are subsequently discussed, followed by highlighting the potential applications of reactive extrusion for future research on flame-retardant polymers.

2. Reactive extrusion in materials science and engineering

Extruders are common devices used in industry for the preparation, formulation, or recycling of a wide range of polymeric materials [19–23]. Such versatility stems from the continuity and relatively short residence time provided by the extrusion process, which results in high output and the good quality of the products obtained. Typically, extrusion provides intensive mixing which allows for easy transfer of viscous and multi-component compounds, which can be hard to process using conventional batch mixers

Table 1. Comparison between the performances of single-, twin-, triple- and planetary-screw extruders (adapted from [18]).

Item	Single-screw extruder	Twin-screw extruder		Multi-screw extruder	
		Counter-rotating	Co-rotating	Triple-screw extruder	Planetary extruder
Screw design	Non-modular	Non-modular ^a	Modular	Modular	Partially modular
Feeding	Fair	Good	Good	Good	Good
Melting	Good	Good	Very good	Excellent	Very good
Distributive mixing	Good	Fair	Very good	Excellent	Excellent
Dispersive mixing	Good	Very good	Very good	Excellent	Very good
Heat generation capability	Very good	Good	Very good	Very good	Very good
Pressure generation capability	Good	Very good	Good	Good	Good
Wiping	Poor	Good	Very good	Very good	Excellent
Degassing	Fair	Good	good	Good	Good

^aIn conical twin screw extruders.

or reactors. Basically, extruders can be classified into piston and screw extruders. Historically, the application of piston extruders has been very limited, although they proved useful for compounding materials that are difficult to process and/or formulate. Teflon pastes, ceramics and rubber compounds are examples of compounds processed by piston extruders. The difficulty of mixing hybrid systems in non-reactive systems can be eliminated by careful selection of the compounding machine. However, most polymer-compounding technologies are based on screw extruders, which benefit from an appropriate level of mixing. Current trends in the development of polymer compounds show that piston extruders are gaining more and more attention mainly in 3D printing technologies applied to the manufacture of tissue engineering scaffolds, concretes, or food [24–26].

Many years of experience have confirmed that screw extruders are better machines for the preparation of materials with a heterogeneous composition. This is mainly due to the higher shear stress generated on materials, and the more efficient heat and mass transfer of screw extruders compared to piston extruders. Melt-compounding via screw-extrusion is an efficient technique for the preparation of novel polymer blends and composites [27–30]. It should be highlighted that a large proportion of the materials studied are based on commercially available components. The continuous nature and repeatability of the extrusion processes enable easier scale-up and commercialization of the results obtained from laboratory- to industrial-scale production. Dealing with this shortcoming has been a driving force behind machine research, which is why there has been growing interest among universities and industrial research and development centers alike to investigate future developments and optimization of this technique for efficient sample preparation. The modification of selected parts in screw extruders, especially screw geometry or extrusion die construction can increase mixing or degassing efficiency (higher quality of the prepared material) and provide additional information about the extrusion process (e.g., rheological measurements based on die pressure). These considerations can have beneficial impacts on the final throughput of the process (cost-effectiveness) [31–34].

Generally, three categories of screw extruders are used for polymer processing, which can be distinguished in terms of the number of screws as single-, twin- and multi-screw extruders [35]. The specifications of each extruder-type are presented in Table 1.

Compared to single-screw extruders, twin-screw and multi-screw extruders offer an intensive mixing and degassing capability. Moreover, both twin-screw and multi-screw extruders usually have a modular construction of the barrel and screws, which increases their application range and may reduce their maintenance cost. These features have resulted in their common use during the preparation of polymer materials with complex compositions for which suitable homogenization is usually very difficult to achieve.

Twin-screw extruders are of two major types, co-rotating or counter-rotating extruders, available in either intermeshing or non-intermeshing configurations. Co-rotating intermeshing twin-screw extruders are common types of intensive mixing machines, which generate higher shear forces than counter-rotating twin-screw extruders. Moreover, co-rotating screw extruders usually work at much higher screw speeds. Co-rotating machines can therefore be used under adiabatic conditions in which heat is generated through friction of materials in the extruder barrel.

Multi-screw extruders can be classified as triple-screw or planetary extruders. Triple-screw extruders were first designed by a research group at the Beijing University of Chemical Technology and patented in 2001 [36]. According to the literature, the first trials with the application of triple-screw extruders on an industrial scale were performed in 2006 [37, 38]. The reason for constructing triple-screw extruders was to increase the residence time of ingredients in the extruder barrel, along with enhancing the mixing intensity. However, similar effects can be achieved by the application of commercially available planetary extrusion, which has been used during the processing of polyvinyl chloride (PVC), the production of hot-melt adhesives, bitumen modification, food-applications, or the drying of polyethylene terephthalate (PET). Although the application of multi-screw extruders is currently rather limited in the production of polymer blends or composites, mainly due to the limited access to laboratory-scale extruders. We strongly believe that using multi-screw extruders in reactive extrusion will be developing in the near future, mainly due to their very efficient heat transfer between the material and plasticizing unit (precise control of processed material temperature).

Physical blending is simple blending of molten components in the absence of any chemical reaction/interaction, which suffers from poor interfacial adhesion or compatibility. This leads to the production of materials with unsatisfactory performance properties, which greatly limits their further applications. The reactive extrusion technique has adopted screw extruders as chemical reactors suitable for continuous transport, mixing and heating of reactants in diverse physical forms (solids, melts/liquids, gases). Therefore, *in situ* processing via reactive extrusion seems to be the most promising approach for the preparation, modification, functionalization or compatibilization of diverse polymeric materials, Fig. 2 [17, 18, 39, 40].

Table 2 presents a summary with examples showing the development of reactive extrusion in polymer science and engineering.

Reactive extrusion is used for significantly improving the interfacial interactions between the various components, resulting in polymer blends or composites presenting higher performances. The comparison of differences in the process characteristics of conventional and reactive extrusion is summarized in Table 3. Compared to conventional extrusion, reactive extrusion is a more complex process, which supports the

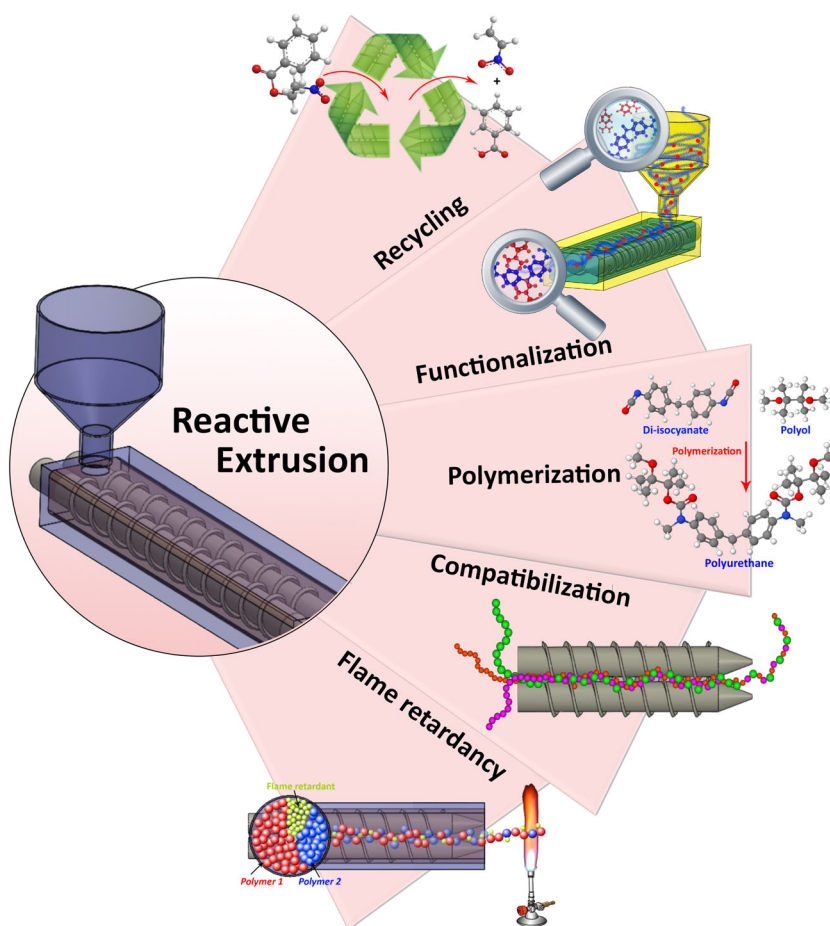


Figure 2. Overview of the reactive extrusion process and its common applications in polymer science and technology.

required mixing intensity and heat removal efficiency. Moreover, other requirements including the knowledge and/or experience of the extruder operator should also be recommended. This is related to the simultaneous physical and chemical interactions between the processed components, which combine different research and engineering fields such as chemistry, chemical and mechanical engineering, or materials science. Moreover, reactions between components performed at high temperatures (or high shear forces) usually result in the emission of volatile organic compounds (risk of fire during extrusion) as by-products that should be characterized, collected, and (when necessary) neutralized. Knowledge of analytical chemistry and environmental engineering needs to be combined to meet such a goal. As already pointed out, conventional extrusion allows for diverse industrial applications. The complexity of reactive extrusion is the reason why the potential of this technique is still unfulfilled.

Though reactive extrusion was proposed many years ago, it was only later applied to the development of flame retardant polymer materials. Figure 3A shows the progression in “reactive extrusion” and “flame-retardant” according to the Scopus® database (data available on 16 May 2021) from 2010 to 2020. The total number of papers on “reactive

Table 2. Summary of selected examples related to polymeric materials prepared via reactive extrusion.

Prepared material	Reaction mechanism	Material details	Reactor type (*d : mm)	Reactive extrusion conditions	Main findings	Ref.
Polymers and blends	<i>In situ</i> polymerization	PA12	Internal batch mixer (60 cm ³) for preliminary studies and a co-rotating twin screw extruder (*d = 25, L/d = 42)	Pre-heated reaction mixture (lactam + initiators/catalysts) were dosed by gear pump to extruder. Barrel temperature: 270 °C. Screw speed: 100-300 rpm Throughput: 3.3-4.2 kg/h Reaction performed under a nitrogen atmosphere.	Anionic polymerization of lauryl lactam takes less than 2 minutes. Torque during extrusion: 14.6-23.8 % Molten lactam with initiator/activator had a tendency to polymerize, which caused extruder feed problems. Molecular weight: 20.8-26.2 kg/mol Polydispersity: 1.8-2.1	[41]
		Polymides	Microcompounder (15 cm ³ capacity) and a co-rotating twin screw extruder (d = 16, L/d = 60)	Feeding of reagents: Solid dianhydride was dosed by twin-screw gravimetric feeder (0.5 kg/h) Liquid diamine was dosed by HPLC pump. Barrel temperature: 180-225 °C Two types of screw profiles in co-rotating twin screw extruder were applied in order to control residence time and improve mixing efficiency. Reaction performed under a nitrogen atmosphere. Temperature: 195 °C	Solvent-free polymerization of polyimides takes less than 10 minutes (usually 4-7 minutes). Molecular weight: 24 kg/mol (microcompounder) and 45.2 kg/mol (twin screw extruder) Polydispersity: 2.2 (microcompounder) and 3.1 For comparison values for solution polymerization: M _w = 38.5 kg/mol and PD = 2.8	[42]
Grafted polymers	Grafting	PMMA/PS blends	mixing/reactor device called RMX [®]	Temperature: 195 °C	Morphological studies of PMMA/PS blends obtained by reactive blending confirmed that domains of PS dispersed in PMMA are much lower (100-200 nm) in comparison to PMMA/PS blends prepared by conventional (physical) melt mixing.	[43]
		PP grafted with maleic anhydride (MA)	A co-rotating twin-screw extruder (d = 25, L/d = unknown)	All the formulations (PP, MA and DCP) were first mixed in a laboratory mixer for approximately 1.5 min and then fed into the extrude hopper. Barrel temperature: 180-210 °C Extrusion performed in a nitrogen atmosphere.	The results showed that DCP concentration affects the MA grafting degree and molecular weight of PP-g-MA, while MA content affects only the molecular weight of PP-g-MA. PP-g-MA has a higher crystallinity degree and lower melting temperature comparing to untreated PP.	[44]

(continued)

Table 2. Continued.

