

Polyester-supported Chitosan-Poly(vinylidene fluoride)-Inorganic Oxide-Nanoparticles Composites with Improved Flame Retardancy and Thermal Stability

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Electronic Supplementary Information

Abstract Polyester (PET) was pre-activated by atmospheric air plasma and coated by various inorganic oxide nanoparticles (MO_x) such as titanium dioxide (TiO_2), zinc oxide (ZnO), and silicon oxide (SiO_2), using poly(vinylidene fluoride) (PVDF) and chitosan (CT) as binders. The resulting PET-PVDF- MO_x -CT composites were thermally compressed and then characterized by scanning electron microscopy, Fourier infrared spectroscopy, thermal gravimetric analysis, and flame retardancy (FR) ability tests. PET modifications resulted in more thermally stable and less harmful composites with weaker hazardous gas release. This was explained in terms of structure compaction that blocks pyrolysis gas emissions. CT incorporation was found to reduce the material susceptibility to oxidation. This judicious procedure also allowed improving flame retardancy ability, by lengthening the combustion delay and slowing the flame propagation. Chitosan also turned out to contribute to a possible synergy with the other polymers present in the synthesized materials. These results provide valuable data that allow understanding the FR phenomena and envisaging low-cost high FR materials from biodegradable raw materials.

Keywords Polyester nonwovens; Composite; PVDF; Flame retardancy; Material oxides; Chitosan

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INTRODUCTION

Materials combustibility is a source of fire risks, and stringent safety measures are usually a major challenge to address.^[1–4] The latter can be tackled through severe rules when using combustible materials (CM) for building, textile manufacturing, or other purposes. Nevertheless, this often imposes increased exploitation costs. Another approach resides in using less combustible materials, which do not necessarily possess the required physico-chemical and rheological properties. A judicious strategy should gather both features through a suitable compromise between low combustibility and physical characteristic needed for the targeted purpose.

Many attempts to reduce the combustibility threshold of

nonwovens materials such as polyester (PET), polyimide, and cellulose through conventional modification procedures turned out to be quite unsatisfactory, resulting in insufficient flame-retardant ability. In this regard, PET has particularly focused interest owing to its interesting features.^[1–4] PET nonwovens have already been functionalized in order to induce its flame retardancy (FR) ability for a series of industrial applications through the incorporation of flame retardant additives.^[5,6] This is the main objective of the present research.

Up to now, inorganic oxides (MO_x)^[7] have been proved possessing FR ability *via* thermal dihydroxylation involving terminal hydroxyl groups conversion into water vapor.^[8,9] Besides, MO_x used as FR agents were also found to improve the mechanical performances of their host materials, to limit the release of toxic volatiles,^[10] and to exhibit many interesting mechanical, electrical, optical, and biological properties.^[11–13] Among these, zinc oxide (ZnO), titanium dioxide (TiO_2), and

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silicon dioxide (SiO_2)^[14,15] are widely investigated for potential uses as UV light-emitters, piezoelectric transducers, and varistors, as well as in transparent electronics, surface acoustic wave devices, and solar cells.^[16,17]

Polymer coating by MO-based FR agents has particularly attracted attention,^[18] given that thermal treatment was found to produce catalyzed char formation without smoke release. Intensive studies have been focused on developing advanced nanocomposites with improved surface properties by using MO_x .^[19] For instance, Fe_3O_4 was found to accelerate the carbonization of chlorinated poly(vinyl chloride) microfibers.^[20]

Poly(vinylidene fluoride) (PVDF) is an interesting polymer with appreciable mechanical, chemical, and ecofriendly features for much industrial and environmental application. The surface area, thermal stability, and impact resistance along with the mechanical, electrical, sensing, and adsorption properties of PVDF can be enhanced by MO_x incorporation.^[21,22] PVDF modification usually involves a mere MO_x incorporation and crosslinking procedure.^[23] Thus, PVDF is expected to act as a host matrix for MO_x and a binder that improves MO stabilization on PET fibers.

