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Henri Vahabi, Hao Wu, Mohammad Reza Saeb, Joseph Koo, Seeram Ramakrishna. Electrospinning for developing flame retardant polymer materials: current status and future perspectives. *Polymer*, 2021, 217, pp.123466. 10.1016/j.polymer.2021.123466 . hal-03126105

HAL Id: hal-03126105

<https://hal.univ-lorraine.fr/hal-03126105>

Submitted on 13 Feb 2023

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Electrospinning for developing flame retardant polymer materials: current status and future perspectives

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Abstract

Polymer processing techniques have experienced continued progress over decades to meet performance requirements in diverse applications. In the same period, various high-performance polymeric materials have been developed rapidly. Fabrication of polymer fibers has been in the center of attention from the origin of synthetic polymers, with applications ranging from textiles to biomedical materials. Electrospinning is a well-known process for developing continuous fibers with diameters of tens of microns to hundreds of nanometers. It benefits from special privilege of *in-situ* modification/functionalization of polymers and nanoscale materials. Flame retardancy is an important performance characteristic of polymer materials. Both material and fabrication aspects have to be taken into account when designing flame retardant polymer materials, but the latter has been rarely dealt with by researchers. This review attempts to categorize state-of-the-art features of flame-retardant polymer materials developed by using electrospinning. Electrospun fibers of natural and synthetic polymers used in developing flame-retardant materials were reviewed and their mechanical properties, advantages and challenging aspects were discussed.

Keywords: Electrospinning; flame retardancy; flame retardant; fire behavior; electrospun fibers; nanofibers

1. Introduction

Flame retardancy is becoming a main dimension of polymer materials and technology in view of the worldwide attention centered to the safety concerns. The growing attention towards development of flame retardant polymer materials is evident in the massive production of commercial flame retardants along with the growing number of patents and research articles on flame retardant polymer materials [1, 2]. Advanced features of the use of polymers are their contribution to the biomedicine, energy devices and aeronautics, but their flammability appears as a serious concern of engineers to be overcome. A huge effort have been undertaken by a wide range of scientists and engineers alike to synthesize and commercialize new flame retardants (FR) [3]. In parallel to the development of new FR, processing technology has evolved considerably and is still experiencing a rapid period of development [4]. From the simple coating treatment in ancient Egypt to the new 3D and 4D printing technologies, novel FR and processing methods have mutually adapted to each other, **Figure 1**.

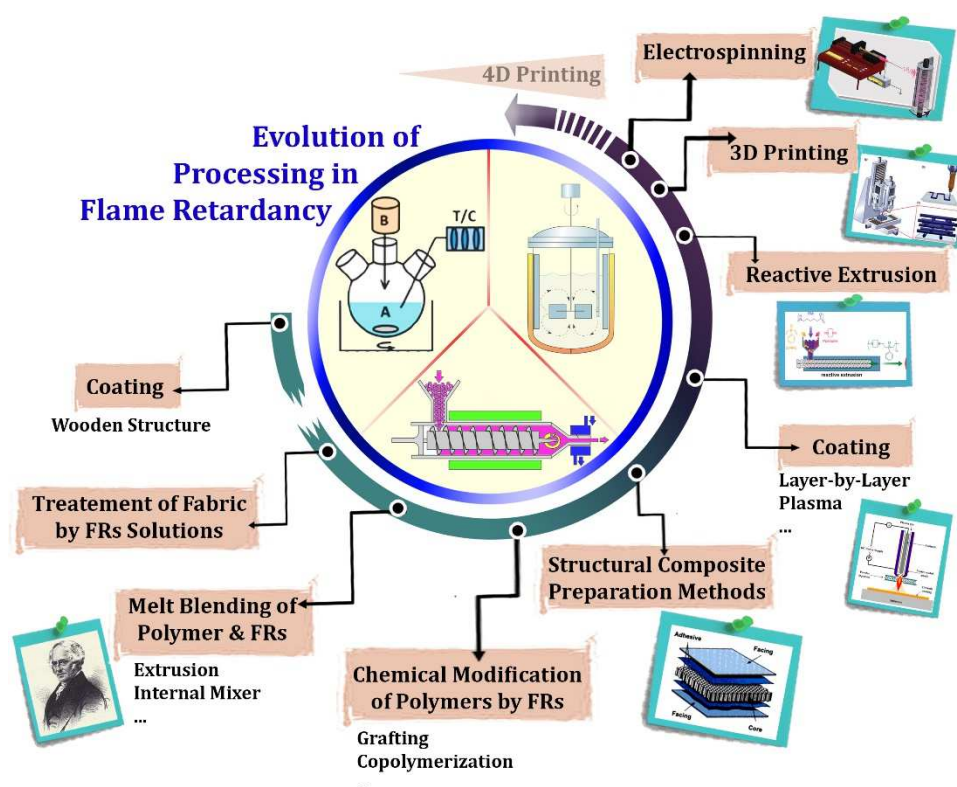


Figure 1. Evolution of processing methods applied in developing flame retardant materials: The simple protective coating is developed by the Egyptians to apply the flame retardants on wood and cotton materials. A similar method has also been used during the siege of Piraeus (86 years B.C.) to apply the alum solutions on wooden battleships. Afterwards, by development of new polymers, various methods have been invented to incorporate the flame retardants into the bulk or onto the surface of polymeric materials including melt extrusion, grafting, layer-by-layer and plasma coating, reactive extrusion, 3D printing and electrospinning. Electrospinning can be privileged because of being facile, versatile and economically reasonable.

Electrospinning is a versatile yet facile methodology for developing polymeric fibers with diameters from micro- to nano-scale [5]. It has been considered over years in diverse applications, such as biomedical [6], tissue engineering [7], drug delivery [8], biosensor [9], filtration [10], protective clothing [11], and catalysis [12]. Electrospinning has recently been undertaken in designing flame retardant polymer materials [13], **Figure 2a**. An electrospinning setup is made of three essential components, including a high voltage power supply, a syringe or spinneret, and a collector, **Figure 2b**. Such a facile one-pot manufacturing process makes it possible to produce functionalized continuous fibers composed of flame retardants of different families.