Prepared material	Reaction mechanism	Material details	Reactor type (*d : mm)	Reactive extrusion conditions	Main findings	Ref.
Poly(lactic acid (PLA) grafted with citrate			A co-rotating twin screw extruder (d = not reported, L/d = 45)	PLA and PLA + 10 wt.% PLA-g-MA are mixed and fed to hopper. Throughput: 2.0 kg/h. Tbc or ATbc (tributyl citrate and tributyl-O-acetyl/citrate) plasticizers are added to the extruder by the aid of a metering pump. Barrel temperature: 160–180 °C Screw speed: 80 rpm	FTIR spectra showed the formation of hydroxyl groups of Tbc and anhydride groups of PLA-g-MA. Selected products showed good storage stability (lack of plasticizer leaching) after 6 months. WAXS, DMA and tensile analyses confirmed that regardless of the plasticizer used, the plasticized PLA materials were amorphous at ambient temperature.	[46]
EPM grafted with vinyltrimethoxysilane			A co-rotating twin screw extruder (d = 18, L/d = 48)	Compound heated up to 130 °C, then the liquid EPM was fed via a dosing pump (throughput: 1.3 kg/h). 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (throughput: 0.5–2.5 g/h) and vinyltrimethoxysilane (VTMS) (throughput: 20–100 g/h) were dosed by syringe pumps. Extrusion performed in an argon atmosphere. Barrel temperature: 80–220 °C Screw speed: 80 rpm	The applied procedure allowed for precise control over grafting degree in the range of 0.14–25 wt.% (calculated based on NMR measurements).	[46]
Starch grafted with acrylamide monomers			A co-rotating twin screw extruder (d = 16, L/d = 40)	Three types of screw profiles in the co-rotating twin-screw extruder were applied in order to control residence time and improve mixing efficiency. Deionized water and acrylamide were dosed by peristaltic pumps. Process stabilization after 10 minutes. Reaction performed under a nitrogen atmosphere.	It was observed that grafting efficiency changed with starch source: - native wheat: 78.0% (soluble fraction: 11.2%) - waxy maize: 74.6% (soluble fraction: 8.5%) - cationic tapioca: 81.3% (soluble fraction: 12.0%) - soluble wheat: 25.2% (soluble fraction: 72.0%)	[47]

Polymer blends or composites	Dynamic cross-linking	PCL/PLA modified by organic peroxides (di-(2-tert-butyl-peroxy)isopropyl) benzene or dicumyl peroxide)	Internal batch mixer (50 cm ³)	PCL/PLA was pre-blended for 4 min, followed by addition of DCP (or BIB), reaction was continued for further 4 min. Mixing temperature: 170 °C Rotor speed: 100 rpm Time of mixing: 8 min.	[47]
		PLA/PBS modified by ethylene-methyl acrylate-glycidyl methacrylate	Self-made triple screw extruder	Barrel temperature: 170–190 °C Screw speed: 80 rpm	[48]
		PLA/ABS blends modified by epoxidized cardanol	Microcompounder (15 cm ³ capacity)	Barrel temperature: 190 °C Screw speed: 100 rpm Time of mixing: 5 min. Batch weight: 10 g	[49]
		PLA/tannin modified by polymeric methylene diphenyl diisocyanate and 3-aminopropyl-triethoxysilane	A co-rotating twin-screw extruder (no details about d or L/d)	The premix of PLA and tannin was dosed directly into the hopper (throughput: 6.6 g/min). The silane was fed directly via a syringe (throughput: 0.8 g/min), while p-MDI was mixed with acetone (p-MDI: acetone = 75:25 v/v) to reduce the viscosity before injection (throughput: 1.0 g/min). Barrel temperature: 185–200 °C Screw speed: 100 rpm	[50]
		PLC/CNC modified by dicumyl peroxide and other components	A co-rotating twin screw extruder (d = not reported, L/d = 48)	PLA granules were covered by a thin layer of dilute DCP solution (1 wt. % in acetone) followed by drying in a vacuum oven for evaporation of excess solvent. PLA/CNC and modifiers (e.g., cellulose/starch; inorganic filler and vegetable oils) were pre-mixed and dosed directly into the hopper.	[51]

(continued)

Table 2. Continued.

Prepared material	Reaction mechanism	Material details	Reactor type (*d : mm)	Reactive extrusion conditions	Main findings	Ref.
Cellulosic filler treatment	Thermo-mechanical degradation	Brewers' spent grain	A co-rotating twin screw extruder (d = 20, L/d = 40)	Barrel temperature: 185-200 °C Screw speed: 200 rpm Barrel temperature: 30-180 °C Screw speed: 75-375 rpm Throughput: 1-5 kg/h	Correct optimization of extrusion parameters allows easy tailoring of the appearance (color, particle size distribution) and performance properties (thermal stability, antioxidant activity) of brewers' spent grain.	[52]
	Chemical surface treatment	Cellulosic fillers modified by isophorone diisocyanate	Internal batch mixer (50 cm ³)	Mixing at room temperature Screw speed: 100 rpm Mixing time: 5 min.	The application of isophorone diisocyanate resulted in a tendency of cellulosic filler agglomeration, which affected the average particle size. Measurement of volatile organic compounds emitted from treated fillers indicated that only part of used filler was deposited on the cellulosic filler.	[53]
		Nanofibrillated cellulose (NFC) isolated from Oat hull	Single screw extruder (d = 1.6, L/d = 40)	The first strategy was that the oat hull was extruded together with NaOH in the first step, then with H ₂ SO ₄ in the second step. The second strategy was that the oat hull was bleached with peracetic acid in the first step and then extruded with H ₂ SO ₄ in the second step. Once the extrusion step was carried out, all the samples were washed with distilled water until reaching pH 5-6. Samples were subsequently dried and milled - average particles obtained 0.297 mm. Barrel temperature: 110 °C Screw speed: 100 rpm	The combination of bleaching with peracetic acid through a single-step extrusion process with H ₂ SO ₄ led to nano-fibrillated cellulose with higher performance (NFC diameters of 12 ± 2 nm, 87.1% cellulose, 80% crystallinity) compared to a two-step extrusion method (nanofibers with diameters of 100 ± 25 nm, 61.2% cellulose, 68% crystallinity)	[54]
	Grafting	Cellulose grafted by PHB	Lab Mixer Molder/Extruder	Dilute DCP solution (4 – 8 mg per mL of acetone) was applied on PHB and cellulose fibers as coating for 30 min.	Radical initiation (by dicumyl peroxide) enabled grafting of PHB onto cellulose via reaction extrusion. Under the applied conditions, the maximum	[55]

				<p>PHB (80%, 1.6 g) and CF1 (20%, 0.40 g) were dried and pre-mixed in a beaker to obtain DCP concentration of about 2–5%. Mixing temperature: 175 °C Mixing time: 5–15 min. The extruded copolymerized product was Soxhlet extracted by the aid of CHCl₃ over 24 h for dissolving the non-reacted PHB in the medium, followed by filtration using a nylon screen to accumulate the gels.</p>	grafting efficiency was acquired after 5 min using 2% DCP. Moreover, electron spin resonance (ESR) was used to detect the radical species present on the cellulose-graft-PHB.
	PLA/ poly(glycerol succinate-co-maleate)-CNC	Microcompounder	<p>Drying of PLA was carried out at 80 °C, while PGSMA – CNC heated to 85 °C followed by addition to other molten ingredients: PLA (8 g), PGSMA – CNC (2 g) (by varying the quantity of CNC: 1, 3, and 5 wt.%), and an initiator (Luperol 101, 0.2 phr) Mixing temperature: 180 °C Screw speed: 100 rpm Mixing time: 2 min.</p>	The results showed that reactive extrusion of PGSMA – CNC with PLA obtained cross-linked PGSMA and PLA-g-PGSMA, while reactive PLA/PGSMA blends in the absence of CNC resulted in more crosslinking. Moreover, optical microscopy analyses revealed some agglomerates of CNC inside the PGSMA – CNC and PLA/ PGSMA – CNC blends.	
Enzymatic treatment	Lignocellulosic biomass	A co-rotating twin screw extruder (d = not reported, L/d = unknown)	<p>Combined thermo-mechano-chemical treatment and the bio-catalytic treatment by enzymatic hydrolysis. Mixing temperature: 40–200 °C Screw speed: 85–250 rpm</p>	Thermo-mechano-chemical pretreatment enables the destruction of the wall polymers, while saccharification begins during bio-extrusion. Such an approach has huge potential to be applied during ethanol production.	
Polymer recycling	Ground tire rubber	A co-rotating twin screw extruder (d = 20, L/d = 40)	<p>Barrel temperature: 60 °C (auto thermal) Screw speed: 250 rpm Throughput: 2.5 kg/h</p>	The results showed that auto-thermal extrusion of GTR enables the preparation of reclaimed rubber with performance properties comparable to commercially available products. Moreover, reduced emission of volatile organic compounds and expected lower energy consumption are also advantages of this method.	
De-cross-linking	Cross-linked polyethylene vitrimers	A co-rotating twin-screw mini-extruder (no	<p>In first step, the pristine PACHE co-polymer (9.78 g) was fed and</p>	Exchange reactions of vinyllogous urethanes performed by reactive	

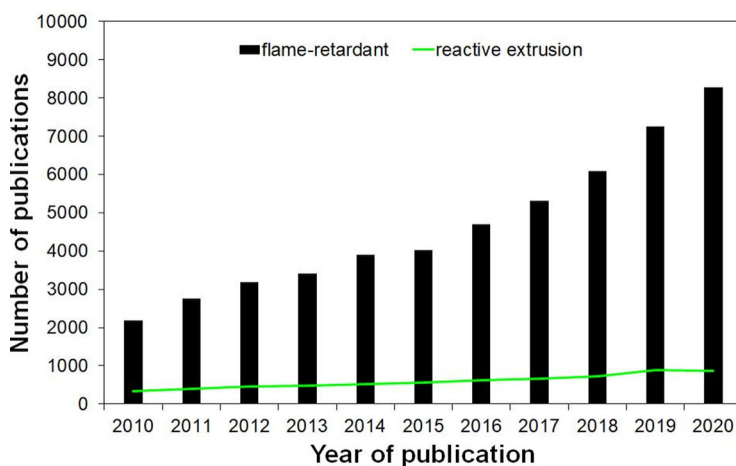
(continued)

Table 2. Continued.

Prepared material	Reaction mechanism	Material details	Reactor type (*d : mm) L/d	Reactive extrusion conditions	Main findings	Ref.
				<p>melted in the extruder for 4-5 min. Subsequently, diamine cross-linker XYDIA (0.221 g) was added dropwise via a syringe and the combined materials were reacted until the torque remained constant (usually ~10 – 15 min). Barrel temperature: 160 °C (auto-thermal) Screw speed: 100 rpm</p>	<p>extrusion enables an easy scale-up of the preparation of cross-linked PE vitrimers. It was found that after four cycles of reprocessing the tensile strength of cross-linked polyethylene vitrimers showed minor degradation.</p>	
		<p>Polyurethane foams treated by dibutyltin dilaurate</p>	<p>Microcompounder (5 cm³ capacity)</p>	<p>Dibutyltin dilaurate as a carbamate exchange catalyst was used during reactive extrusion. Prior to extrusion, thirty grams of commercial PU foam was suspended in 1.5l of benchtop dichloromethane. DBTDL (4.5 grams) was added to the suspension and the resulting 30 mg/mL catalyst solution was stirred overnight. The resulting swollen polymer was filtered, collected, and dried for 24 hours to remove residual dichloromethane. Barrel temperature: 200-220 °C Screw speed: 100 rpm Time of mixing: 1 min. Reaction performed under a nitrogen atmosphere.</p>	<p>Microscopy and thermomechanical experiments show that air can be efficiently removed by extrusion. Recycling products were formed as filaments or films, which confirms that thermoset PU foams were successfully converted into easily processable material.</p>	[59]
	Chain extension /branching	<p>waste PET modified by 5-amino isophthalic acid</p>	<p>A co-rotating twin screw extruder (d = 27, L/d = 36)</p>	<p>Barrel temperature: 265 °C Screw speed: 100 rpm Throughput: 5 kg/h</p>	<p>During research two strategies were considered: i) physical blending of virgin and waste PET and ii) reactive extrusion of virgin and waste PET with 5-amino isophthalic acid. The viscosity decreased whichever process was used, with conservation of mechanical properties.</p>	[60]

Table 3. Comparison between the conventional and reactive extrusion processes in brief.