The use of natural polymers such as chitosan (CT) to reinforce MO stabilization was justified by the numerous advantages of CT over artificial materials.^[24,25] CT is known to display biodegradability, biocompatibility with plants, antimicrobial, non-toxicity, and fiber formation properties,^[26] and is still investigated for a series of potential applications in wastewater treatment, pulp and paper manufacturing, agriculture, and textile industry.^[27] Incorporation of CT for improving the stability of the targeted high FR modified PET fibers could be a judicious route to be explored. To the best of our know-

ledge, such an approach has not been tackled up to now.

In this research, polyester nonwoven fabric (PET) was employed as organic support for TiO_2 , ZnO , and SiO_2 in the presence of poly(vinylidene fluoride) (PVDF) as binder. Chitosan (CT) was employed as a natural polymer to reinforce the immobilization of PVDF- MO_x composite on PET fibers. The FR ability of the obtained PET-PVDF- MO_x -CT material was herein investigated. Different modified nonwovens were systematically characterized by field emission scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and thermogravimetric analysis (TGA). The surface compatibility and FR properties were examined in terms of materials structure and stability.

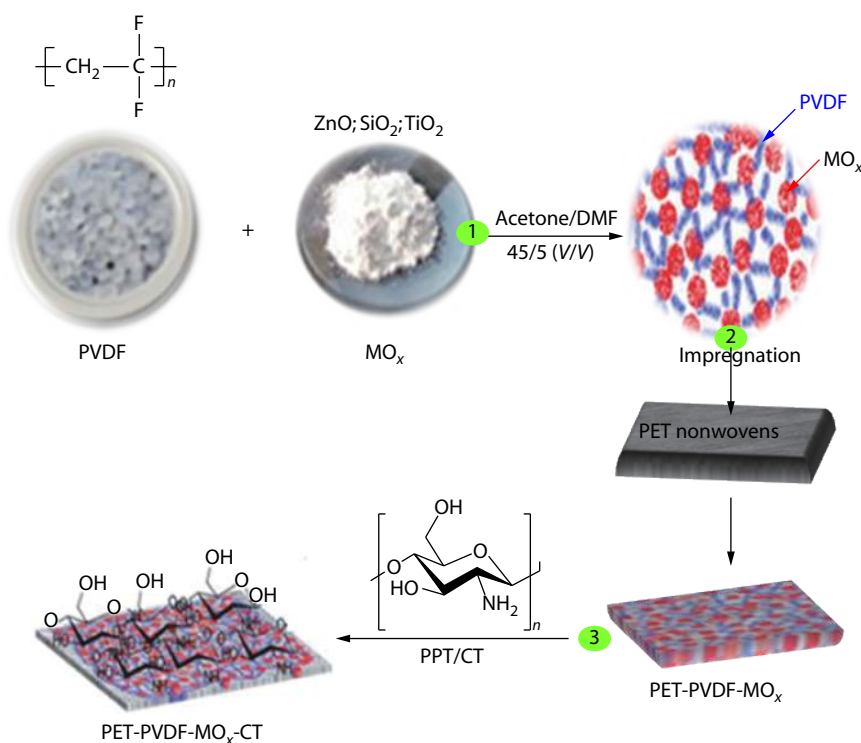
EXPERIMENTAL

Materials and Methods

Poly(vinylidene fluoride) (PVDF) and inorganic oxide nanoparticles ZnO and TiO_2 were purchased from Sigma-Aldrich. Polyester nonwovens (PET) with 0.9 μm fiber diameter were obtained from CETI (Table S1 in the electronic supplementary information, ESI). SiO_2 nanoparticles were synthesized by sol gel synthesis according to a procedure described in ESI. Acetone and *N,N*-dimethylformamide (DMF), ethanol, sodium triphosphate (PPT), distilled water, ammonia hydroxide (NH_4OH , NH_3 basis), sodium hydroxide (NaOH), and tetraethoxysilane (TEOS) were obtained and used as received.

Preparation and Design of Composite Materials

The preparation and design procedure for the material synthesis involved many successive steps (Scheme 1). PET was first cleaned from impurities and spinning oil present on the surface



Scheme 1 Schematic illustration of the synthesis procedure for PET-PVDF- MO_x -CT composites.

according our previously published work.^[28,29] Briefly, PET was activated by atmospheric air plasma to introduce both —OH and —COOH groups on the fiber surface according to specific operating conditions (Table S2 in ESI). In the meantime, three 3/5 (W/W) mixtures containing different inorganic oxides (*i.e.* TiO₂, ZnO, or SiO₂) and PVDF as reagents were completed with an acetone-DMF solution (45/5, V/V) as solvent. The resulting suspensions were stirred for 2 h at 50 °C, and PET nonwovens were then immersed for 2 h. The coated nonwovens were removed from the solution and dried at 50 °C for 24 h.