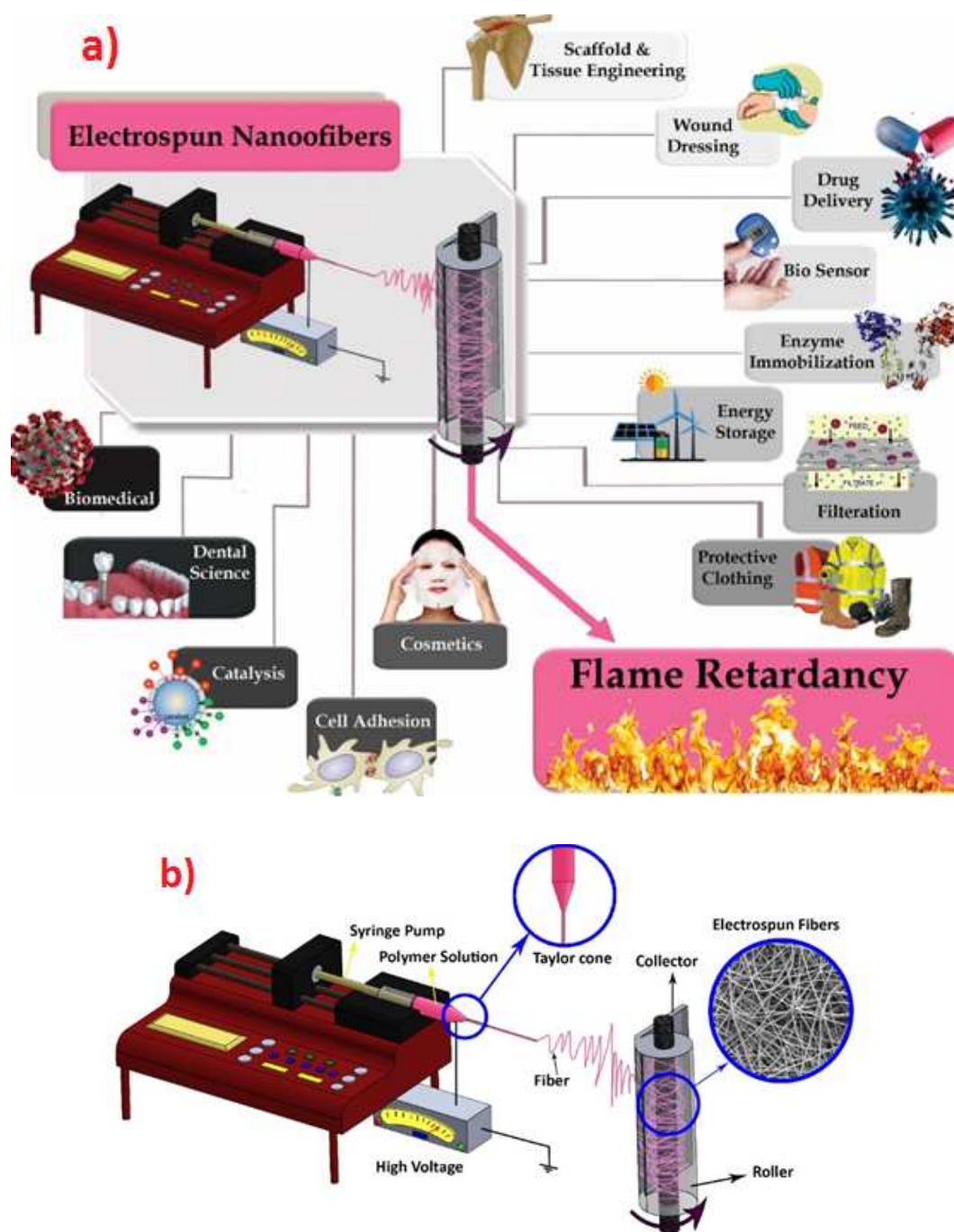


Figure 2. a) A quick view over diverse applications of fibers prepared via electrospinning; b) schematic illustration of a typical electrospinning setup.

The principle of electrospinning consists of injection of a polymer solution or melt through a nozzle under high voltage. The use of high voltage enables user to create an electrical charge and polarity into the polymer solution. The accumulation of charge leads to apparition of a conical shaped polymer flow at the tip of the dispensing nozzle, namely Taylor cone. Then,

the charged jet of polymer solution is expelled from the tip of the Taylor Cone. Thus, the solution jet is highly stretched and the fibers with nano- or micro-size are deposited on the collector. The fibers prepared are in non-woven (felt mat) form and can be deposited on a substrate/support. Moreover, electrospinning offers the possibility to incorporate micro or nanoparticles into the polymer solution and to obtain composite fiber materials with multiple functionalities. Accordingly, electrospinning allows for facile *in-situ* production of flame-retardant composites.

In recent years, the electrospinning method has been progressively considered in improving the flame retardancy of materials. A survey of the literature showed that the electrospun fibers are supporting flame retardancy improvement by making possible the preparation of safe membranes in lithium-ion batteries (LIBs), **Table 1**. LIBs are currently considered as one of the most promising energy-storage devices [14]. A membrane inside the LIBs is responsible for keeping the anode and cathode electrodes separate in the battery and at the same time allowing the Li^+ ions to pass through it. Currently, the majority of commercially available membranes are made of polyethylene or polypropylene due to their excellent properties including mechanical strength and chemical stability [15]. However, these materials are highly flammable and; therefore, the fire safety issues related to them in LIBs are of critical significance [16, 17]. In this sense, several research works have been devoted to the preparation of membranes with high flame retardancy and porous character, which is necessary for the application, using electrospinning method, **Table 1**. The flammable character of electrolytes in LIBs is another key fire safety concern. In other words, the electrolytes used in LIBS are inherently flammable organic liquids and incidental fluctuations in temperature or leakage can cause spontaneous ignition of electrolytes. Therefore, some solutions have already been recommended to diminish the flammability of electrolytes, *e.g.*, the addition of flame retardants into electrolyte or the use of fluorinated electrolytes.

However, these solutions in an inverse way are detrimental and decrease the ionic conductivity of electrolytes. A new strategy has been developed to overcome this problem that consists in the preparation of electrospun core/shell fibers with a flame retardant core and a polymer shell [18]. These electrospun core/shell fibers can be added to the membrane or the electrolyte to be released in case of fire. In such a composite material, the flame retardant is not directly in contact with the electrolyte but will be released to extinguish fire when the polymer shell is degraded at high temperatures. Electrospinning can create a conformal coating on the surface of a support material. Once the electrospun coating layer is formed, the high-performance polymer fibers in which flame retardant is encased will cover the surface of support, making it flame retardant. Therefore, electrospinning appears to be a promising method to bring new features to the field of flame retardancy.

The present review mainly focuses on the potential of electrospinning method for improving the flame retardancy of polymer materials. The literature in this field were carefully reviewed and classified by the type of polymer used in preparation of electrospun fibers. **Table 1** summarizes all papers published in the field of electrospinning having flame retardancy as the main responding variable. It is apparent from the table that flame retardant electrospun fibers are experiencing an early stage of development and research in this filed is of crucial importance and significance.

2. Principle of flame retardancy of polymer materials

Flame retardancy is becoming a key performance characteristic of polymer materials. To make a polymer flame retardant, one can choose one method among the two possible choices [19]. In the first method, known as melt processing, a flame retardant or flame-retardant system/blend of two or more flame retardant additives are incorporated into the polymer matrix batch-wise (injection molding) or continuously (extrusion). The second method is known as reactive processing, through which molecules/monomers of flame-retardant

additive(s) are covalently situated in the polymer chains through polymerization with monomers of the main polymer or chemically anchor to the side chains of polymers through covalent bonding. In some cases, the flame retardant is applied on the surface of the polymeric sample (coating). Among well-known flame-retardant families are minerals, halogens, phosphorus, and nitrogen-based chemicals.