Process characteristics	Conventional extrusion	Reactive extrusion
Required mixing efficiency	Normal	High
Required heat removal	Normal	High
Component interactions	Physical	Physical and chemical
By-products or volatile compounds emission	Low	High
Process stabilization	Regular	Complex
Risk of instability or fire during trials	Low	High
Knowledge and experience of extruder operator	Limited	High
Potential applications in industry	Diverse	Still not discovered

**Figure 3.** Research works devoted to the flame-retardant and reactive extrusion topics published from 2010 to 2020 (source of data: Scopus® database – data from 16 May 2021); (B).

extrusion” is 6,503 (2010–329/2020–871; increased by 265%/10 years) and in the case of “flame-retardant” it is 51,084 (2010–2180/2020–8271; increased by 380%/10 years). The data presented in the open literature indicate that the combination of research in both fields, reactive extrusion and flame retardancy of polymer blends and composites, will result in progressive development in the near future. Our analysis also disclosed that there are two possible issues dealing with “flame retardancy” and “reactive extrusion”: the chemical modification of polymers with flame retardant elements during reactive extrusion and the *in situ* preparation of flame retardants through reactive extrusion with polymers. Nevertheless, the field is very recent and will take a long time reach maturity. Current trends in this regard are reviewed in the next part of this paper.

3. Reactive extrusion for developing flame-retardant polymers

Commercial flame retardant polymers can be obtained through grafting of flame retardant additives/molecules onto polymer chains or by using chain extenders and manipulating the polymer backbone [61]. For reactive modification using chain extenders, functional groups need to be anchored to the end of polymer chains. Fascinatingly, this can be acquired through *in situ* thermal degradation of polymer chains and enchainment of molecules in the course of melt processing, as for polyamides, polyesters and

polycarbonates [62]. The grafting of reactive/functional groups onto polymer chains is also used in developing flame-retardant polymers. In a classical free-radical grafting process, the reactive radical-ended chains participate in hydrogen abstraction, through which reactive molecules graft onto growing chains *in situ* in a single- or two-step process. In a two-step method, a reactive precursor such as MA enables free-radical grafting to accept flame retardant molecule *via* the ring-opening of the anhydride moiety. The use of reactive extrusion for developing flame-retardant polymers has remained relatively limited in view of processing considerations, while chemical modification of flame-retardant polymer materials itself has progressed significantly over the past two decades. Development of flame retardants using reactive extrusion is experiencing an ascending trend, Table 4. In this regard, using some tests is essential for understanding the importance and efficiency of reactive extrusion, mainly cone calorimeter, UL94, and limiting oxygen index (LOI) [5]. There is the belief that cone calorimetry appears to be the most useful semi-real scale test to demonstrate the fire scenario and behavior of polymers. In this test, the oxygen consumption during irradiation-assisted combustion is monitored. Some key parameters obtained by this test include peak of heat release rate (pHRR) (kW/m^2), total heat release (THR) (kJ/m^2), and time to ignition (TTI) (s). Moreover, the amount of CO and CO₂ produced as well as the opacity of the smoke present in the exhaust duct is monitored. Some easier and faster, industrially accepted, tests are also used for evaluating the flame retardancy of polymers, like UL94 for quick analysis of the flammability of polymers. There are various possibilities in terms of flammability features in horizontal (H) or vertical (V) configurations with small- and large-scale options. When a sample is vertically exposed to small flame, the ignitability and spread of flame can be appropriately evaluated by UL94 V testing, with V-0, V-1 or V-2 classes representing high, medium and low flammability, respectively. Another test is LOI, working and evaluating on the basis of the minimal oxygen concentration [O₂] in an oxygen/nitrogen mixture [O₂/N₂] which assists vertical combustion of 5 cm of standard polymer sample under direct flame for 3 min. Inspired by oxygen content in the air (21% in volume), materials with LOI less than 21 are considered as “combustible”, while above this value they are classified as “self-extinguishing”. Therefore, the higher LOI values the better the flame retardancy performance. In conclusion, UL94 results depend on the thickness of sample, while heat flux additionally affects the analyses based on cone calorimetry. Thus, it seems difficult to find an explicit correlation between results of different tests, where sample dimension and test circumstances play key roles. Moreover, LOI results are sometimes chaotic because of fire behavior complexity, which is not considered in this test [63].

There is a general approach for incorporating phosphorus monomers into growing polymer chains *in situ* in a classical reactive extrusion process [64]. Mincheva et al. [8] developed flame-retardant poly(lactide) (PLA) through the covalent incorporation of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-diamine into PLA chain applying a reactive process. First, they pre-synthesized DOPO-diamine initiator and used it to catalyze the ring-opening polymerization (ROP) of L,L-lactide (L,L-LA) in the bulk and the formation of phosphorylated poly(lactide) oligomers (DOPO-PLA). Then, the resulting ROP of L, i.e., L-LA, was performed in a 250 mL InoXTM reactor at 180 °C for 90 min under an inert atmosphere. The so-obtained phosphorylated poly(lactide)

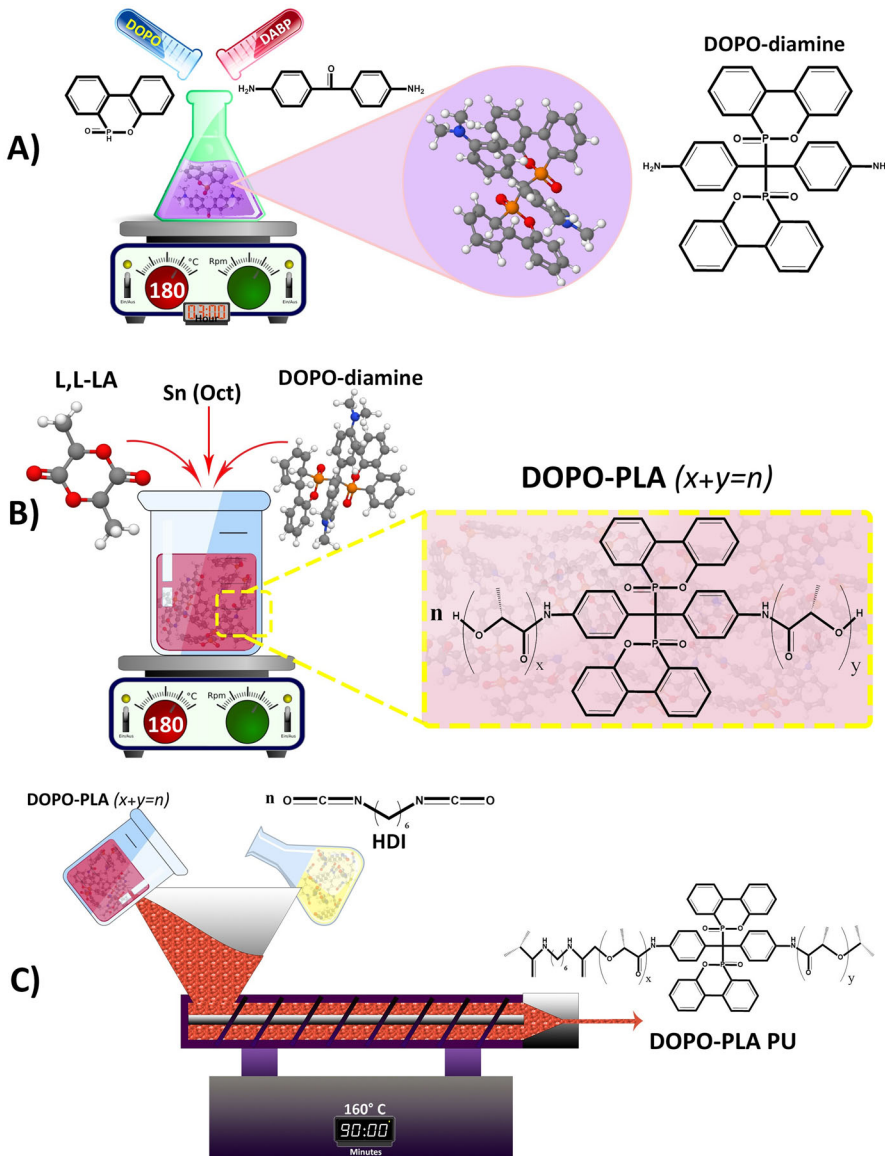


Figure 4. Schematic representation of the synthesis of DOPO-PLA-PU by Mincheva et al. with the preparation of phosphorylated PLA by a reactive process: (A) Synthesis of DOPO-diamine; (B) L,L-lactide ring-opening polymerization (ROP) initiated by DOPO-diamine; and (C) chain coupling reaction [8].

oligomers (DOPO-PLA) then participated in a chain extension reaction, which increased the molecular weight, using hexamethylene diisocyanate (HDI) via reactive extrusion. The chain extension reaction was performed at 160 °C inside a 15 cm³ vertical co-rotating twin-screw DSM Xplore microcompounder equipped with a nitrogen inlet. **Figure 4** illustrates the synthesis pathway of the flame retardant developed in this work.

The so-obtained phosphorylated PLA (DOPO-PLA-polyurethane (PU)) showed superior flame retardant properties in cone calorimeter and UL-94 tests, with respect to

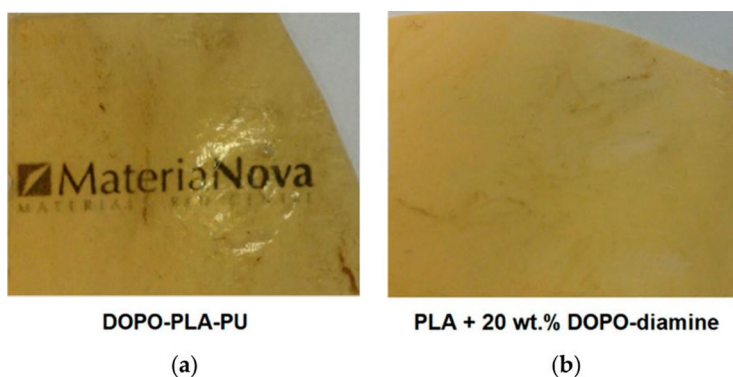


Figure 5. Comparison between the transparency level of phosphorylated-PLA obtained by the reactive processes (a) and the additive route (b) [8].

both neat commercially available PLA and PLA blends containing DOPO-diamine as additive (10 and 20 wt.%). In contrast to the other blends that did not obtain any classification based on the UL-94 test, phosphorylated polylactide reached V0 classification and a lower peak heat release rate (pHRR) and total heat release (THR) were detected in calorimetric analysis. Unfortunately, phosphorylated PLA (DOPO-PLA-polyurethane (PU)) also presented a significant reduction in the time to ignition (TTI) with respect to pristine PLA. The authors attributed the enhanced flame-retardant properties to the formation of a char residue during cone calorimeter and UL-94 tests. However, this char was not thermally stable since only some pieces remained at the end of cone calorimeter tests. On the other hand, the contribution of gas phase flame retardancy to the fire protection efficiency was not explicitly determined as a consequence of phosphorylated PLA (DOPO-PLA-PU) films (0.8 mm thickness) not being easily ignitable. In other words, a possible flame inhibition mechanism could have been induced by the DOPO. However, the obtained phosphorylated PLA presents a major defect because of its lower thermal stability than that of commercial PLA. The authors discussed that the lower molecular weight of DOPO-PLA-PU compared to the commercial PLA could explain the reduction in the TTI observed in cone calorimeter tests. Chemically speaking, DOPO-PLA-PU presented another interesting feature by allowing the formation of transparent films (0.8 mm), in contrast to the PLA/DOPO-diamine blends, Fig. 5. The preservation of the transparency of the films prepared by reactive extrusion results from the good dispersion of the flame retardant within the material on a molecular scale, which is one of the major positive effects offered by the use of reactive extrusion.