The resulting PET-PVDF-TiO₂, PET-PVDF-SiO₂, and PET-PVDF-ZnO composites were further immersed under mild stirring in a 3 g/L aqueous CT solution in the presence of sodium triphosphate (PPT). Each treated fabric was then dried (110 °C, 3 min) and cured (170 °C, 30 s) using a hot air dryer (Werner Mathis AG, Switzerland). The final PET-PVDF-MO_x-CT materials were then hot-pressed at 80 °C and 5 Pa for 5 min before further characterization and tests.

Characterizations

The starting and treated PET nonwovens were first characterized without any further preparation through Fourier transform IR spectroscopy (FTIR, Tensor 27 (Bruker) spectrometer with a ZnSe ATR crystal). The particle morphology and chemical composition were examined by scanning electron microscopy (SEM, JEOL JEM-ARM200F HR instrument with a field emission gun and probe aberration corrector) after previous metallization by a gold layer at 18 mA for 360 s with a Biorad E5200 device and Energy Dispersion of X-rays fluorescence (ED-XRF). The thermal stability was assessed by thermal gravimetric analysis (TGA) by means of a TG-DTA A6300R equipment.

Flame Retardancy Tests

Prior to flame retardancy (FR) tests, all materials were subjected to a hot press for 5 min between two heating metal plates at 120 °C and 50 × 10⁴ Pa into 125 mm × 125 mm × 3 mm pills. The flammability was evaluated on all samples by vertical flame

spread test method according to a French standard NF-G 07-113;1972.^[30] In this test, a sample was placed in the middle of the flame, and the size (cm²) of the burnt surface was measured. Data such as burning rate, ignition time, and time up to flame extinction allowed classifying the flame exposed surface during the FR tests according to Table S3 (in ESI).

RESULTS AND DISCUSSION

Morphology and Particle Dispersion

Preliminary SEM observations showed a random network of overlapped fibers and multiple connected pores with a fairly smooth surface for the starting PET material. Almost thorough PET surface coverage was achieved by PVDF/MO_x deposit. This must be due to PET-PVDF compatibility and affinity of both polymers towards MO_x. SEM images of PET-PVDF-TiO₂ showed a high amount of dispersed particles and of bulkier clusters of much smaller particles on the fiber surface. This quite heterogeneous particle dispersion appears to be a common feature for all composites, and can be explained in terms of stronger PVDF-TiO₂ interactions as compared to those occurring between both polymers. Chitosan (CT) incorporation was found to significantly influence such morphology, resulting in much more uniform particle dispersion for all three samples (Fig. 1).

Multi-spot ED-XRF analysis allowed detecting the presence of ZnO, silica, and titania in the grains of the corresponding PET-PVDF-ZnO-CT, PET-PVDF-SiO₂-CT, and PET-PVDF-TiO₂-CT samples, respectively (Fig. 2). This provides clear evidence of the beneficial role of CT in the PVDF-MO_x particle dispersion and stabilization on PET surface.

Structure and PET-coating Interactions

According to FTIR analysis (Fig. 3), the structure of the starting PET was commonly identified through IR bands in the region 1720–650 cm⁻¹, attributed to the stretching vibration of CH₂, C=O, and aromatic C=C bond, at 3100 cm⁻¹ assigned to CH