Flame-retardant integrated into the bulk or surface of polymer materials can act in two ways in order to make polymers resistant against fire. They assist in retardancy of flame in the gas, condensed or both phases [20]. In the first scenario, flame retardant assists in dilution of the combustible gases through emission of inert gases like NH_3 and CO_2 , or trap the active radicals in the gas phase like H^\bullet and OH^\bullet by release of reactive moieties like HPO^\bullet , PO^\bullet , and halogenated radicals [21]. Therefore, flame retardants acting in gas phase help one to control over flame propagation. In a different manner, flame retardants acting in condensed phase make possible formation of a residue/char protective layer on the top layer of the substrate blocking the emission of combustible gases from the bottom to the top layer and mutually prevents the penetration of oxygen molecules and the generated heat from the top of surface in the gas phase to the combustion front at the bottom of substrate. Once the polymer is infinitesimally converted from substrate into the char in the time span of combustion, lower flammable parts of polymer remained in the sample use less fuel and flame becomes controlled.

Typically, limiting oxygen index (LOI), UL94, microscale combustion calorimetry (MCC) also known as pyrolysis combustion flow calorimeter (PCFC) analysis and cone calorimetry are general techniques utilized in evaluation of flame retardant properties of polymers. LOI and MCC are the most common tests for the analysis of electrospun fibers, which are briefly dealt here. LOI is a quantity which takes into account the lowest amount of oxygen in a mixture of oxygen and nitrogen needed for protecting sample against combustion. The

minimum concentration of oxygen required in this test is the amount that sample receives and resists against flame for 3 min or a length of 5 cm of a standard sample burns in a vertical configuration [22]. As ISO 4589 outlines, LOI is conducted on a rectangular sample having dimension of 80×10×4 mm³. The higher the LOI the more appropriate the flame retardancy of a sample. MCC is also known as a useful measure for flammability of polymers. According to ASTM D7309, MCC analyzes degradation of polymers of very low amount (typically 2-4 mg) which takes place in pyrolysis in a small chamber in the presence of nitrogen as atmosphere. According to standard protocol, polymer receives heat at heating rate of 0.-4 °C/s until it approaches 750 °C as maximum temperature. Pyrolysis assists in the release of gases from sample and a combustor with constant temperature of 900 °C burns gases and measures the amount of oxygen used in and the heat release rate of combustion process [23]. The apparatus works on the basis of Huggett's relation, where 1 kg of the oxygen consumed in combustion is equivalent of 13.1 MJ of the energy released in this process. The most vital parameters obtained from MCC are the peak of the heat release rate (pHRR) and the total heat release (THR). A higher flame retardancy performance is corresponded to the minimum of pHRR and THR.

2. Electrospinning and flame retardancy

2.1. Electrospun polyamide fibers

Cai et al. [24] prepared polyamide 6 (PA6) fibers containing Fe-montmorillonite (Fe-MMT) by electrospinning and then sputter coated these fibers with silicon (Si). The authors reported that the yield of the charred residue in TGA has been increased to 13.42% for the electrospun coated fibers against 10.56% for the electrospun fibers. They also performed MCC analysis on these samples and showed the decrease in pHRR by around 18% and 25% for PA/Fe-MMT fibers and sputter coated PA/Fe-MMT fibers, respectively compared with electrospun PA fibers. The synergistic effect between Fe-MMT and Si as well as catalysis effect of Fe³⁺

which can contribute to the molecular crosslinking and char promotion has been suggested as mechanism in flame retardancy improvement. Selvakumar et al. [25] investigated the effect of electrospun PA6 nanofibers containing boric acid nanoparticles on flame retardancy of cotton fabrics. Boric acid particles have been incorporated into PA6 solution and then directly coated on cotton fabrics. The flame spread test performed (CPSC Test, method CFR part 1610 standard for the flammability of clothing textiles) on coated samples showed that PA nanofibers containing 0.05 wt.% boric acid increase the flame spread time by 82%, in respect of pure PA6. Wu et al. [26] studied thermal and flame retardant properties of electrospun PA6 nanocomposite fibers. Nanofibers with varying concentrations of MMT nanoclay and intumescent flame retardant electrospun into nanofibers with diameters in the 100nm range. A uniform distribution of well dispersed and highly aligned nanoclay platelets were observed in TEM images, **Figure 3**. Fibers with intumescent FR started to degrade at lower temperatures due to the early decomposition of the flame retardants but the overall char yield was increased significantly. MCC results showed that both FR and nanoclay were effective in reducing the pHRR. Similarly, Yin et al. [27] fabricated electrospun PA6 nanocomposite fibers incorporated with carbon nanotube (CNT), nanoclay and intumescent FRs. A synergistic effect between CNT and nanoclay were reported based on MCC heat release results.

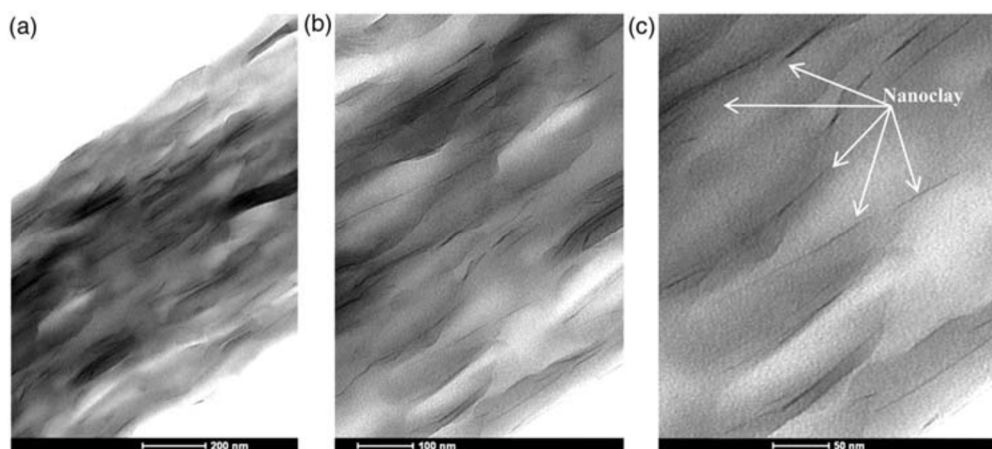


Figure 3. TEM images of electrospun PA6 fibers containing nanoclay platelets with scale bars of (a) 200 nm, (b) 100 nm, and (c) 50 nm [28].

Dhineshababu et al. [29] incorporated MgO nanoparticles into PA6 and then coated on cotton fabric using electrospinning. The burning time for cotton sample coated with PA6/MgO was slightly increased (18.5 s) compared with the cotton sample coated with neat PA6. They proposed that these cotton fabrics are suitable for protective clothing for soldiers.

A core-shell nanofibrous material has been prepared by Liu et al. [30] using electrospinning. The shell was made of PA6 and triphenyl phosphate (TPP) was used as the core. The above-mentioned material was designed for the dust filtration application in which both filtration and flame retardancy functionalities are needed. The flame retardancy is needed for the dust filters because the accumulated combustible dusts on filters can be a source of fire hazard. The electrospun core-shell nanofibers were deposited on filters and then wetted by vegetable oil. From the vertical burning test, the filter treated with core-shell nanofiber showed self-extinguishing behavior and was not ignited even after 14 s of exposure to a direct flame. In contrast, the filter treated with neat PA6 burnt entirely.