Simonetti et al. [65] proposed a new concept for developing flame retardant polymeric materials by reactive extrusion. It is based on *in situ* generation of new flame retardant macromolecules during the polymer extrusion, starting from reagents introduced as additives. The authors prepared a polyamide 6 (PA6)-based flame-retardant material by a reactive process through *in situ* synthesis of phosphine oxide-based macromolecules during the extrusion, Fig. 6. During PA6 melt processing, divinyl phenyl phosphine oxide (DVPPPO) and piperazine were introduced as additives and both reacted together via the Michael addition reaction to form phosphine oxide-based macromolecules. The so-obtained material, which was a blend of PA6 with phosphorylated oligomers and low molecular weight polymers, presented a non-leaching behavior owing

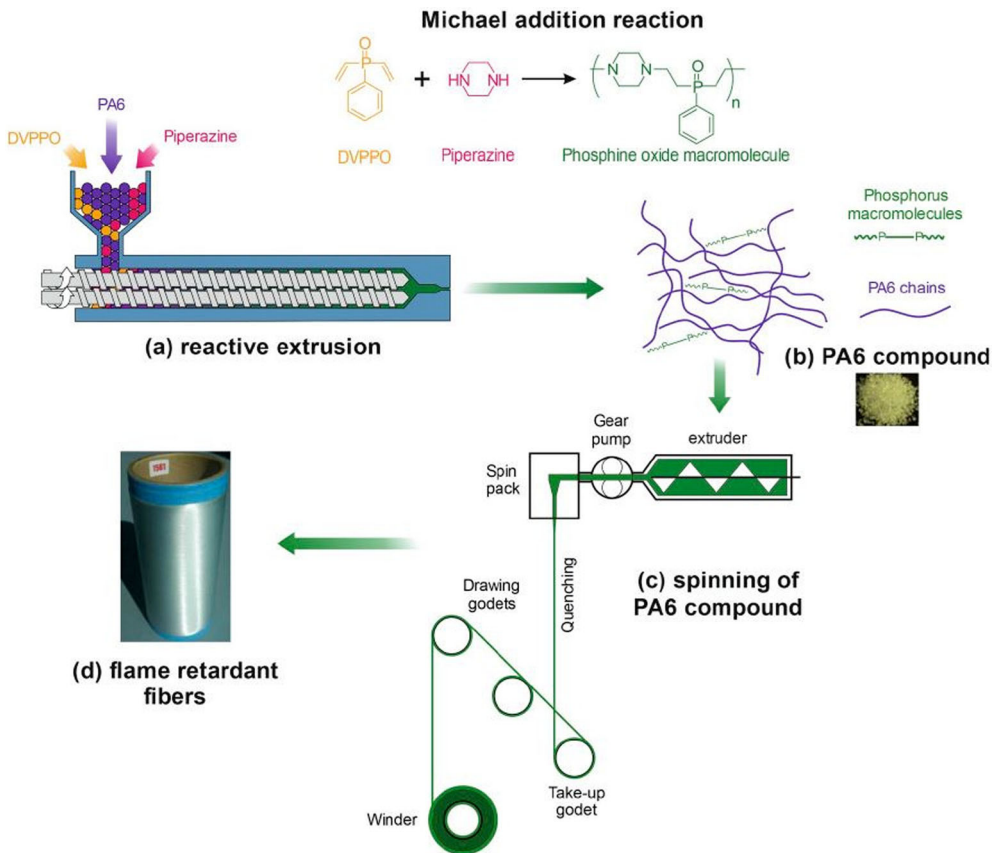


Figure 6. Schematic representation of the flame-retardant PA6 preparation steps [65]. Reproduced/Adapted with permission from [65]. Copyright (2021, Elsevier).

to the large size of the phosphorous-based macromolecules. The flame retardancy of the modified PA6 was evaluated on small-scale fire tests. Limiting oxygen index (LOI) measurements performed on specimens of 1 mm thickness of PA6 and PA6/DVPPPO/piperazine presented higher LOI values (30.2%) than unmodified PA6 (25.6%). BKZ-VB vertical burning tests (Swiss standard) showed superior flame retardant behavior of the modified PA6 with a shorter after-flame compared to unmodified PA6.

Sahyoun et al. [66] prepared flame retardant agents by melt processing of polyamide 6.6 (PA66)/PA6 copolymers. They synthesized organophosphorous silica nanoparticles through the hydrolysis-condensation reactions of a diethylphosphatoethyltriethoxysilane precursor during the extrusion process of the PA66 copolymer. The so-obtained polyamide nanocomposites presented interesting flame retardant properties, i.e., a considerable reduction in the pHRR (-57%) owing to the formation of an expanded char layer. This result was very impressive since the nanocomposite contained only 0.91 wt.% silicon and 0.96 wt.% phosphorus. However, the presence of ethanol (trapped in the material and produced during further hydrolysis-condensation reactions) in the core of the material as well as the formation of phosphoric acid induced a faster ignition of the composite (lower TTI) during cone calorimeter tests. The efficiency of this system also

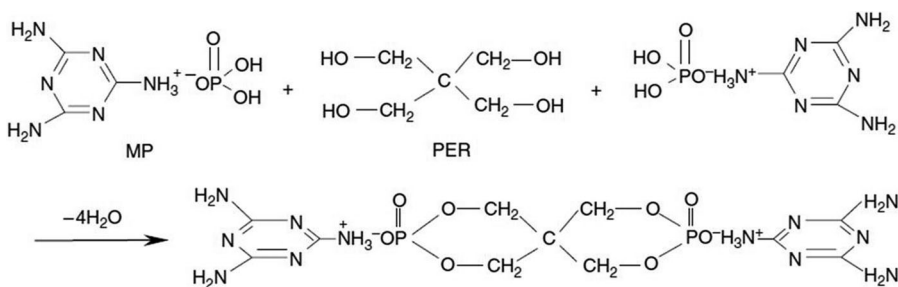


Figure 7. Chemical reaction between pentaerythritol and melamine phosphate to synthesize melamine salt of pentaerythritol phosphate (MPP) [7]. Reproduced/Adapted with permission from [7]. Copyright (2021, Wiley).

comes from the fact that this method enables good dispersion of the phosphorylated silica nanoparticles within the material.

4. Preparation of flame-retardant additives via reactive extrusion

Liu et al. [67] investigated the preparation of an intumescent flame retardant (IFR) through reactive extrusion. Their hypothesis was based on the fact that a conventional IFR containing three polar components (acid source, char-forming and blowing agent) would show poor compatibility in non-polar polypropylene (PP). They considered that integration of these components into a molecule, melamine salt of pentaerythritol phosphate (MPP), would reduce the polarity of the IFR obtained, leading to better compatibility with PP. Moreover, MPP had already been synthesized using POCl₃, a chemical representing some safety issues. Nevertheless, the authors noticed that the reaction between pentaerythritol and melamine phosphate, Fig. 7, necessitates a high activation energy, over 240 °C, which can be harmful due to some side reactions including the condensation of melamine phosphate (MP) and the etherification of pentaerythritol leading to a decrease in their flame retardant properties. Moreover, MPP's high viscosity was a constraint for its preparation in a conventional reactor. To overcome these problems, the authors suggested a reactive extrusion of PP as a carrier resin with the aforementioned triple flame retardant. In addition, a solid acid, silicotungstic acid (STA), was added to the formulation as a catalyst to reduce the activation energy and obtain the synergistic effect with the flame retardant. Moreover, STA was not corrosive to the equipment.

Their investigations on the preparation of flame retardants via reactive extrusion focused on three parameters including the extrusion temperature, residence time, and carrier resin content, Fig. 8. They showed that the conversion rate increases with the increase in processing temperature (Fig. 8a) and residence time (Fig. 8b). However, at the same time an undesirable foaming of the flame retardant occurred. It was also shown that the conversion rate was first increased by increasing of the carrier resin percentage, Fig. 8c and then decreased due to an increase in viscosity, which limited the interaction between PER and MP. The addition of STA to the formulation facilitated reactive extrusion such that a higher conversion rate and shorter residence time were achieved at a lower temperature of 230 °C, which limited the foaming effect. The IFR

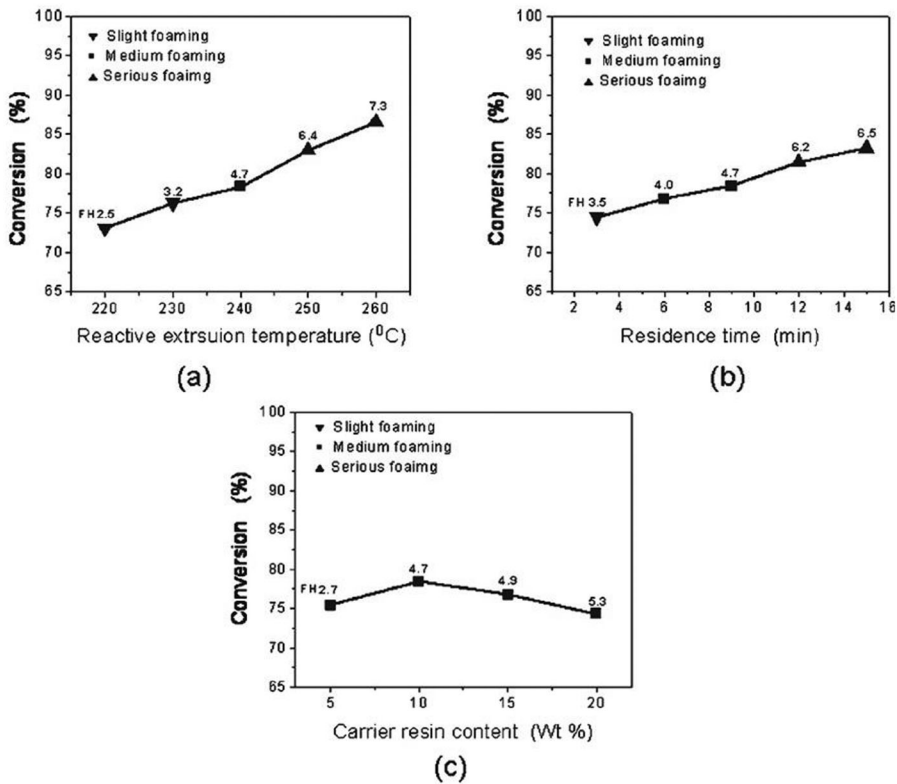


Figure 8. The efficiency of the reactive extrusion process in foaming terms of conversion: (a) the effect of extrusion temperature; (b) the effect of residence time; and (c) the effect of resin content [67]. Reproduced/Adapted with permission from [67]. Copyright (2021, Wiley).

obtained (MPP) via reactive extrusion was then ground into pellets and used as flame retardant and melt-extruded with PP. The flame-retardant performance of the MPP obtained via reactive extrusion was compared with a commercial IFR at 23 wt.% loading. The PP sample containing MPP obtained via reactive extrusion had an LOI of 31.5 and rated V0 in UL94, while for the flame retardant PP containing a commercial MPP the LOI was 29.1 and the sample was non-rated in UL94. Furthermore, oriented MPP in fibrillar morphology was obtained via reactive extrusion (by mixing PER and MP). They compared the effect of the fibrillar MPP, obtained in reactive extrusion, with that of a conventional spherical MPP on the flame retardancy of PP. The LOI value for PP containing 25 wt.% of fibrillar MPP was 32 and rated V0 in UL94, compared with 29 and a V2 rating for PP containing spherical MPP. They interpreted the higher flame retardancy of the reactively extruded sample as being due to the increased interfacial area between the flame retardant and polymer in the case of fibrillar MPP.

Wang et al. [68] also reported the reaction between pentaerythritol and melamine phosphate in the reactive extrusion of polyethylene (PE) compounds. They additionally used ammonium polyphosphate (APP) and copper chelates to enhance the flame retardancy of PE. At 30 wt.% of additive loading, a V0 rating in UL94 and LOI of 28.7 were achieved. In another study, Wang et al. [69] investigated the same reaction by reactive extrusion using PP and added montmorillonite (MMT) at 1 wt.%. The total loading

percentage of additive was fixed at 25 wt.% and resulted in an LOI of 35, compared with 18 for neat PP.

Chen et al. [70] investigated the synthesis of melamine cyanurate (MCA) in reactive extrusion. They explained that the traditional method of synthesizing MCA based on the reaction of melamine and cyanuric acid taking place in hot water using alkali salt or alkali hydroxide as catalyst has some drawbacks including low efficiency, high energy consumption, generation of wastewater, and coloring the product. Moreover, the presence of an alkali-based catalyst deteriorated the flame retardant properties. Therefore, they investigated the synthesis of MCA by reaction between melamine and cyanuric acid in the presence of water, pentaerythritol and a water-bound dioctyl phthalate (DPT) plasticizer via the reactive extrusion method. They reported that the reaction was close to 100% conversion. Furthermore, the radial size of MCA particles obtained *in situ* was between 80 nm and 300 nm, uniformly dispersed throughout the PA6. Their results showed that it is possible to achieve a V0 rating in UL94 test. They also compared the PA6 containing *in-situ* prepared MCA with a PA6 extruded with a commercially available MCA (Melapur®MC50). Although similar flame retardant behavior was observed for these samples, the sample prepared *in situ* by reactive extrusion showed a better mechanical property in terms of elongation at break 106.3%, compared with that of PA6 containing Melapur® MC50, 35%.