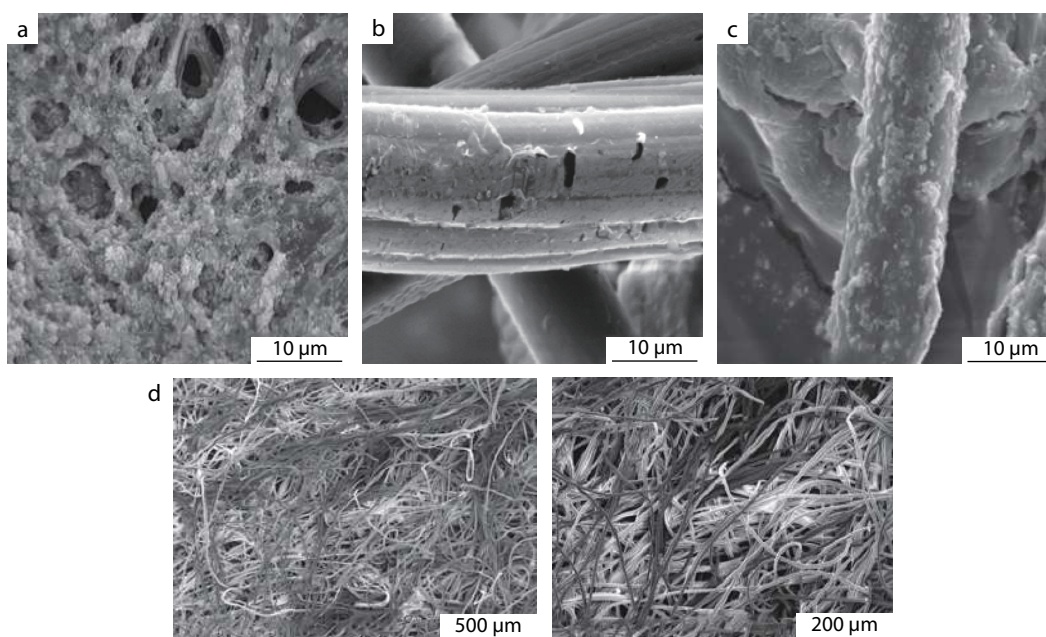


Fig. 1 SEM images of (a) PET-PVDF-TiO₂-CT, (b) PET-PVDF-SiO₂-CT, (c) PET-PVDF-ZnO-CT, and (d) PET-PVDF composites.

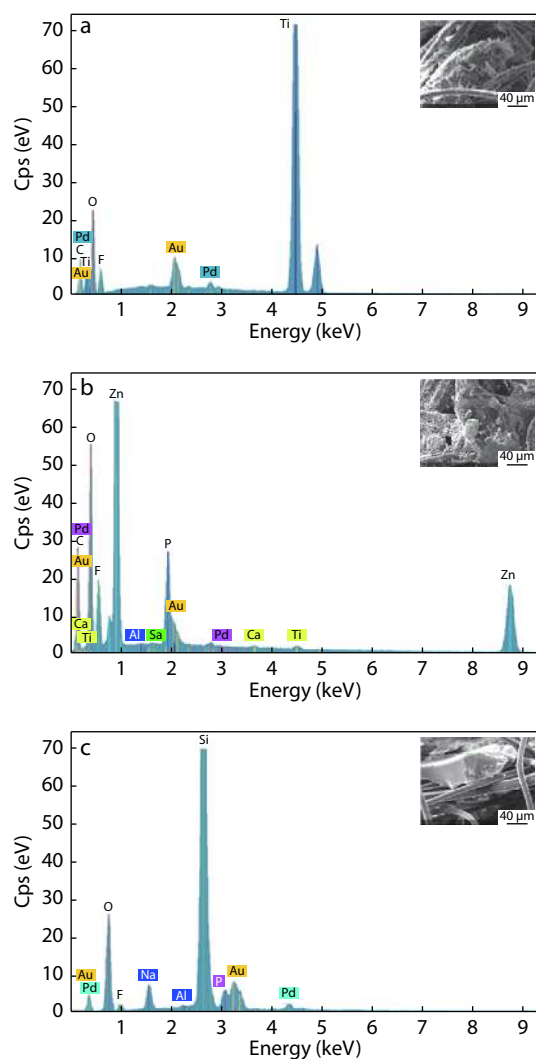


Fig. 2 ED-XRF spectra of (a) PET-PVDF-TiO₂-CT, (b) PET-PVDF-ZnO-CT, and (c) PET-PVDF-SiO₂-CT.

stretching vibration, and the broad ones around 3437 and 1456 cm⁻¹ related to OH stretching vibrations. PVDF incorporation generated a new band at 869 cm⁻¹ attributed to ν_{CF_2} vibration for amorphous PVDF.^[31,32] MO_x dispersion was confirmed by the appearance of new bands at 515 cm⁻¹ due to Zn—O stretching vibration, a special feature of pure ZnO.^[32] SiO₂ deposition was supported by the 1100 cm⁻¹ band broadening assigned to O—Si—O stretching vibration, while that of TiO₂ by the 700 cm⁻¹ band attributed to Ti—O bond stretching vibration.^[33]