Mazzocchetti et al. [31] used poly(meta-phenylene isophthalamide) (PMIA) electrospun fibrous mats for coating of prepreg epoxy based carbon fiber reinforced polymers (CFRP) to improve their flammability. Since PMIA is inherently flame retardant and self-extinguishing, no additives were incorporated to the electrospun fibers. The thickness of applied mats was around 50-80 μm . From the obtained results in cone calorimeter tests, it has been demonstrated that the electrospun coating mats were able to increase the TTI significantly from 46 s for uncoated sample to 94 s. In spite of a significant change in TTI, the variation of pHRR was limited, from $470 \pm 50 \text{ kW/m}^2$ for uncoated sample to $391 \pm 30 \text{ kW/m}^2$. The authors claimed that the thin and light ($24\text{--}27 \text{ g/m}^2$) character of the PMIA coating is a useful method to improve the flame retardancy regardless the object dimensions and geometry.

Electrospun PMIA fibers have also been used as coating to improve the flame retardancy of wood panels. Merighi et al. [32] prepared two types of electrospun PMIA fibers: randomly

aligned (mat) and highly aligned fibers. Then, these fibers were applied on wood panels using a polyurethane paint and a vinyl glue as adhesive. The authors claimed that the fire behavior of wooden samples was improved. However, the HRR curves obtained in cone calorimetry test showed a slight difference between treated and non-treated wooden samples. The pHRR and THR values were nearly identical when the accuracy of cone calorimetry test is considered. Nevertheless, the TTI increased for all treated samples.

2.2. Electrospun polyimide fibers

Gallo et al. [13] used electrospinning for preparation of two types of electrospun nanofiber mats based on polyamic acid (PAA) and polyimide (PI) which were then deposited onto PA66 plate samples (100×100×3 mm) in order to have the coating effect of nanofiber mats and thus improve the flame retardancy of PA66. Based on cone calorimetry tests performed on plate samples coated by PI and PAA nanofiber mats, they concluded that the main effect of nanofibers mats was the increase in time to ignition (TTI), at the best from 38 s for PA66 to 85 s with PI nanofiber mats coating. However, other parameters such as pHRR did not change notably.

Development of new separator in rechargeable metal–sulfur batteries is a great concern due to the safety issues associated with the flammability of current commercially available separators, generally fabricated by porous polyolefin. Zhou et al. [33] prepared a multilayer structure in which electrospun PI membrane was used as an inner layer and two external coating layers was from copper nanowire-graphene nanosheet (CuNWs-GN) film and lithium lanthanum zirconium oxide polyethyleneoxide (LLZO-PEO) film (CuNWs-GN/PI/LLZO). They performed a simple lighter test to compare the flame retardant character of PI layer as well as the sandwich structure with a PP sample and presented some photos of samples during burning, **Figure 4**.

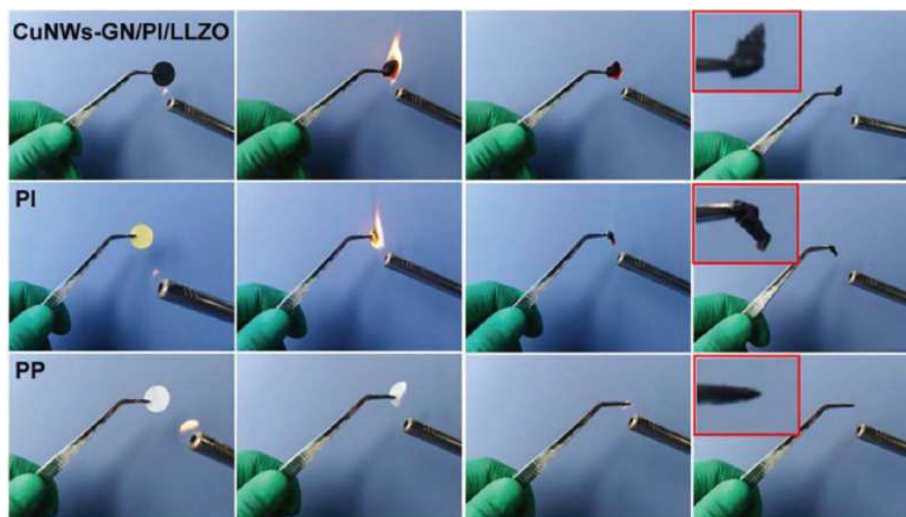


Figure 4. Flame tests realized by Zhou et al. on PI, PP, and CuNWs-GN/PI/LLZO samples [33].

Wang et al. [34] reported the preparation of electrospun nanofibers based on PI as membrane for lithium-ion batteries. The authors simply tested the electrospun nanofibers PI membranes using a lighter and compared its behavior with a commercially available membrane (Celgard). The photographs presented in the paper show a greater flame in the case of Celgard membrane and a self-extinguishing behavior for the electrospun PI membrane. Kong et al. [35] prepared PI nanofibers by electrospinning in which pendant fluorinated groups ($-\text{CF}_3$) was incorporated into the polymer backbone. They also performed a simple flame test using a lighter and demonstrated non-flammability of fluorinated PI film compared with a commercial polyethylene film used in lithium-ion batteries.

2.3. Electrospun cellulose fibers

A new method for preparation of nanoparticle-coated electrospun fibers have been reported by Zheng et al. [36]. They prepared a solution of divided cellulose pulp and a room temperature ionic liquid (RTILs) solvent. This solution was electrospun onto a bath containing an aqueous suspension of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) nanoparticles. Thus, the $\text{Mg}(\text{OH})_2$ nanoparticles were coated onto the cellulosic fibers. For the sake of comparison,

they also prepared the electrospun fibers from a solution of cellulose and Mg(OH)_2 . TGA results showed that when the Mg(OH)_2 nanoparticles (50 nm) were coated onto cellulose fiber surfaces, the remaining residue significantly increased to 31%, against 11% in the case of Mg(OH)_2 nanoparticles incorporated inside the electrospun fibers. The authors also examined the electrospun fibers using a simple flame test and observed higher resistance of coated sample compared with the other method. The authors attributed this behavior to the physical voids created when nanoparticles are incorporated inside the fibers which will lead to rapid combustion because of increased the internal surface area of the cellulose fibers. Moreover, the liberation of water from nanoparticles during the combustion and the increased surface area also contribute to the rapid burning of fibers. On the other hand, these undesirable effects can be limited when the nanoparticles are coated onto the fiber surface. Pirzada et al. [37] elaborated a porous 3D nanofiber aerogels (NFA) using electrospinning. They prepared a solution of cellulose diacetate and silica sol and this solution was electrospun to obtain nanofibers. Freeze-drying of these electrospun nanofibers in tertiary butanol and then a thermal treatment led to a hybrid nanofibers aerogel. The obtained hybrid aerogel was exposed to flame and showed self-extinguishing properties. The mechanism proposed for this behavior was the accumulation of thermally stable silica on the sample surface and its barrier effect to limit the heat transfer to material.