Aluminum hydroxide (ATH) and hydromagnesite (HM) are widely used in ethylene-vinyl acetate (EVA) as flame retardants. However, a large amount of these fillers is usually needed to achieve an acceptable level of flame retardancy. Therefore, one solution could be the combination of these flame retardants with other ones to gain a synergistic effect at a low loading level. Silica is one of the fillers used in combination with other flame retardants in polymers. Battegazzore et al. [71] investigated the generation of silica particles via a sol-gel reaction in reactive extrusion in the presence of ATH or HM in EVA to obtain a well-dispersed silica. First, EVA was melt-blended with ATH or HM at 60 wt.% loading percentage, Fig. 9. The sol-gel reaction was performed in another twin-screw extruder (Twin screw SHJ-20 Nanjijg Giant M., screw diameter = 21.7 mm, L/D = 39, screw speed = 25 rpm, heating temperature = 90-130 °C, residence time = 2-2.5 min). EVA was added to the extruder and then a premix of tetraethyl orthosilicate (TEOS)/water/catalyst was fed into the extruder at 20 wt.%. They also extruded EVA and commercially available silica using the aforementioned extruder under the same conditions. Then, the masterbatch containing ATH or HM at 55 wt.% and the masterbatch containing sol-gel silica or commercial silica at 5 wt.% were extruded with EVA. It was demonstrated that sol-gel silica prepared via reactive extrusion was not totally condensed and Si-C bonds between sol-gel-silica and EVA were created. The flame retardancy behavior was evaluated using LOI, UL94 and cone calorimetry tests. Here, we focus on the results obtained for the sol-gel silica obtained in reactive extrusion in combination with ATH or HM, as well as their comparison with a combination using commercial silica. LOI tests showed that the sol-gel silica was less efficient than commercial silica to increase the LOI value when combined with ATH, which resulted in an LOI value of 37 for EVA/ATH/commercial silica, compared with 31.5 for the EVA/ATH/sol-gel silica sample. In UL94 tests, both samples were rated V-1. The LOI value in the case of the combination of HM and sol-gel silica was 36.7,

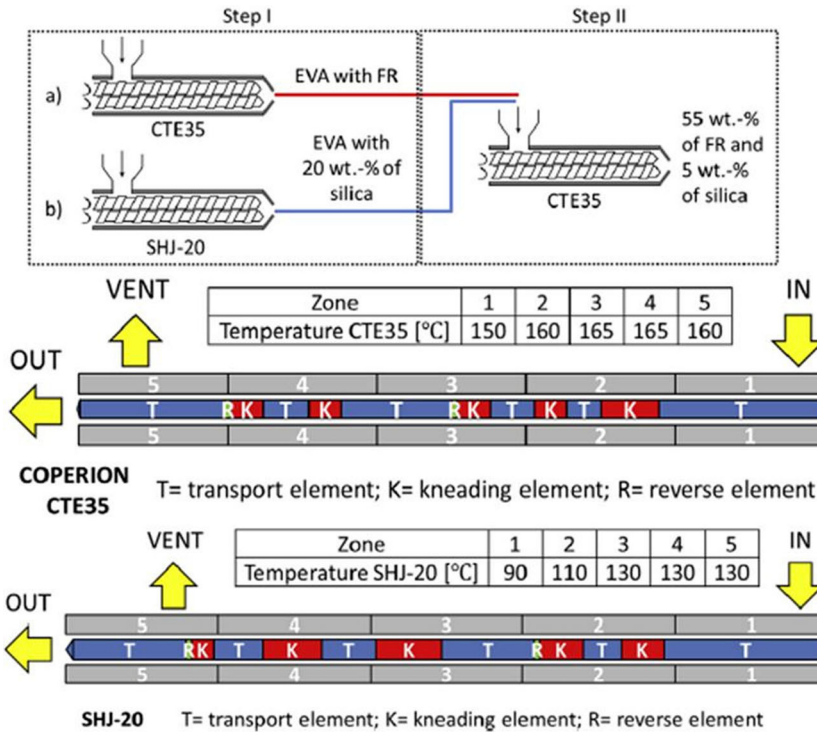


Figure 9. Schematic representation of different steps taken in the preparation of EVA/ATH/HM containing silica obtained from sol-gel in reactive extrusion by Battezzore et al. [71] (FR: flame retardant (ATH or HM), CTE35: twin screw extruder from Coperion Keya, SHJ-20: twin screw extruder from Nanjij Giant M.) [71]. Reproduced/Adapted with permission from [71]. Copyright (2021, Elsevier).

compared with 29.1 for the combination of HM and commercial silica. The EVA sample containing HM and sol-gel silica was rated V-0, while EVA/HM/commercial silica was not rated. Figure 10 displays the HRR curves obtained in cone calorimeter tests for EVA and all composites. It can be clearly observed that there was no significant difference in flame behavior for combinations of ATH with sol-gel or with commercial silica, Fig. 10a. Interestingly, the combination of HM and sol-gel silica was remarkably efficient for improving the flame retardancy behavior. The combination of HM and commercial silica gave a pHRR value around 179 kW/m^2 , while for EVA/HM/sol-gel silica the pHRR was around 97 kW/m^2 . Characterization of the char residue obtained at the end of cone calorimeter tests showed that the sol-gel method via extrusion was able to form a 3D condensed silica network structure inside the EVA, which was more efficient in the formation of a compact and consistent char residue and produced a better barrier effect during combustion.

Reactive extrusion is also used to synthesize *in situ* various polymers including PU [72, 73], PA [74, 75], PLA [18]. In this process, it is also possible to add the flame retardant into the extruder from a secondary feeding zone or a metering pump to obtain a flame-retardant polymer. This method is not directly related to the use of reactive extrusion to add flame retardancy to polymers. However, the *in-situ* synthesis of polymers in the presence of flame retardants can impact the dispersion state of the

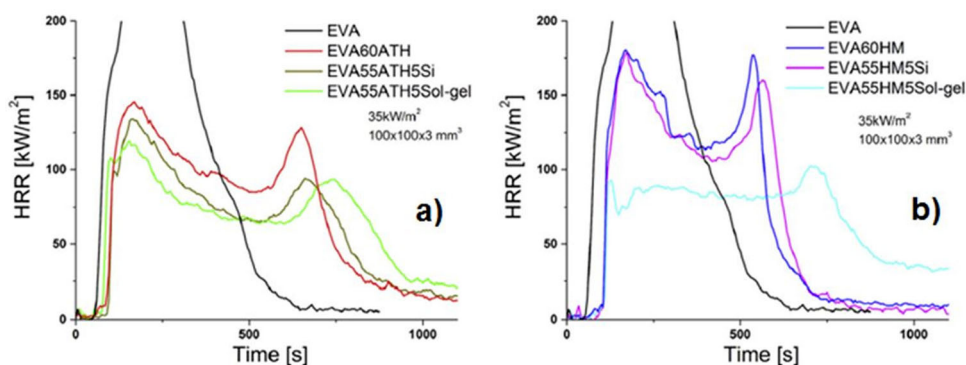


Figure 10. Heat release rate (HRR) curves as a function of time obtained from cone calorimeter tests for EVA and a) EVA containing ATH at 60 wt.% (EVA60ATH), ATH at 55 wt.%/commercial silica at 5 wt.% (EVA55ATH5Si), ATH at 55 wt.%/sol-gel silica at 5 wt.% (EVA55ATH5Sol-gel), b) HM at 60 wt.% (EVA60HM), HM at 55 wt.%/commercial silica at 5 wt.% (EVA55HM5Si), HM at 55 wt.%/sol-gel silica at 5 wt.% (EVA55HM5Sol-gel) [71]. Reproduced/Adapted with permission from [71]. Copyright (2021, Elsevier).

flame retardants and thus may change the flame behavior [76]. Reactive extrusion is also used to prepare foam materials [77].

5. Concluding remarks and future perspectives

Processing is of vital importance when designing efficient and high-performance flame retardant polymer materials. This technique enables good dispersion/distribution of the flame retardant agents within the polymeric matrices, reducing their migration during the materials' period of use and aging, obtaining good mechanical properties and at the same time conserving transparency.

Reactive extrusion presents a promising process for developing inherent flame retardant polymers, mainly by the chemical modification of their chains through the incorporation of chemical functions presenting flame retardant effect.

The reactive extrusion process can be also used as an open polymerization reactor in which inherent flame retardant polymers can be prepared from monomers and reactive flame retardant species. On the other hand, reactive extrusion can be applied to the preparation of flame retardant additives, which are not reactively bonded to polymer chains, but can be dispersed more appropriately compared to simple extrusion process. Besides the aforementioned advantageous features of reactive extrusion for developing flame retardant polymeric materials, there are some challenging aspects to be considered for future developments. For example, storage stability and aging of the products developed by reactive extrusion should be taken into account since some post-extrusion reactions could occur. Moreover, there is a need to evaluate the extrusion circumstances and processing details which affect natural or artificial aging as well as the fire-retardancy behavior of composites. The risk of formation and emission of volatile organic compounds (VOCs) during the extrusion process, which can present serious risks for workers and the environment, should also be considered.

Table 4. Summary of the literature on “flame-retardant polymers” prepared via reactive extrusion.

Polymer	Flame retardant/additive	Fire tests	Extrusion condition	Year	Ref.
PLA	9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and hexamethylene diisocyanate (chain extender)	Mass loss calorimetry, UL94	Microcompounder (15 cm ³) Mixing temperature: 160 °C Screw speed: 30 rpm 14 g DOPO-PLA was added to the micro-compounder and processed for 3 min, then 0.98 mL HDI was introduced, and the mixture reacted for a further 90 min. Reaction performed in a nitrogen atmosphere.	2020	[8]
PLA	Ammonium polyphosphate (APP), melamine and organoclay	Mass loss calorimetry	Microcompounder (15 cm ³) Mixing temperature: 185 °C Screw speed: 100 rpm Mixing time: ~50 min per step. Step I, 20 g of L-lactide, tin (II) octanoate and triphenylphosphine were incorporated, while polymerization efficiency was measured by torque increment. After stabilization (~50 min), half of the produced PLLA was discharged and replaced by a mixture of 10 g of D-lactide mixed, tin (II) octanoate and triphenylphosphine in the extruder. Finally, when the torque stabilized (~ 50 min.) 0.75 wt.% a-tropolone was introduced to deactivate the catalyst. Next, 24.2 wt.% of ammonium polyphosphate, 4.8 wt.% of melamine and 1 wt.% of nanoclay were added. Reaction performed in a nitrogen atmosphere.	2012	[78]
Polyamide 6 (PA6)	Ukanol RD, 3-(hydroxyphenyl)-phosphinyl) propanoic acid (HPP) and commercial linear chain extender dedicated to polyamides	UL94	Twin-screw extruder (d = 25, L/d = unknown) Screw speed: 100 rpm Throughput: 3 kg/h Chain extender content: 1 wt.% No details about exact composition of samples (the content of flame retardancy in the polymer unknown)	2020	[79]
PA6	Divinyl phenyl phosphine oxide (DVPPPO), piperazine	LOI	Twin-screw extruder (d = 16, L/D = 36), Barrel temperature: 250-265 °C Screw speed: 110 rpm PA6/DVPPPO (5 wt.%)/piperazine (2.5 wt. %) were pre-mixed a dosed directly into the hopper with throughput = 8 g/min (dosing in a nitrogen atmosphere)	2019	[65]
PA66/PA6 copolymer (90:10 wt.%)	Organophosphorous silica (precursor (diethylphosphatoethyl-triethoxysilane)	Cone calorimetry, PCFC	A co-rotating twin screw extruder (d = 30, L/d = 34) Barrel temperature: 250 °C Organophosphorous silica was added into the matrix in the	2015	[66]

(continued)

Table 4. Continued.