Chitosan insertion induced a shift of the ν_{CF_2} bands from 869 cm⁻¹ to 875 cm⁻¹, indicating the interaction with PVDF.^[34] The 1625, 1420, and 1156 cm⁻¹ bands assigned to NH₂ group bend scissoring, OH bending in primary alcohols, and C—N stretching vibrations in chitosan indicate the presence of CT on the modified PET fibers.^[35] Both amino (—NH₂) and hydroxyl groups (—OH) of plasma-treated PET and chitosan are expected to interact through H-bridges with OH-functionalized species such as PET and MO_x. This should generate a crosslinked entanglement around PET fibers

(Scheme 2) that stabilizes PET coating.^[36,37]

Interestingly, PVDF incorporation induced the disappearance of 1108 cm⁻¹ band assigned to C—O—C stretching vibration in PVDF, providing clear evidence of the contribution of such groups in PET coating stabilization. Additional evidence in this regard arises from the marked intensity decrease noticed for all the above mentioned IR bands. The most plausible explanation should consist in the appearance of

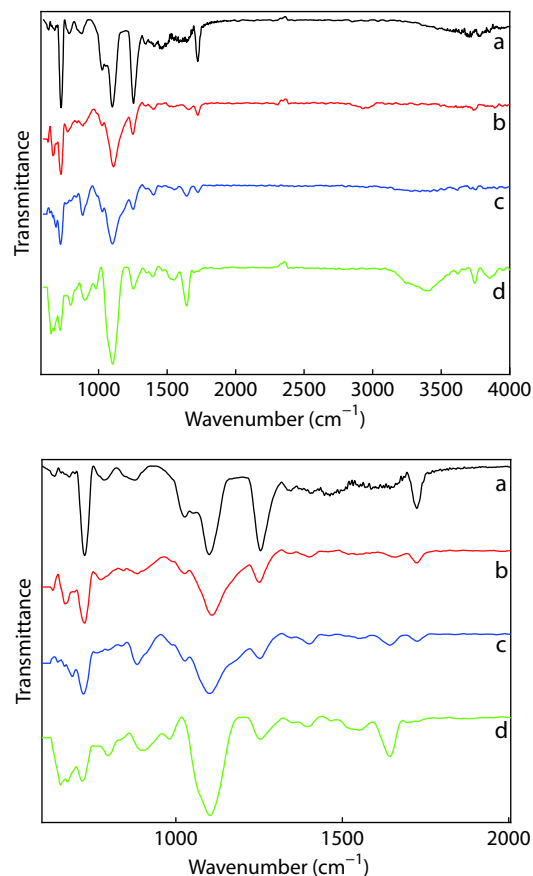
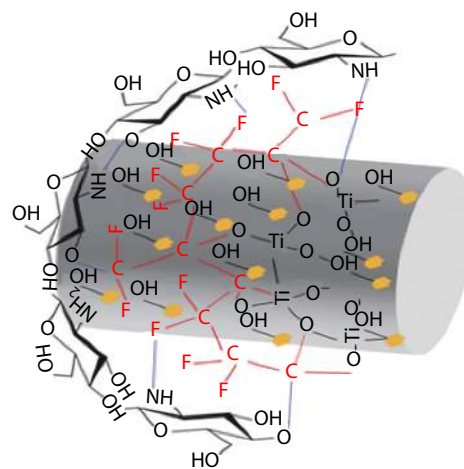


Fig. 3 FTIR spectra of (a) PET, (b) PET-PVDF-SiO₂-CT, (c) PET-PVDF-TiO₂-CT, and (d) PET-PVDF-ZnO-CT composites.



Scheme 2 Representation of the fiber structure after functionalization with PVDF/TiO₂/CT.

strong interactions that restrict bond vibrations and cause a coating structure compaction around PET fibers.