2.4. Electrospun polyacrylonitrile fibers

Cai et al. [38] studied the effect of ferric chloride (FeCl_3) on combustion property of electrospun polyacrylonitrile (PAN) nanofibers. Solutions of PAN and FeCl_3 at 1 and 3 wt.% (in a solution containing 12 wt.% PAN and DMF) were prepared after which nanofibers of PAN containing FeCl_3 were obtained by electrospinning. PCFC analysis showed around 17% decrease in pHRR in presence of 5 wt.% FeCl_3 , with respect to the neat PAN nanofibers. Based on the activity of FeCl_3 reported in the literature, the authors considered the action of

FeCl_3 as a Lewis acid. Since PAN has strong electronegative groups (cyano groups: $-\text{CN}$), it coordinates with FeCl_3 and thus the mechanism of PAN degradation changes. Moreover, FeCl_3 has some catalyzing effect which helps the crosslinking of polymer and char promotion. Moon and Emrick [39] prepared the electrospun fibers of PAN containing carbon nanotubes (CNT) and ochre and evaluated their flame retardancy using PCFC and LOI tests. They discovered that when the electrospun nanofibers containing both CNT and ochre were thermally treated (in a furnace with preheated air and then heated to a specific temperature), the best results in terms of flammability can be obtained. Thus, the electrospun nanofibers prepared by a combination of CNT at 0.1 wt.% and ochre at 1 wt.% in a solution of 10 wt.% PAN in DMF, and followed by a thermal treatment led to significantly improved the flammability properties. For the above-mentioned sample, the LOI value increased to 34.5 against 19.5 for the pure PAN electrospun fiber. For the same sample, the heat release capacity (HRC) also significantly decreased to 24 J/g.K, against 253 J/g.K for the pure PAN electrospun fiber. Pu et al. [40] investigated the effect of poly(m-phenylene isophthalamide) (PMIA) and multi-walled carbon nanotube on flammability of PAN electrospun fibers. Solutions of these materials were prepared (CNT at 0.3, 0.6, 0.9, and 1.2 wt.% in a solution of PMIA/PAN (12 wt.%, w/w, 1/1)) and highly oriented, non-woven electrospun fiber membrane were obtained. The authors performed a simple test using a lighter and presented some photos to show the improvement of flammability of the sample prepared.

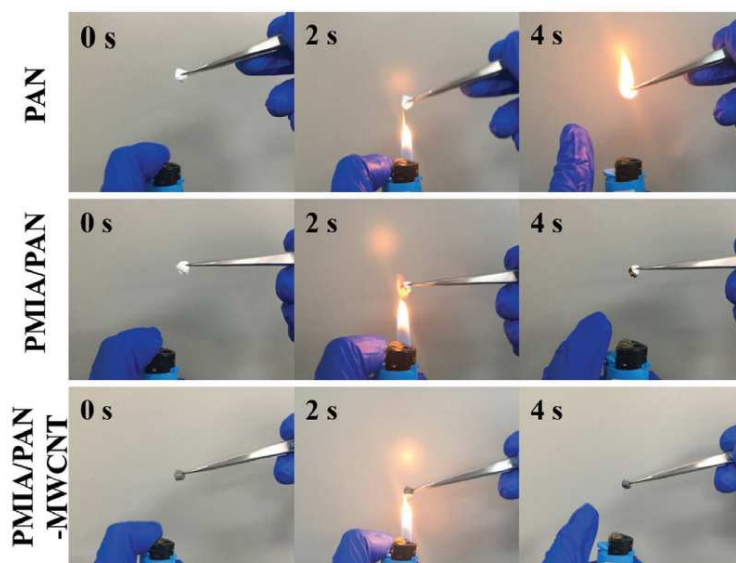


Figure 5. Flame test realized by Pu et al. [40] on PAN, PMIA/PAN and, PMIA/PAN-MWCNT samples.

2.5. Electrospun polyurethane fibers

Using electrospinning method, Zhai et al. [41] prepared polyetherimide/polyurethane (PEI/PU) nanofibers as a separator for lithium ion batteries. After obtaining the PEI-PU electrospun fibers, a coating based on SiO_2 nanoparticles was applied on these fibers using a dip-coating process. Using this method, the porous character of PU, the excellent flame properties of PEI and the barrier effect of SiO_2 were gathered in one material. A simple non-conventional flame test using a lighter was used to demonstrate the better FR property of SiO_2 /PEI-PU sample compare with a commercially available separator (Celgard).

Yang et al. [42] investigated the flame behavior of electrospun PU-polysulfonamide (PSA) non-woven fibers containing barium titanate (BaTiO_3) as membrane for filtration in dust removal. Again, the porous character of PU was used along with the FR property of PSA. BaTiO_3 was incorporated in order to use its known positive effect on surface roughness, strength and charge storage capacity due to its high dielectric constant. A simple lighter flame test was also performed to show a better FR behavior of the electrospun BaTiO_3 /PU-PSA fibers as compared with pure PU fibers.

2.6. Electrospun poly(vinylidene fluoride) fibers

A core-shell electrospun structure have been designed by Liang et al. [18] for separators in Li-ion batteries in which poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) was used as shell and TPP flame retardant as core, **Figure 6,a-b**. The preparation of core-shell structure was performed using a dual nozzle coaxial electrospinning method. The main idea behind this design was the degradation of the PVDF-HFP shell allows for liberation of the flame retardants into the electrolyte, in case of an ignition. The TPP can be immediately dissolved in the electrolyte and convert it to a non-flammable liquid. The flame test showed that TPP/PVDF-HFP samples were resistant to flame and cannot be ignited by a lighter.

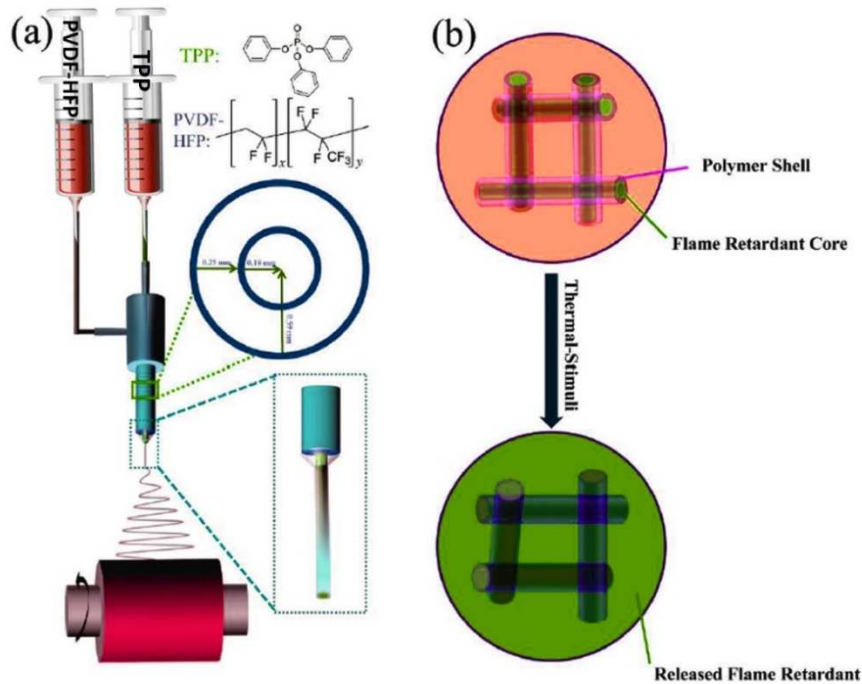


Figure 6. Schematic illustration of the setup used by Liang et al. [18] to prepare the core/shell fibers.