Polymer	Flame retardant/additive	Fire tests	Extrusion condition	Year	Ref.
PA66/PA6 copolymer (90:10 wt.%)	Si-DOPO precursor (DOPO, 9,10-dihydro-9-oxa-10-phosphaphenanthrene)	Cone calorimetry, PCFC	molten state using an external liquid pump. No detailed information about throughput or screw speed. A co-rotating twin screw extruder ($d = 30L/d = 34$) Barrel temperature: 250 °C Screw speed: 150 rpm Throughput: 3 kg/h Si-DOPO precursor was added to the matrix in the molten state using an external liquid pump.	2015	[80]
PP	Melamine phosphate (MP), Pentaerythritol	UL94	Two step procedure: Step I – production of a master batch of MP and PER in certain proportions was prepared in a high-speed mixer and dosed into a twin-screw extruder ($d = 30$ mm, $L/d = 32$) Barrel temperature: 260-270 °C No information about screw speed and throughput. The extrudate was cut into pellets and then repeatedly extruded 1–3 times. Step II. The master batch from Step I was mixed with PP in a twin-screw extruder. Barrel temperature: 190 °C No information about throughput or screw speed.	2003	[81]
PP	MP, Pentaerythritol	–	Two-step procedure: Step I –master batch production Step I – production of a master batch of MP and PER in certain proportions was prepared in a high-speed mixer and dosed into a twin-screw extruder ($d = 30$ mm, $L/d = 32$) Barrel temperature: 260-270 °C No information about screw speed and throughput. The extrudate was cut into pellets and then repeatedly extruded up to 3 times. Step II. The master batch from Step I was mixed with PP in a twin-screw extruder. Barrel temperature: 190 °C No information about throughput or screw speed.	2004	[7]
PA6	Melamine (MEL), cyanuric acid (CA)	UL94	Twin-screw extruder ($d = 30$ mm, $L/d = 32$) Barrel temperature = 235 °C, Residence time in extruder: 2-5 min. Prior to extrusion the studied compositions were blended using a high-speed mixer. No information about throughput or screw speed.	2006	[70]

(continued)

Table 4. Continued.

Polymer	Flame retardant/additive	Fire tests	Extrusion condition	Year	Ref.
PP	Melamine salt of pentaerythritol phosphate	–	Twin-screw extruder. No information about extruder specifications or extrusion conditions	2007	[82]
Polyethylene (PE)	Pentaerythritol, MP, copper chelates	Cone calorimetry, LOI, UL94	Polyethylene/flame retardant (29.8 wt.%) systems were prepared using a counter-rotating twin-screw extruder (no information about extruder specifications) Barrel temperature: 150 °C Screw speed: 80 rpm Residence time in extruder: 25 s For selected samples copper chelates were added into the PE/flame retardant at a concentration of 0.2 wt.% using a two-roll mill at 150-160 °C	2007	[68]
Polypropylene (PP)	Pentaerythritol, MP, silicotungstic acid (STA)	–	Twin-screw extruder (d = 30, L/d = 32). All components were mixed in a high-speed mixer prior to extrusion. Two-step procedure: Step I: master batch with flame retardant modifiers Step II: blending of master-batch with PP. No details about extrusion conditions.	2008	[67]
PP	Pentaerythritol, melamine phosphate as flame retardant, organomodified-montmorillonite (OMMT)	Cone calorimetry, LOI, UL94	A counter-rotating twin-screw extruder (d = 20.5 mm, L/d = 44) Barrel temperature: 240-260 °C Screw speed: 100 rpm No information about throughput. A two-step procedure was used: Step I: master batch with flame retardant modifiers Step II: blending of master-batch with PP (barrel temperature: 170-200 °C).	2014	[69]
Ethylene-vinyl acetate copolymer (EVA)	Aluminum trihydroxide (ATH), -hydromagnesite (HM), fumed silica, , <i>in situ</i> sol-gel silica	Cone calorimetry, LOI, UL94	Depending on the composition studied, two types of twin-screw extruders were used. Twin screw extruder (d = 21.7, L/D = 39), Screw speed: 25 rpm Barrel temperature: 90-130 °C Residence time of material in extruder = 2-2.5 min Twin screw extruder (dr= 35, L/d = 40) Screw speed: 100 rpm Barrel temperature: 150-165 °C In all cases, the total final filler content was fixed at 60 wt.% During application of sol-gel silica -> pre-gel solution was pumped directly into the hopper.	2019	[71]

(continued)

Table 4. Continued.

Polymer	Flame retardant/additive	Fire tests	Extrusion condition	Year	Ref.
Poly(ethylene terephthalate) (PET)	HFR-DEPZn-PSMP-DOP	Cone calorimetry, Single flame source	No information about extrusion throughput PET foams were prepared using a tandem extrusion line based on a twin-screw ($d = 25$, $L/d = \text{no data}$) and a single-screw extruder ($d = 45$, $L/d = \text{no data}$) Die temperature: 240-255 °C Screw speed: no data Throughput: 6 kg/h PET bulk samples were prepared using a co-rotating twin screw extruder ($d = 11$, $L/d = \text{unknown}$). Barrel temperature: 240-270 °C Screw speed: 150 rpm Throughput: no data	2020	[83]
Poly(lactide) (PLA) <i>in situ</i> polymerization via reactive extrusion	Multi-walled carbon nanotubes (MWCNT)	Mass loss calorimetry	Microcompounder (15 cm ³) capacity about 12 g of polymer. Mixing temperature: 185-195 °C Screw speed: 100 rpm Mixing time: ~50 min. Reaction performed in a nitrogen atmosphere. During nanocomposite preparation, MWCNT was mixed with the L,L-lactide and with the catalyst in nitrogen before feeding the extruder with a manual stirrer for 10 min.	2011	[76]

The lack of details concerning reactive extrusion processes and sample preparation details may also make it very difficult to collect data with an acceptable level of repeatability. Thus, future developments should consider some forgotten aspects in the development of flame retardant polymer materials through reactive extrusion. First, on-line/in-line monitoring of the progress and stabilization of reactive extrusion should be further discussed by performing coupled flame retardancy evaluations with rheological, optical, gas-chromatography, etc. methods. Commercialization of products or up-scaling trials are not very difficult to achieve, but a global experimental design with materials and processing details would be necessary. It is also believed that reactive extrusion can be coupled with 3D printing techniques to create flame-retardant polymer materials or devices by the production of filaments through direct reactive extrusion, e.g., a combination of extrusion and cross-linking in precisely controlled single-stage 3D printing.

References

1. Morgan, A. B.; Gilman, J. W. An Overview of Flame Retardancy of Polymeric Materials: application, Technology, and Future Directions. *Fire Mater* **2013**, *37*, 259–279. DOI: 10.1002/fam.2128.
2. Wilkie, C. A.; Morgan, A. B. *Fire Retardancy of Polymeric Materials*; Boca Raton, Florida: CRC Press, **2009**.
3. Morgan, A. B.; Wilkie, C. A. *The Non-Halogenated Flame Retardant Handbook*; Salem, Massachusetts: John Wiley & Sons, **2014**.

4. Subramanian, M. *Basics of Polymers: fabrication and Processing Technology*; New York: Momentum Press, **2015**.
5. Vahabi, H.; Laoutid, F.; Mehrpouya, M.; Saeb, M. R.; Dubois, P. Flame Retardant Polymer Materials: An Update and the Future for 3D Printing Developments. *Mater. Sci. Eng.: R Rep.* **2021**, *144*, 100604. DOI: [10.1016/j.msere.2020.100604](https://doi.org/10.1016/j.msere.2020.100604).
6. Liang, S.; Neisius, N. M.; Gaan, S. Recent Developments in Flame Retardant Polymeric Coatings. *Prog. Org. Coat.* **2013**, *76*, 1642–1665. DOI: [10.1016/j.porgcoat.2013.07.014](https://doi.org/10.1016/j.porgcoat.2013.07.014).
7. Wang, Q.; Chen, Y.; Liu, Y.; Yin, H.; Aelmans, N.; Kierkels, R. Performance of an Intumescent-Flame-Retardant Master Batch Synthesized by Twin-Screw Reactive Extrusion: effect of the Polypropylene Carrier Resin. *Polym. Int.* **2004**, *53*, 439–448. DOI: [10.1002/pi.1394](https://doi.org/10.1002/pi.1394).
8. Mincheva, R.; Guemiza, H.; Hidan, C.; Moins, S.; Coulembier, O.; Dubois, P.; Laoutid, F. Development of Inherently Flame—Retardant Phosphorylated PLA by Combination of Ring-Opening Polymerization and Reactive Extrusion. *Materials* **2019**, *13*, 13. DOI: [10.3390/ma13010013](https://doi.org/10.3390/ma13010013).
9. Morgan, A. B. The Future of Flame Retardant Polymers—Unmet Needs and Likely New Approaches. *Polym. Rev.* **2019**, *59*, 25–54. DOI: [10.1080/15583724.2018.1454948](https://doi.org/10.1080/15583724.2018.1454948).
10. Vahabi, H.; Sonnier, R.; Ferry, L. Effects of Ageing on the Fire Behaviour of Flame-Retarded Polymers: A Review. *Polym. Int.* **2015**, *64*, 313–328. DOI: [10.1002/pi.4841](https://doi.org/10.1002/pi.4841).
11. Vahabi, H.; Movahedifar, E.; Saeb, M. R. Flame Retardancy of Reactive and Functional Polymers. In *Reactive and Functional Polymers Volume Three: Advanced Materials*; Gutiérrez T. J., Ed.; Springer International Publishing: Cham, **2021**; pp 165–195
12. Zhang, H.; Li, Z.; Gong, X.; Wang, Y. Synthesis of a New Flame Retardant Curing Agent with Phosphorus and Their Application to Epoxy Resins. *J. Phys.: Conf. Ser.* **2020**, *1626*, 012177. DOI: [10.1088/1742-6596/1626/1/012177](https://doi.org/10.1088/1742-6596/1626/1/012177).
13. Vahabi, H.; Rastin, H.; Movahedifar, E.; Antoun, K.; Brosse, N.; Saeb, M. R. Flame Retardancy of Bio-Based Polyurethanes: Opportunities and Challenges. *Polymers* **2020**, *12*, 1234. DOI: [10.3390/polym12061234](https://doi.org/10.3390/polym12061234).
14. Nguyen, Q.-B.; Vahabi, H.; Rios de Anda, A.; Versace, D.-L.; Langlois, V.; Perrot, C.; Nguyen, V.-H.; Naili, S.; Renard, E. Dual UV-Thermal Curing of Biobased Resorcinol Epoxy Resin-Diatomite Composites with Improved Acoustic Performance and Attractive Flame Retardancy Behavior. *Sustain. Chem.* **2021**, *2*, 24–48. DOI: [10.3390/suschem2010003](https://doi.org/10.3390/suschem2010003).
15. Rad, E. R.; Vahabi, H.; de Anda, A. R.; Saeb, M. R.; Thomas, S. Bio-Epoxy Resins with Inherent Flame Retardancy. *Prog. Org. Coat.* **2019**, *135*, 608–612. DOI: [10.1016/j.porgcoat.2019.05.046](https://doi.org/10.1016/j.porgcoat.2019.05.046).
16. Beyer, G.; Hopmann, C. *Reactive Extrusion: Principles and Applications*; Hoboken, New Jersey: John Wiley & Sons, **2018**.
17. Li, T.-T.; Feng, L.-F.; Gu, X.-P.; Zhang, C.-L.; Wang, P.; Hu, G.-H. Intensification of Polymerization Processes by Reactive Extrusion. *Ind. Eng. Chem. Res.* **2021**, *60*, 2791–2806. DOI: [10.1021/acs.iecr.0c05078](https://doi.org/10.1021/acs.iecr.0c05078).
18. Formela, K.; Zedler, Ł.; Hejna, A.; Tercjak, A. Reactive Extrusion of Bio-Based Polymer Blends and composites-Current Trends and Future Developments. *Express Polym. Lett.* **2018**, *12*, 24–57. DOI: [10.3144/expresspolymlett.2018.4](https://doi.org/10.3144/expresspolymlett.2018.4).
19. Hyvärinen, M.; Jabeen, R.; Kärki, T. The Modelling of Extrusion Processes for Polymers—A Review. *Polymers* **2020**, *12*, 1306. DOI: [10.3390/polym12061306](https://doi.org/10.3390/polym12061306).
20. Gonzalez-Gutierrez, J.; Cano, S.; Schuschnigg, S.; Kukla, C.; Sapkota, J.; Holzer, C. Additive Manufacturing of Metallic and Ceramic Components by the Material Extrusion of Highly-Filled Polymers: A Review and Future Perspectives. *Materials* **2018**, *11*, 840. DOI: [10.3390/ma11050840](https://doi.org/10.3390/ma11050840).
21. Ab Rahim, S.; Lajis, M.; Ariffin, S. A Review on Recycling Aluminum Chips by Hot Extrusion Process. *Proc. CIRP* **2015**, *26*, 761–766. DOI: [10.1016/j.procir.2015.01.013](https://doi.org/10.1016/j.procir.2015.01.013).
22. Pranzo, D.; Larizza, P.; Filippini, D.; Percoco, G. Extrusion-Based 3D Printing of Microfluidic Devices for Chemical and Biomedical Applications: A Topical Review. *Micromachines* **2018**, *9*, 374. DOI: [10.3390/mi9080374](https://doi.org/10.3390/mi9080374).