Thermal Stability Improvement

Thermogravimetric analysis under nitrogen stream and at 20 °C/min heating rate from 20 °C to 800 °C (Fig. 4 and Figs. S1 and S2 in ESI) revealed low hydrophilic character reflected by a barely detectable water loss at 70–140 °C. This result is of great importance, because it confirms the involvement of the hydrophilic amino and hydroxyl groups in PET coating stabilization. Such composites start decomposing at 180–200 °C via depolymerization of both PVDF and CT, which agrees with previous reports.^[29,38,39]

A quick overview shows two major thermal processes for PET, suggesting the occurrence of two decomposition steps. Considering 375 and 500 °C as common endsets of the first and second thermal degradation processes (Fig. S3 in ESI), a first mass loss of ca. 26 wt% was noticed for PET in the temperature range of 300–375 °C and another one of approximately 58 wt% between 355 and 500 °C (a).

Unlike with ZnO, the incorporation of the two other oxides (SiO₂ and TiO₂) and/or polymers resulted in a beneficial shift of the thermal degradation threshold from 274 °C towards higher temperatures (Table 1), indicating an improvement of the thermal stability. This was supported by the significant

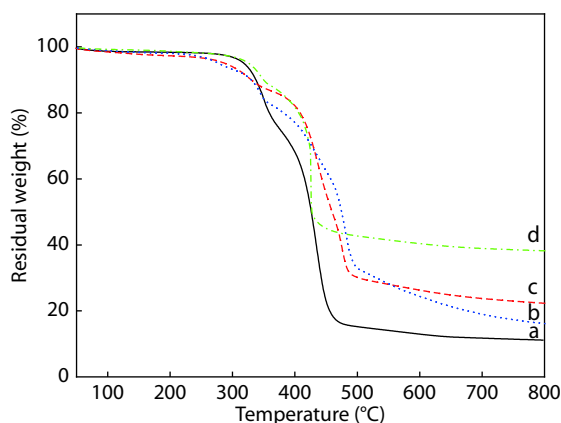


Fig. 4 TGA curves of (a) PET, (b) PET-PVDF-ZnO-CT, (c) PET-PVDF-SiO₂-CT, and (d) PET-PVDF-TiO₂-CT composites.

decreases in mass loss for PET-TiO₂ (c) and PET-ZnO (d) (Fig. S1 in ESI), much less pronounced after addition of PVDF (a), CT (b), or their mixture (d) on PET fibers (Fig. S2 in ESI).

The most plausible explanation resides in the higher thermal stability of MO_x as compared to that of polymers. The lower thermal stability induced by ZnO incorporation may involve oxide dehydroxylation and polymerization. These processes appear as being a specific feature of ZnO, as supported by the 14% mass loss for the first thermal decomposition, which was not noticed for SiO₂ and TiO₂. Here, a massive water loss from dihydroxylation is supposed to attenuate the second thermal degradation process, resulting in a much lower mass loss as supported by the highest amount of char residue (49%).

PET modifications revealed that the first weight loss depleted markedly down to 14 wt%–15 wt% for PET-PVDF-SiO₂-CT (c) and PET-PVDF-TiO₂-CT (d) and to a less extent of 19 wt%–20 wt% for PET-PVDF-ZnO-CT (b) (Table 1). This provides evidence of the decrease of hazardous gas release. Similar effect but not in the same sequence was noticed for the second mass loss, which decreased down to ca. 57 wt% for PET-PVDF-SiO₂-CT (c), 48 wt% for PET-PVDF-ZnO-CT (b), and 42 wt% for PET-PVDF-TiO₂-CT (d). This indicates that this second thermal decomposition also produced fewer volatile compounds. This must be attributed either to an increase in thermal stability and/or to a structure compaction that blocks gas emissions. Thus, PET-PVDF-TiO₂-CT appears as being the least harmful material when exposed to heating with the lowest mass losses for both degradation processes.

Flame Retardancy Ability Assessment

Preliminary flame retardancy (FR) tests showed that PET is a highly flammable, as well illustrated by a completely burned surface (Fig. 5a). Modified PET exhibited high FR ability, which appears to increase in the following sequence: PET-PVDF < PET-MO_x < PET-CT < PET-PVDF-MO_x < PET-PVDF-MO_x-CT. The smallest burnt surface was obtained for PET-PVDF-TiO₂-CT (Fig. 5d). The required time delay for triggering combustion increased from 30 s for PET to more than three times longer (92.13 s) for PET-PVDF-MO_x-CT (Table 2), providing evidence of the key role of PET modifications.