Zhang et al. [43] incorporated polyhedral oligomeric silsesquioxane (POSS) (at 5, 10 and 15 wt.%) into a solution of PVDF and the obtained electrospun fibers obtained from the aforementioned solution have been collected on a PP separator for the Li-ion battery applications. They used POSS with the chloropropyl groups to improve the compatibility with PVDF and to benefit from cage structure of POSS which help the migration of conductive

medium. The PP supported POSS-(C₃H₆Cl)₈/PVDF samples have been exposed to flame and their behavior compared with the pure PP separator sample. They observed that no shrinkage happened to the PP supported POSS-(C₃H₆Cl)₈/PVDF sample, while the PP sample immediately shrunk. The best flame behavior has been observed on the sample containing 15 wt.% POSS with a self-extinguishing property after burning for 2 s. The improvement in flame behavior was explained by the presence of Cl and F in POSS and PVDF as well as the thermal stability of POSS cages.

Wang et al. [44] investigated the flame behavior of a separator for the Li-ion batteries made of poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) and containing 2 wt.% Sb₂O₃ by electrospinning. The Sb₂O₃ particles were added to a solution of PVDF-CTFE and then the electrospun nanofibers were prepared. The results obtained from MCC test showed a significant decrease in heat release capacity (HRC) from 1,356 J/g.K for commercially available PE membrane to 75 J/g.K for Sb₂O₃/PVDF-CTFE electrospun fibrous membrane. This behavior was related to the low flammability of PVDF-CTFE as well as the interaction between Sb₂O₃ and Cl and formation of SbCl₃ and its action in gas phase. Chen et al. [45] studied the flame behavior of electrospun PVDF fibrous membrane containing TPP and cellulose acetate (CA) which showed a better flame resistance compared with a PE separator sample. The percentage of TPP and CA in PVDF was not mentioned.

2.7. Electrospun melamine formaldehyde resin fibers

A thermoset resin was used by Wang et al. [46] to produce electrospun non-woven mat as separator in Li-ion batteries. Melamine formaldehyde resin (MFR) was used due to its higher thermal stability and flame retardancy compared with the commercially available PE or PP separators. The electrospun nanofibers were prepared by dissolving melamine and formaldehyde in polyvinyl alcohol (PVA) at 8 wt.% in order to increase the thermal stability of fibers. The LOI value for the obtained MFR membrane was 38 against 18 for a

commercially available PP membrane. Moreover, in the case of graphite/LiMn₂O₄ battery, the use of MFR separator was beneficial to overcome the problem related to the diffusion of Mn²⁺ ions through the membrane and its deposition on the graphite anode surface that led to decreased battery efficiency, **Figure 7**. The presence of lone pair electron in nitrogen from the MFR causes the chelation between its macromolecular chains and Mn²⁺ ions and these ions are captured by the MFR separator.

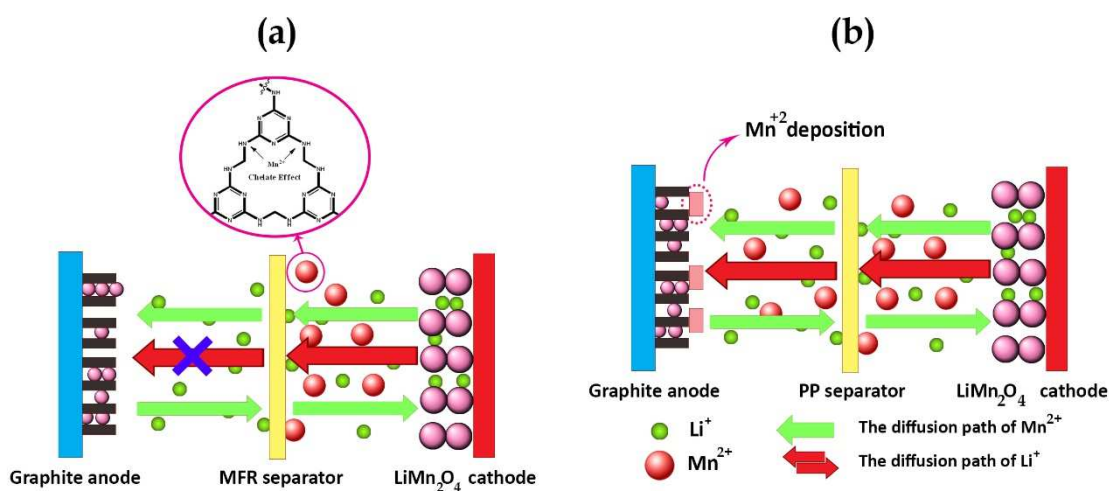


Figure 7. Schematic illustration of the Li⁺ and Mn²⁺ diffusion in the case of MFR separator (a) and PP separator (b) [46].

2.8. Electrospun polycarbonate fibers

Moon et al. [47] prepared electrospun polycarbonate (PC) fibers containing ochre at 2.5 wt.% and single-walled carbon nanotube at 1 wt.% (SWNT). The aim of using these fillers was to improve the dispersion state of SWNT in PC and to enhance flame retardancy. Then, they prepared thin films of these fibers using compression molding. PCFC test was used to evaluate the flame retardancy and some moderate improvement in flammability behavior was observed. For example, the value of HRC was around 464 J/g.K for the PC/SWNT/ochre composite electrospun fibers against 514 J/g.K for the electrospun PC fibers.

2.9. Electrospun ceramic fibers in polylactic acid

Besides all aforementioned strategies for improving flame retardancy, ceramic fibers can also be used as reinforcement in polymers. The composites resulted from the incorporation of electrospun fibers into a polymer matrix generally showed enhanced properties [48, 49]. Zhang et al. [50] studied the flame retardancy of PLA by incorporation of nickel oxide (NiO) electrospun fibers. First, the submicronic NiO fibers was prepared by electrospinning method. Then, PLA was melt blended with the NiO fibers (at 3 and 5 wt.%) and the nanosized carbon black (CB), in a micro compounder and the sheet samples were prepared using a hot press. They compared the performance of this composite with a similar composite prepared by commercially available NiO particles. LOI and cone calorimetry tests were performed to evaluate the flame retardancy performance of these samples. The highest LOI value (21%) was obtained from the combination of NiO electrospun fibers at 5 wt.% and CB at 3 wt.%, while the same formulation containing commercially available NiO particles showed a LOI value of 19.9. For the pure PLA samples, the value of LOI was 19. The best performance in terms of pHRR was also obtained from the same samples, containing NiO electrospun fibers at 5 wt.% and CB at 3 wt.%. The effect of the combination of these additives on flame retardancy was explained by their action to catalyze the carbonization of degradation products of PLA. The difference of behavior in the presence of NiO fibers and spherical particles was explained by a better quality char formed during combustion without cracks in the case of NiO fibers which can play its barrier role better in contrast to that of NiO particles. A better dispersion state of the NiO electrospun fibers was presented as the main reason for a better char quality.