23. Offiah, V.; Kontogiorgos, V.; Falade, K. O. Extrusion Processing of Raw Food Materials and by-Products: A Review. *Crit. Rev. Food Sci. Nutr.* **2019**, *59*, 2979–2998. DOI: [10.1080/10408398.2018.1480007](https://doi.org/10.1080/10408398.2018.1480007).
24. Lee, J.; Kim, K. E.; Bang, S.; Noh, I.; Lee, C. A Desktop Multi-Material 3D Bio-Printing System with Open-Source Hardware and Software. *Int. J. Precis. Eng. Manuf.* **2017**, *18*, 605–612. DOI: [10.1007/s12541-017-0072-x](https://doi.org/10.1007/s12541-017-0072-x).
25. Hack, N.; Dressler, I.; Brohmann, L.; Gantner, S.; Lowke, D.; Kloft, H. Injection 3D Concrete Printing (I3DCP): Basic Principles and Case Studies. *Materials* **2020**, *13*, 1093. DOI: [10.3390/ma13051093](https://doi.org/10.3390/ma13051093).
26. Kim, N. P.; Eo, J.-S.; Cho, D. Optimization of Piston Type Extrusion (PTE) Techniques for 3D Printed Food. *J. Food Eng.* **2018**, *235*, 41–49. DOI: [10.1016/j.jfoodeng.2018.04.019](https://doi.org/10.1016/j.jfoodeng.2018.04.019).
27. Kim, J. H.; Hong, J. S.; Ishigami, A.; Kurose, T.; Ito, H.; Ahn, K. H. Effect of Melt-Compounding Protocol on Self-Aggregation and Percolation in a Ternary Composite. *Polymers* **2020**, *12*, 3041. DOI: [10.3390/polym12123041](https://doi.org/10.3390/polym12123041).
28. Clarkson, C. M.; Azrak, S. M. E. A.; Schueneman, G. T.; Snyder, J. F.; Youngblood, J. P. Crystallization Kinetics and Morphology of Small Concentrations of Cellulose Nanofibrils (CNFs) and Cellulose Nanocrystals (CNCs) Melt-Compounded into Poly (Lactic Acid)(PLA) with Plasticizer. *Polymer* **2020**, *187*, 122101. DOI: [10.1016/j.polymer.2019.122101](https://doi.org/10.1016/j.polymer.2019.122101).
29. Mysiukiewicz, O.; Barczewski, M. Crystallization of Polylactide-Based Green Composites Filled with Oil-Rich Waste Fillers. *J. Polym. Res.* **2020**, *27*, 1–17. DOI: [10.1007/s10965-020-02337-5](https://doi.org/10.1007/s10965-020-02337-5).
30. Gomez, J.; Villaro, E.; Karagiannidis, P. G.; Elmarakbi, A. Effects of Chemical Structure and Morphology of Graphene-Related Materials (GRMs) on Melt Processing and Properties of GRM/Polyamide-6 Nanocomposites. *Results Mater.* **2020**, *7*, 100105. DOI: [10.1016/j.rinma.2020.100105](https://doi.org/10.1016/j.rinma.2020.100105).
31. Bauer, H.; Matic, J.; Khinast, J. Characteristic Parameters and Process Maps for Fully-Filled Twin-Screw Extruder Elements. *Chem. Eng. Sci.* **2021**, *230*, 116202. DOI: [10.1016/j.ces.2020.116202](https://doi.org/10.1016/j.ces.2020.116202).
32. Chen, H.; Pandey, V.; Carson, S.; Maia, J. Enhanced Dispersive Mixing in Twin-Screw Extrusion via Extension-Dominated Static Mixing Elements of Varying Contraction Ratios. *IPP* **2020**, *35*, 37–49. DOI: [10.3139/217.3857](https://doi.org/10.3139/217.3857).
33. Teixeira, P.; Covas, J.; Hilliou, L. In-Process Assessment of Clay Dispersion in PLA during Melt Compounding: Effects of Screw Speed and Filler Content. *Polym. Degrad. Stab.* **2020**, *177*, 109190. DOI: [10.1016/j.polymdegradstab.2020.109190](https://doi.org/10.1016/j.polymdegradstab.2020.109190).
34. Barczewski, M.; Barczewski, R.; Chwalczuk, T. The in-Line Detection Method of Sharkskin Melt Flow Instability during Polyethylene Extrusion Based on Pressure Analysis. *J. Manuf. Processes* **2020**, *59*, 153–166. DOI: [10.1016/j.jmapro.2020.09.046](https://doi.org/10.1016/j.jmapro.2020.09.046).
35. Mack, M. Compounding Options for Heat Sensitive Products. *Adv. Polym. Technol.* **1984**, *4*, 69–75. DOI: [10.1002/adv.1984.060040107](https://doi.org/10.1002/adv.1984.060040107).
36. Nan, J.; Baorui, Y.; Yingsheng, X. Three Screw Rod Extruder for Polymer. Chinese Patent CN.2471522.
37. Zhu, X.; Wang, G.; He, Y.; Cheng, Z. Study of Dynamic Flow and Mixing Performances of Tri-Screw Extruders with Finite Element Method. *Adv. Mech. Eng.* **2013**, *5*, 236389. DOI: [10.1155/2013/236389](https://doi.org/10.1155/2013/236389).
38. Wang, G.; Zhu, X.; He, Y.; Chen, L. Effects of Screw Clearance and Blend Ratio on the Flow and Mixing Characteristics of Tri-Screw Extruders in Cross Section with CFD. *Eng. Appl. Comput. Fluid Mech.* **2013**, *7*, 74–89. DOI: [10.1080/19942060.2013.11015455](https://doi.org/10.1080/19942060.2013.11015455).
39. Zedler, L.; Kowalkowska-Zedler, D.; Vahabi, H.; Saeb, M. R.; Colom, X.; Cañavate, J.; Wang, S.; Formela, K. Preliminary Investigation on Auto-Thermal Extrusion of Ground Tire Rubber. *Materials* **2019**, *12*, 2090. DOI: [10.3390/ma12132090](https://doi.org/10.3390/ma12132090).
40. Andrzejewski, J.; Nowakowski, M. Development of Toughened Flax Fiber Reinforced Composites. Modification of Poly (Lactic Acid)/Poly (Butylene Adipate-co-Terephthalate) Blends by Reactive Extrusion Process. *Materials* **2021**, *14*, 1523. DOI: [10.3390/ma14061523](https://doi.org/10.3390/ma14061523).

41. Wollny, A.; Nitz, H.; Faulhammer, H.; Hoogen, N.; Mülhaupt, R. In Situ Formation and Compounding of Polyamide 12 by Reactive Extrusion. *J. Appl. Polym. Sci.* **2003**, *90*, 344–351. DOI: [10.1002/app.12577](https://doi.org/10.1002/app.12577).
42. Verny, L.; Ylla, N.; Cruz-Boisson, F. D.; Espuche, E.; Mercier, R.; Sudre, G.; Bounor-Legaré, V. Solvent-Free Reactive Extrusion as an Innovative and Efficient Process for the Synthesis of Polyimides. *Ind. Eng. Chem. Res.* **2020**, *59*, 16191–16204. DOI: [10.1021/acs.iecr.0c02881](https://doi.org/10.1021/acs.iecr.0c02881).
43. Pierrot, F. X.; Ibarra-Gómez, R.; Bouquey, M.; Muller, R.; Serra, C. A. In Situ Polymerization of Styrene into a PMMA Matrix by Using an Extensional Flow Mixing Device: A New Experimental Approach to Elaborate Polymer Blends. *Polymer* **2017**, *109*, 160–169. DOI: [10.1016/j.polymer.2016.12.045](https://doi.org/10.1016/j.polymer.2016.12.045).
44. Bettini, S. H. P.; Agnelli, J. A. M. Grafting of Maleic Anhydride onto Polypropylene by Reactive Extrusion. *J. Appl. Polym. Sci.* **2002**, *85*, 2706–2717. DOI: [10.1002/app.10705](https://doi.org/10.1002/app.10705).
45. Hassouna, F.; Raquez, J.-M.; Addiego, F.; Toniazzo, V.; Dubois, P.; Ruch, D. New Development on Plasticized Poly(Lactide): Chemical Grafting of Citrate on PLA by Reactive Extrusion. *Eur. Polym. J.* **2012**, *48*, 404–415. DOI: [10.1016/j.eurpolymj.2011.12.001](https://doi.org/10.1016/j.eurpolymj.2011.12.001).
46. Bäuerle, T.; Ulitzsch, S.; Lorenz, A.; Rebner, K.; Chassé, T.; Kandelbauer, A.; Lorenz, G. Effects of Process Parameters on Silane Grafting of Liquid Ethylene-Propylene Copolymer by Reactive Extrusion as Quantified by Response Surface Methodology. *Polymer* **2020**, *202*, 122601. DOI: [10.1016/j.polymer.2020.122601](https://doi.org/10.1016/j.polymer.2020.122601).
47. Siyamak, S.; Laycock, B.; Luckman, P. Synthesis of Starch Graft-Copolymers via Reactive Extrusion: Process Development and Structural Analysis. *Carbohydr. Polym.* **2020**, *227*, 115066. DOI: [10.1016/j.carbpol.2019.115066](https://doi.org/10.1016/j.carbpol.2019.115066).
48. Xue, B.; He, H.; Zhu, Z.; Li, J.; Huang, Z.; Wang, G.; Chen, M.; Zhan, Z. A Facile Fabrication of High Toughness Poly(Lactic Acid) via Reactive Extrusion with Poly(Butylene Succinate) and Ethylene-Methyl Acrylate-Glycidyl Methacrylate. *Polymers* **2018**, *10*, 1401. DOI: [10.3390/polym10121401](https://doi.org/10.3390/polym10121401).
49. Rigoussen, A.; Raquez, J.-M.; Dubois, P.; Verge, P. A Dual Approach to Compatibilize PLA/ABS Immiscible Blends with Epoxidized Cardanol Derivatives. *Eur. Polym. J.* **2019**, *114*, 118–126. DOI: [10.1016/j.eurpolymj.2019.02.017](https://doi.org/10.1016/j.eurpolymj.2019.02.017).
50. Liao, J.; Brosse, N.; Hoppe, S.; Du, G.; Zhou, X.; Pizzi, A. One-Step Compatibilization of Poly(Lactic Acid) and Tannin via Reactive Extrusion. *Mater. Des.* **2020**, *191*, 108603. DOI: [10.1016/j.matdes.2020.108603](https://doi.org/10.1016/j.matdes.2020.108603).
51. Dhar, P.; Gaur, S. S.; Soundararajan, N.; Gupta, A.; Bhasney, S. M.; Milli, M.; Kumar, A.; Katiyar, V. Reactive Extrusion of Polylactic Acid/Cellulose Nanocrystal Films for Food Packaging Applications: Influence of Filler Type on Thermomechanical, Rheological, and Barrier Properties. *Ind. Eng. Chem. Res.* **2017**, *56*, 4718–4735. DOI: [10.1021/acs.iecr.6b04699](https://doi.org/10.1021/acs.iecr.6b04699).
52. Hejna, A.; Barczewski, M.; Skórczewska, K.; Szulc, J.; Chmielnicki, B.; Korol, J.; Formela, K. Sustainable Upcycling of Brewers' Spent Grain by Thermo-Mechanical Treatment in Twin-Screw Extruder. *J. Cleaner Prod.* **2021**, *285*, 124839. DOI: [10.1016/j.jclepro.2020.124839](https://doi.org/10.1016/j.jclepro.2020.124839).
53. Hejna, A.; Marć, M.; Skórczewska, K.; Szulc, J.; Korol, J.; Formela, K. Insights into Modification of Lignocellulosic Fillers with Isophorone Diisocyanate: structure, Thermal Stability and Volatile Organic Compounds Emission Assessment. *Eur. J. Wood Prod.* **2021**, *79*, 75–90. DOI: [10.1007/s00107-020-01604-y](https://doi.org/10.1007/s00107-020-01604-y).
54. Debiagi, F.; Faria-Tischer, P. C. S.; Mali, S. A Green Approach Based on Reactive Extrusion to Produce Nanofibrillated Cellulose from Oat Hull. *Waste Biomass Valor.* **2021**, *12*, 1051–1060. DOI: [10.1007/s12649-020-01025-1](https://doi.org/10.1007/s12649-020-01025-1).
55. Wei, L.; McDonald, A. G.; Stark, N. M. Grafting of Bacterial Polyhydroxybutyrate (PHB) onto Cellulose via in Situ Reactive Extrusion with Dicumyl Peroxide. *Biomacromolecules* **2015**, *16*, 1040–1049. DOI: [10.1021/acs.biomac.5b00049](https://doi.org/10.1021/acs.biomac.5b00049).
56. Brown, E.; Abdelwahab, M.; Valerio, O.; Misra, M.; Mohanty, A. K. In Situ Cellulose Nanocrystal-Reinforced Glycerol-Based Biopolyester for Enhancing Poly(Lactic Acid) Biocomposites. *ACS Omega* **2018**, *3*, 3857–3867. DOI: [10.1021/acsomega.8b00056](https://doi.org/10.1021/acsomega.8b00056).