A deep analysis of the data presented in Table 2 showed

Table 1 TGA data of PET and modified counterparts.

Sample	Pyrolysis temperature (°C)		Mass loss (wt%)		Char residues (wt%)
	Onset	Endset	20–375 °C ^a	375–500 °C ^a	
PET	274	627	26	58	11.15
PET-PVDF	344	624	2–3	74	18.69
PET-CT	347	697	3–4	73	19.65
PET-PVDF-CT	345	651	27	59	19.08
PET-SiO ₂	349	765	0	54	14.44
PET-PVDF-SiO ₂	267	706	9	61	23.06
PET-ZnO	236	640	14	25–26	49.19
PET-PVDF-ZnO	222	696	12	46	32.61
PET-TiO ₂	325	742	0	30	40.92
PET-PVDF-TiO ₂	341	703	3	53	38.21
PET-PVDF-SiO ₂ -CT	242	771	14–15	57	23.13
PET-PVDF-ZnO-CT	294	718	19–20	48	16.09
PET-PVDF-TiO ₂ -CT	262	778	14–15	42	38.43

^a The temperatures 375 and 500 °C were taken as common endsets of the first and second thermal degradation processes only for comparison.

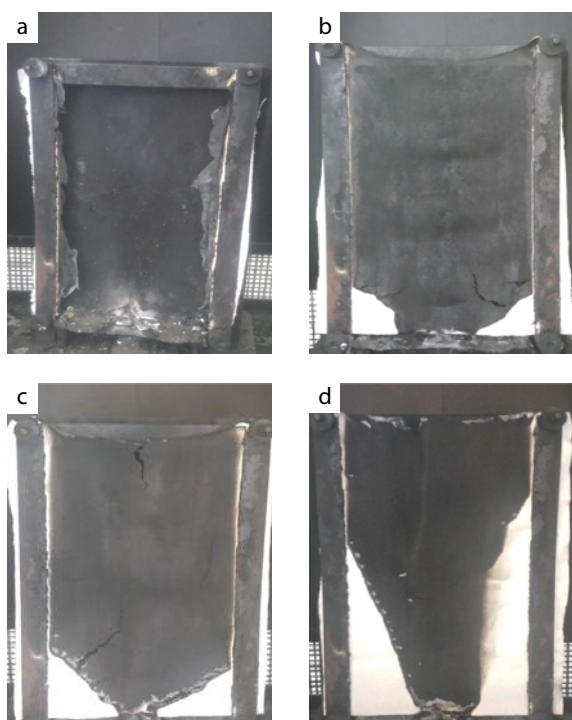


Fig. 5 Flame retardancy tests on (a) original PET, (b) PET-PVDF-SiO₂-CT, (c) PET-ZnO-CT, and (d) PET-PVDF-TiO₂-CT composites.

Table 2 Main features in flame retardancy test of PET and its modified counterparts.

Sample	Combustion time delay (s)	Linear propagation velocity (cm/s)
PET	25.00	1.20
PET-PVDF	50.81	0.59
PET-CT	58.13	0.51
PET-PVDF-CT	59.48	0.53
PET-ZnO	30.00	0.48
PET-PVDF-ZnO	30.00	0.39
PET-PVDF-ZnO-CT	77.45	0.38
PET-SiO ₂	60.10	0.49
PET-PVDF-SiO ₂	67.60	0.44
PET-PVDF-SiO ₂ -CT	72.03	0.40
PET-TiO ₂	61.65	0.48
PET-PVDF-TiO ₂	77.60	0.38
PET-PVDF-TiO ₂ -CT	92.13	0.32

that the combustion time delay (CTD) was at least doubled upon incorporation of PVDF (50.81 s), CT (58.13 s), or their mixture (59.48 s), the highest contribution being noticed for chitosan. These results are in agreement with the small burnt surface upon FR tests (Figs. S4b and S4c in ESI). The weakest CTD lengthening was registered upon ZnO and PVDF loadings (30 s), while the strongest improvements were obtained after CT insertion, namely 72.03 s for PET-PVDF-SiO₂-CT, 77.45 s for PET-PVDF-ZnO-CT, and 92.13 s for PET-PVDF-TiO₂-CT.