2.10. Mechanical properties evaluation

It is certainly of vital importance to enhance the flame-retardant properties of polymer materials without deteriorating their mechanical properties [51]. However, almost fifty percent of the published reports suffer from the lack of information. Overall, incorporation of

flame-retardant additives into polymers unavoidably deteriorates mechanical strength and elongation of break as a consequence of poor filler-polymer interaction. Therefore, having flame retardancy of polymers without serious damage to mechanical properties would be enough. In the case of electrospinning process, researchers working on flame retardancy have taken two different strategies when mechanical properties are considered. Some researchers report the mechanical properties of electrospun fibers along with their flame-retardant properties, whereas some others report the mechanical properties of the resulting composite/mat/coating sample. Therefore, the lack of data or diversity of mechanical tests and samples makes it difficult to compare mechanical properties and/or to find a general pattern for variation of mechanical response of electrospun fibers. Moreover, claims about enhanced mechanical properties in some reports are plunged into methodical chaos and complexity. For instance, back to the last case addressed in the previous section, Zhang et al. [50] studied mechanical properties in detail. PLA electrospun fibers strengthened with submicronic NiO as metal oxide particles or fibers and CB nanoparticles, individually or combined with the aforementioned additives, experienced an irregular mechanical behavior. It is reported that the tensile strength of PLA sample containing 3 wt.% NiO nanoparticles+3 wt.% CB (52.7 ± 1.0 MPa) or PLA sample containing 5 wt.% NiO nanoparticles+3 wt.% CB (51.9 ± 0.2 MPa) are lower than neat electrospun PLA (56.0 ± 0.8 MPa). The corresponding nanocomposite samples in which NiO electrospun fibers are replaced by NiO nanoparticles increased tensile strengths from 56.2 ± 0.6 MPa to 58.0 ± 0.6 MPa, which are in the order of standard deviation. Nevertheless, Young's modulus has improved meaningfully even up to 50% with respect to the neat PLA electrospun fiber by hybridizing CB either with NiO nanoparticle or NiO electrospun fiber. As discussed earlier, authors properly served microscopic micrographs and discussed the improvements in both flame retardant and mechanical properties in terms of dispersion. Table 1 summarizes the mechanical properties of electrospun fibers and/or their

composites. It can be seen that the availability of mechanical properties is the matter of concern.

Table 1. Summary of the literature on flame retardant and mechanical properties of electrospun fibers or the resulting mat/coating/composites (*V: Voltage, **WD: Working Distance, ***ER: Ejection Rate, NR: Not Reported). Due to the diversity of mechanical tests and their application modes, tests and results (“+” when mechanical response increases with respect to the blank sample, “-“ for cases in which mechanical properties decreased after flame retardant incorporated, and ND (Not Deteriorated) for cases mechanical properties remained almost unchanged and) are briefly given and detailed information can be extracted from the assigned reference. It is worthy of mentioning that improvement or deterioration of mechanical properties are determined based on the results by the authors of the present review paper, not based on what has been conceded by the authors of the original papers. Moreover, we leave judgment about the ultimate shape of the sample to the respected reader, because in some cases fibers and composites have not been clearly specified in the methodology or results by the authors.

Electrospun fiber	Substrate	Additive	Loading percentage of additive	Electrospinning specification	Electrospun fiber diameter-thickness of sample	Mechanical properties of fibers/composites/mats/coatings	Application	[Ref.]
Polyamide 6 (PA6)	-	Fe-MMT (PA6/Fe-MMT) fibers have been sputter coated with Si)	4 wt. %	*V=14 kV **WD=10 cm ***ER=0.5 mL/h	100-300 nm- 100 nm	NR	NR	[24]
PA6	Cotton	Boric acid	0.05 wt. %	V= 5–15 kV WD=80 mm ER= 0.2-0.6 mL/h	120-400 nm- NR	NR	Fabric	[25]
PA6	-	MMT, Exolit® OP1312	5 wt. %: MMT 15 and 20 wt. %: Exolit	V=25 kV WD =8 cm ER=4 mL/min	100-200 nm-NR	NR	Protective clothing	[26]
PA6		MMT, CNT, Exolit® OP1312	3.75 and 1.875 wt. % MMT and CNT, 15 wt. %: Exolit	-	100-200 nm-NR	NR	Not specified	[27]
PA6	Cotton	MgO	5 wt. %	V=18 kV WD=18 cm ER=0.09 mL/h	170-240 nm- ~ 30 µm	NR	Protective clothing	[29]
PA6	Filter framework	Triphenyl phosphate (TPP)	-	V=15 kV WD=15 cm ER=0.06 mL/h	100-200 nm-NR	NR	Dust filtration	[30]
Poly(meta-phenylene isophthalamide) (PMIA)	Prepreg epoxy Carbon Fiber Reinforced panels	-	-	V=16-25 kV WD=15 cm ER=0.1-.04 mL/h	220 µm- 80 µm	Young’s modulus (+)	Coatings	[31]
PMIA	Wood	-	-	Spinbow® electrospinning- no more information is available	micrometric- 80 µm	Elastic modulus (+)	Coating	[32]
Polyamic acid (PAA) and polyimide (PI)	PA66	-	-	V=15 kV WD=12 cm	100-400 nm- 80-108 µm	NR	-	[13]
PI	-	-	-	V=15-25 kV WD=30 cm ER=0.8 mL/h		NR	Membrane	[33]
PI	-	-	-	V=15 kV WD =15 cm ER=0.45 mL/h	200-600 nm-35-38 µm	Young’s modulus (+) Tensile strength (+) Elongation at break (+)	Membrane	[35]
PI	-	-	-	V=21 kV WD =25 cm ER=1.5 mL/h	800 nm- 100 µm	Young’s modulus (+) Elongation at break (ND)	Membrane	[34]
Cellulose	-	Magnesium	Coating on	V=30 kV	500 nm to 1 µm-	NR	Coating	[36]