57. Vandenbossche, V.; Brault, J.; Vilarem, G.; Hernández-Meléndez, O.; Vivaldo-Lima, E.; Hernández-Luna, M.; Barzana, E.; Duque, A.; Manzanares, P.; Ballesteros, M.; et al. A New Lignocellulosic Biomass Deconstruction Process Combining Thermo-Mechano Chemical Action and Bio-Catalytic Enzymatic Hydrolysis in a Twin-Screw Extruder. *Ind. Crops Prod.* **2014**, *55*, 258–266. DOI: [10.1016/j.indcrop.2014.02.022](https://doi.org/10.1016/j.indcrop.2014.02.022).
58. Tellers, J.; Pinalli, R.; Soliman, M.; Vachon, J.; Dalcanale, E. Reprocessable Vinylogous Urethane Cross-Linked Polyethylene via Reactive Extrusion. *Polym. Chem.* **2019**, *10*, 5534–5542. DOI: [10.1039/C9PY01194C](https://doi.org/10.1039/C9PY01194C).
59. Sheppard, D. T.; Jin, K.; Hamachi, L. S.; Dean, W.; Fortman, D. J.; Ellison, C. J.; Dichtel, W. R. Reprocessing Postconsumer Polyurethane Foam Using Carbamate Exchange Catalysis and Twin-Screw Extrusion. *ACS Cent. Sci.* **2020**, *6*, 921–927. DOI: [10.1021/acscentsci.0c00083](https://doi.org/10.1021/acscentsci.0c00083).
60. Asensio, M.; Nuñez, K.; Guerrero, J.; Herrero, M.; Merino, J. C.; Pastor, J. M. Rheological Modification of Recycled Poly(Ethylene Terephthalate): Blending and Reactive Extrusion. *Polym. Degrad. Stab.* **2020**, *179*, 109258. DOI: [10.1016/j.polymdegradstab.2020.109258](https://doi.org/10.1016/j.polymdegradstab.2020.109258).
61. Vahabi, H.; Movahedifar, E.; Saeb, M. Flame Retardancy of Reactive and Functional Polymers. In *Reactive and Functional Polymers*; New York City: Springer, **2021**; pp. 165–195, Vol. 3.
62. Mohammadi, Y.; Khonakdar, H. A.; Jafari, S. H.; Saeb, M. R.; Golriz, M.; Wagenknecht, U.; Heinrich, G.; Sosnowski, S.; Szymanski, R. Simulation of Microstructural Evolution during Reactive Blending of PET and PEN: Numerical Integration of Kinetic Differential Equations and Monte Carlo Method. *Macromol. Theory Simul.* **2015**, *24*, 152–167. DOI: [10.1002/mats.201400086](https://doi.org/10.1002/mats.201400086).
63. Weil, E. D.; Patel, N. G.; Said, M.; Hirschler, M. M.; Shakir, S. Oxygen Index: correlations to Other Fire Tests. *Fire Mater.* **1992**, *16*, 159–167. DOI: [10.1002/fam.810160402](https://doi.org/10.1002/fam.810160402).
64. Joseph, P.; Tretsiakova-Mcnally, S. Reactive Modifications of Some Chain-and Step-Growth Polymers with Phosphorus-Containing Compounds: effects on Flame Retardance—A Review. *Polym. Adv. Technol.* **2011**, *22*, 395–406. DOI: [10.1002/pat.1900](https://doi.org/10.1002/pat.1900).
65. Simonetti, P.; Nazir, R.; Gooneie, A.; Lehner, S.; Jovic, M.; Salmeia, K. A.; Hufenus, R.; Rippl, A.; Kaiser, J.-P.; Hirsch, C.; et al. Michael Addition in Reactive Extrusion: A Facile Sustainable Route to Developing Phosphorus Based Flame Retardant Materials. *Compos. Part B: Eng.* **2019**, *178*, 107470. DOI: [10.1016/j.compositesb.2019.107470](https://doi.org/10.1016/j.compositesb.2019.107470).
66. Sahyoun, J.; Bounor-Legare, V.; Ferry, L.; Sonnier, R.; Bonhommé, A.; Cassagnau, P. Influence of Organophosphorous Silica Precursor on the Thermal and Fire Behaviour of a PA66/PA6 Copolymer. *Polym. Degrad. Stab.* **2015**, *115*, 117–128. DOI: [10.1016/j.polymdegradstab.2015.02.017](https://doi.org/10.1016/j.polymdegradstab.2015.02.017).
67. Liu, Y.; Wang, Q. Reactive Extrusion to Synthesize Intumescent Flame Retardant with a Solid Acid as Catalyst and the Flame Retardancy of the Products in Polypropylene. *J. Appl. Polym. Sci.* **2008**, *107*, 14–20. DOI: [10.1002/app.26220](https://doi.org/10.1002/app.26220).
68. Wang, D.-Y.; Liu, Y.; Wang, Y.-Z.; Artilles, C. P.; Hull, T. R.; Price, D. Fire Retardancy of a Reactively Extruded Intumescent Flame Retardant Polyethylene System Enhanced by Metal Chelates. *Polym. Degrad. Stab.* **2007**, *92*, 1592–1598. DOI: [10.1016/j.polymdegradstab.2007.04.015](https://doi.org/10.1016/j.polymdegradstab.2007.04.015).
69. Wang, J.-S.; Wang, G.-H.; Liu, Y.; Jiao, Y.-H.; Liu, D. Thermal Stability, Combustion Behavior, and Toxic Gases in Fire Effluents of an Intumescent Flame-Retarded Polypropylene System. *Ind. Eng. Chem. Res.* **2014**, *53*, 6978–6984. DOI: [10.1021/ie500262w](https://doi.org/10.1021/ie500262w).
70. Chen, Y.; Wang, Q.; Yan, W.; Tang, H. Preparation of Flame Retardant Polyamide 6 Composite with Melamine Cyanurate Nanoparticles in Situ Formed in Extrusion Process. *Polym. Degrad. Stab.* **2006**, *91*, 2632–2643. DOI: [10.1016/j.polymdegradstab.2006.05.002](https://doi.org/10.1016/j.polymdegradstab.2006.05.002).
71. Battegazzore, D.; Lavaselli, M.; Cheng, B.; Li, D.; Yang, R.; Frache, A.; Paul, G.; Marchese, L. Reactive Extrusion of Sol-Gel Silica as Fire Retardant Synergistic Additive in Ethylene-Vinyl Acetate Copolymer (EVA) Composites. *Polym. Degrad. Stab.* **2019**, *167*, 259–268. DOI: [10.1016/j.polymdegradstab.2019.07.011](https://doi.org/10.1016/j.polymdegradstab.2019.07.011).

72. Verhoeven, V.; Padsalgikar, A.; Ganzeveld, K.; Janssen, L. The Reactive Extrusion of Thermoplastic Polyurethane and the Effect of the Depolymerization Reaction. *Int. Polym. Proc.* **2006**, *21*, 295–308.
73. Semsarzadeh, M.; Navarchian, A.; Morshedian, J. Reactive Extrusion of Poly (Urethane-Isocyanurate). *Adv. Polym. Technol.* **2004**, *23*, 239–255. DOI: [10.1002/adv.20014](https://doi.org/10.1002/adv.20014).
74. Kim, H.; Oh, K.; Seo, Y. Rheological and Mechanical Properties of a Novel Polyamide 6 Synthesized by Anionic Polymerization of ϵ -Caprolactam in a Twin-Screw Extruder. *Polymer* **2019**, *177*, 196–201. DOI: [10.1016/j.polymer.2019.06.008](https://doi.org/10.1016/j.polymer.2019.06.008).
75. Tuna, B.; Benkreira, H. Reactive Extrusion of Polyamide 6 Using a Novel Chain Extender. *Polym. Eng. Sci.* **2019**, *59*, E25–E31. DOI: [10.1002/pen.24944](https://doi.org/10.1002/pen.24944).
76. Bourbigot, S.; Fontaine, G.; Gallos, A.; Bellayer, S. Reactive Extrusion of PLA and of PLA/Carbon Nanotubes Nanocomposite: processing, Characterization and Flame Retardancy. *Polym. Adv. Technol.* **2011**, *22*, 30–37. DOI: [10.1002/pat.1715](https://doi.org/10.1002/pat.1715).
77. Misiura, D.; Majka, T. M. An Overview on Obtaining Foamed PET by Reactive Extrusion. *Tech. Trans.* **2018**, *115*, 97–102.
78. Gallos, A.; Fontaine, G.; Bourbigot, S. Reactive Extrusion of Intumescent Stereocomplexed Poly-L, D-Lactide: characterization and Reaction to Fire. *Polym. Adv. Technol.* **2013**, *24*, 130–133. DOI: [10.1002/pat.3058](https://doi.org/10.1002/pat.3058).
79. Pagel, S.; Benz, J.; Mourgas, G.; Buchmeiser, M.; Bonten, C. Reactive Compounding of Intrinsically Flame-Resistant Polyamides. *AIP Conference Proceedings*: AIP Publishing LLC, **2020**; p. 020043. doi: [10.1063/5.0028391](https://doi.org/10.1063/5.0028391)
80. Sahyoun, J.; Bounor-Legaré, V.; Ferry, L.; Sonnier, R.; Da Cruz-Boisson, F.; Melis, F.; Bonhommé, A.; Cassagnau, P. Synthesis of a New Organophosphorous Alkoxysilane Precursor and Its Effect on the Thermal and Fire Behavior of a PA66/PA6 Copolymer. *Eur. Polym. J.* **2015**, *66*, 352–366. DOI: [10.1016/j.eurpolymj.2015.02.036](https://doi.org/10.1016/j.eurpolymj.2015.02.036).
81. Chen, Y.; Liu, Y.; Wang, Q.; Yin, H.; Aelmans, N.; Kierkels, R. Performance of Intumescent Flame Retardant Master Batch Synthesized through Twin-Screw Reactively Extruding Technology: effect of Component Ratio. *Polym. Degrad. Stab.* **2003**, *81*, 215–224. DOI: [10.1016/S0141-3910\(03\)00091-0](https://doi.org/10.1016/S0141-3910(03)00091-0).
82. Liu, Y.; Wang, Q.; Chen, Y. Preparation and Application of Deformable and Orientable Intumescent Flame Retardants Incorporated with Polypropylene. *Polym.-Plast. Technol. Eng.* **2007**, *46*, 455–460. DOI: [10.1080/03602550701247413](https://doi.org/10.1080/03602550701247413).
83. Bethke, C.; Goedderz, D.; Weber, L.; Standau, T.; Döring, M.; Altstädt, V. Improving the Flame-Retardant Property of Bottle-Grade PET Foam Made by Reactive Foam Extrusion. *J. Appl. Polym. Sci.* **2020**, *137*, 49042. DOI: [10.1002/app.49042](https://doi.org/10.1002/app.49042).