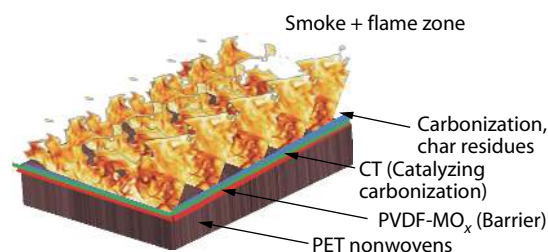
This must be associated with the relatively low flammability of CT, most likely due to its saccharides structure and higher number of oxygen atoms, which confers a lower ability to oxidation. This was in good concordance with the lowest linear propagation velocity (LPV) registered for almost all CT-

containing samples (0.51 cm/s for PET-CT, 0.38 cm/s for PET-PVDF-ZnO-CT, 0.40 cm/s for PET-PVDF-SiO₂-CT, and 0.32 cm/s for PET-PVDF-TiO₂-CT) as compared to their CT-free counterparts. The general tendency is that judicious successive incorporation of polymers, oxide insertion, and then CT loading produced increasingly improved FR ability expressed in terms of long CTD and low LPV, as observed for all PET-PVDF-MO_x-CT samples. Chitosan contribution is thereby fully demonstrated, but a possible CT/PVDF synergy should also be envisaged, for their combination may play a certain role in the attenuation of the composite flammability.^[40]

Interestingly, in the present work, smoke and gases released were employed to evaluate the fire toxicity of the composites. The curves of the amount of CO and CO₂ and their estimated yields are showed in Fig. S5 (in ESI). The decreased intensity peaks corresponding to CO and CO₂ are observed after the treatment, *i.e.* PVDF/CT/MO_x addition. As discussed in the following section, the transfer of degraded products can be blocked by these barriers. Then, the CO and CO₂ gases from the prepared composite are released. Here, the reduction in yield of these gases indicates the decrease in fire toxicity and may further lead to the decrease in CO₂ amount.

Effect of PET Functionalization on FR Ability

The low amount of char residue obtained with PET-PVDF and PET-CT (Table 1) is due to simultaneous polymer combustion and melting on the material surface. On such materials, the high flame temperature also favors pyrolysis in the inner melted phase, progressively producing an increasingly dense coke layer through carbonization that blocks oxygen diffusion inside the composite bulk (Scheme 3).



Scheme 3 Possible mechanisms of flame retardancy phenomena.

This phenomenon is supposed to be more pronounced after MO_x incorporation which should produce structure compaction, as previously stated. This is expected to be even more accentuated due to the continuous formation of carbon dioxide (CO₂), and subsequently a possible formation of carbonates and/or carbonate-like associations with terminal hydroxyls and lattice oxygen atoms belonging to the inorganic moiety. Consequently, the FR ability enhancement can be explained by the appearance of a protective-char layer hindering oxygen diffusion inside the composite. This barrier should also reduce the flammable mass reservoir and heat transfer, in agreement with previous work.^[41,42]

Here, the thermal compression procedure (TCP) employed under specific conditions (120 °C and 50 × 10⁴ Pa) for the prepared composite PET-PVDF-MO_x-CT is expected to reduce the void space between polymer fibers and MO_x particles up to total removal of entrapped air. Besides, TCP should also im-

prove direct contact between M-OH groups belonging to both MO_x and organic fibers, thereby improving the flame retardancy ability.

CONCLUSIONS

PET modifications by the incorporation of poly(vinylidene difluoride), chitosan, and oxides such as silica and titania allowed affording composite materials with higher thermal stability and lower harmfulness. This was reflected by a marked depletion of hazardous gas release. A structure compaction appeared to be a key factor in blocking pyrolysis gas emissions. Chitosan incorporation reduced the material flammability due to its saccharides structure that confers a lower ability to oxidation. Successive incorporation of polymers, metal oxides, and then CT turned out to be a judicious procedure for tailoring improved flame retardancy ability, affording material composites with long combustion delay and low linear flame propagation velocity. This beneficial effect of chitosan contribution appears to involve a possible synergy with the other polymers present in the synthesized materials.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-020-2336-7>.

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