		hydroxide Mg(OH) ₂ nanoparticles	cellulose	WD=10 cm ER=60 µL/min	NR			
Cellulose	-	Silica	-	V=20 kV WD=15 cm ER=0.5 mL/h	143 ± 74 nm- NR	Fatigue residency (+) Compressive strength (+)	Aerogels	[37]
Polyacrylonitrile (PAN)	-	Ferric chloride (FeCl ₃)	1, 3 and 5 wt.% (in solution of 12 wt.% PAN And DMF)	V=14 kV WD=15 cm ER=0.4 mL/h	50-250 nm-NR	NR	Anode material for high performance lithium-ion batteries	[38]
PAN	-	Carbon nanotubes (CNT) - Ochre	CNT: 0.1 and 0.2 wt.% Ochre: 0.5, 1 and 2 wt.% (both filler in a solution of 10 wt.% PAN and DMF)	V=9-14 kV ER= 0.003- 0.004 mL/min	155-176 nm-NR	Young's modulus (-) Tensile strength (+) Elongation at break (+)	Interior of airplane, automobile, and protective textiles	[39]
Poly(m-phenylene isophthalamide) (PMIA)/PAN	-	CNT	CNT/ 0.3, 0.6, 0.9, and 1.2 wt.% (In a solution of PMIA/PAN (12 wt.%, w/w, 1/1))	V=20 kV WD=15 cm ER= 3 µL/min	1100-150nm (estimated from microscopy images) -30 µm	Young's modulus (+) Elongation at break (+) Stress at break (+)	Membrane	[40]
Polyetherimide- polyurethane (PEI-PU)	-	SiO ₂ coated on the PEI-PU fibers	-	V=30 kV WD=25 cm ER= 1 mL/h	544 nm- 35 µm	Tensile strength (+)	Membrane	[41]
PU-Polysulfonamide (PSA)	-	Barium titanate (BaTiO ₃)	5 wt.% in solution of 15 wt.% PU-PSA	V=25 kV WD=18 cm ER= 10 mL/min	196-248 nm-30 µm	Young's modulus (+) Tensile strength (+) Elongation at break (+)	Membrane	[42]
Poly(vinylidene fluoride– hexafluoropropylene) (PVDF-HFP)	-	TPP	60 wt.% in injected solution	V=15 kV WD=15 cm ER= 1.08 mL/h (core) and 0.54 mL/h (shell)	200-500 nm-30-35 µm	NR	Membrane	[18]
PVDF	polypropylene (PP) separator	Polyhedral oligomeric silsesquioxane (POSS)	5, 10 and 15 wt.%	V=15 and 18 kV WD=15 cm ER= 1.8 mL/h	600-1060 nm- 9 µm	Tensile strength (+) Elongation at break (+)	Membrane	[43]
Poly(vinylidene fluoride-co- chlorotrifluoroethylene) (PVDF-CTFE)	-	Sb ₂ O ₃	2 wt.%	V= 12 kV WD=25 cm ER= 33.6 mL/min	300-400 nm-42 µm	Young's modulus (+) Tensile strength (+) Elongation at break (+)	Membrane	[44]
PVDF	-	TPP/ Cellulose acetate (CA)	-	V= 18 kV WD=20 cm ER= 0.6 mL/h	430 nm for PVDF/CA/TPP fibers-NR	Young's modulus (ND) Tensile strength (+) Elongation at break (+)	Membrane	[45]
Melamine formaldehyde resin	-	Polyvinyl alcohol (PVA)	8 wt.%	V= 18.5 kV WD=16 cm	200-400 nm-30 µm	NR	Membrane	[46]
Polycarbonate	-	Ochre/SWCNT	2.5/1	V= 16 kV WD=14 cm ER=0.08 mL/min	1785-2215 nm-NR	Young's modulus (+) Elongation at break (+) Tensile strength (+)	-	[47]
Nickel oxide (NiO) in PLA	-	-	-	V= 25 kV WD=15 cm ER=0.08 mL/h	200-400 nm-NR	Young's modulus (+) Elastic modulus (+) Tensile strength (ND) Hardness (+)	Improvement of flame retardancy for PLA	[50]

3. Concluding remarks and future perspectives

Electrospinning process presents some emerging potential to be considered further in the field of flame retardancy. In this work, literature dealing with the use of electrospinning in developing flame-retardant materials were reviewed. The survey unveiled that the use of electrospinning in the field of flame retardancy is not widely adopted yet. Moreover, the conventional fire characterization methods have not been systematically used to evaluate flame retardancy characteristics of electrospun sample. In almost half of the reports the mechanical properties are not involved in evaluation. For other cases, the addition of a flame retardant into the polymer inevitably deteriorated the mechanical properties of electrospun fibers. Nevertheless, due to the nature of this method which produces fibers under stretching, results on mechanical properties are more promising compared to conventionally prepared sample like extrusion and injection molding. Thus, there are plenty of opportunities and challenges to fill the gap in the field of flame retardancy and electrospinning. We discussed the topic to prove that the potential of electrospinning could open some new doors to the preparation of flame-retardant materials in view of the fast developments highlighted in this review, **Figure 8**. Some of these possibilities are unique, such as the preparation of core/shell structures in which a flame retardant takes position in the core wrapped in a polymer shell, or preparation of nanofiber mats with integration of flame retardant inside the fibers provided by the of pores present between the nanofibers. Electrospinning also gives the possibility to prepare well-dispersed nanofillers inside a polymer, which can facilitate the incorporation of fibers into a given polymer and to guarantee an acceptable dispersion of flame retardant. Electrospun fibers and mats can play the role of heat shielding on the polymer surface. Moreover, electrospinning can be used to bring the flame-retardant characteristics to

miniature components when the incorporation of flame retardant via conventional methods, such as extrusion which is difficult or may degrade the other properties of materials.

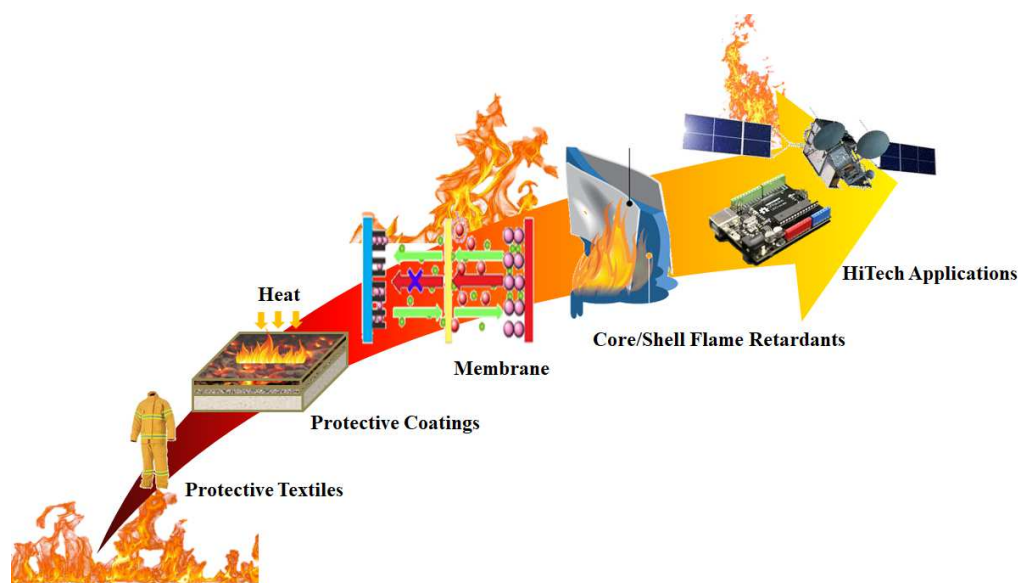


Figure 8. Schematic representation of present status and potential future applications of flame-retardant materials prepared via electrospinning.

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