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Thermal Degradation and Thermal Decomposition of Plasticized PVC Including POSS Additives for PVC Compounds: Mechanisms, Impact, and Performance of Standards

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ABSTRACT

Poly(vinyl chloride) has been a key polymeric material since its commercial production in 1931, demonstrating versatility across numerous industries due to its compatibility with various additives. PVC's inherent properties, flame retardance, durability, and recyclability make it ideal for building and construction, which accounts for a significant portion of its consumption in Europe. This paper reviews the thermal degradation, decomposition, and combustion behavior of plasticized PVC, focusing mainly on classical stabilization systems and novel nanostructured additives such as polyhedral oligomeric silsesquioxane (POSS), which offer promising advances in improving PVC's thermal stability and fire performance. The review highlights how these aspects, mainly when addressed with innovative additives, could shape the future of PVC compounds in high-performance applications, especially in the cable industry, where fire performance and regulatory compliance are increasingly important.

1 | Introduction

The aim of this work is to present an overview of PVC degradation and stabilization mechanisms, the relevant regulatory framework, and their implications for recyclability and sustainability, with particular attention to stabilizers that include nanostructured polyhedral oligomeric silsesquioxanes (POSS).

1.1 | PVC, Evolution, Uses, and Fire Performances

Polyvinylchloride (PVC) is a polymeric material used in many applications since 1931, when its commercial production began in Germany [1]. In the early stages of its introduction to the market, flexible PVC with different plasticizers was the synthetic replacement for natural rubber in various finished items. Then, PVC became strategic during World War II due to disruptions to the natural rubber supply chain following the Japanese invasion of Malaysia. After the war, flexible PVC was widely utilized in the cable industry and various other applications [1]. The benefit of PVC resin is its extreme versatility due to its compatibility with many additives, imparting specific characteristics needed by articles in particular applications, such as flexibility, impact strength, weatherability, flame retardance, and many others. That is why PVC resin, then as now, is used for producing a plethora of goods such as wires and cables, coated fabrics, pleather, floorings, profiles and sheets, pipes and fittings, hoses, tubes, gaskets, and rigid and flexible films for packaging [2–4].

Highlights

- Review of the thermal degradation, decomposition, and combustion behavior of PVC
- Review of the classical stabilization systems for PVC
- Review of novel nanostructured additives like polyhedral oligomeric silsesquioxane as PVC thermal stabilizers and flame retardants

When mixed with various additives, the resulting PVC/additive mixture is commonly called a "PVC compound." These additives serve multiple purposes: Some facilitate PVC processing, whereas others enhance the final properties of the products. Processing additives might include thermal stabilizers, plasticizers, processing aids, and lubricants that help to improve heat stability and flow characteristics during the manufacturing process. Performance-enhancing additives can include, among others, thermal and UV stabilizers, impact modifiers, processing aids, fillers, plasticizers, and pigments, which can improve the durability, strength, appearance, and resistance to environmental factors of the final PVC products. Other additives as fillers can be used not only to impart some properties but also to reduce the cost of the compound. PVC compounds are designed to perform well in a wide range of service temperatures (−50°C—125°C), having, among others, good mechanical properties, clarity, weatherability, and chemical resistance to oils, greases, and hydrocarbons. From a technological point of view, PVC compounds' advantages are related to the ease of being shaped into finished items across various production systems such as extrusion, calendering, injection, blow, dip and slush molding, coating, casting, and many others. PVC compounds can be flexible or rigid. Indeed, pure PVC is a rigid and stiff material, but when mixed with plasticizers, it becomes softer and more flexible. Rigid goods are called unplasticized PVC or PVC-U, and flexible plasticized PVC or PVC-P [5]. In 2021, Reagens statistical data [6] shows a consumption of 5100 kTon of PVC in the EU 27, including Norway, Switzerland, and the United Kingdom. PVC-U profiles (27%), rigid plates (2%), rigid films (6%), miscellaneous rigid and bottles (7%), and pipes and fittings (22%) accounted for 64% of the total consumption of PVC resins. Flexible tubes and profiles (3%), flexible film and sheets (6%), cables (6%), flooring (7%), coated fabrics (3%), and other flexible (12%) covered the remaining 36%. Most PVC-finished items, like floorings, pipes and fittings, wall coverings, window and technical profiles, and wires and cables, are used in building and construction (B&C). These items account for almost 70% of the average PVC compounded volume in the European Union (EU) [7–9]. It must be highlighted that certain plasticizers (phthalates) cannot be used in the manufacture of specific articles, such as, for example, toys (as of REACH Annex XVII entry 51) [10]. Additionally, PVC-P is excluded from cable manufacturing for B&C in high-risk locations where the highest additional classification for acidity is required [7].

The durability of PVC goods is a well-known and valuable characteristic. They have medium-long and extra-long lifespans, [11] with some items, pipes, and fittings, for example, commonly having an expected life of at least 100 years, [12] and window profiles, roofing membranes, and cables more than 20 years [11, 13]. Furthermore, PVC goods are easily recyclable and reshapable into new articles [14]. The combination of excellent durability, lower processing temperatures than those of alternative plastics, and the recyclability of PVC items leads to reduced consumption of non-renewable resources, with consequent reductions in environmental impacts such as CO_2 emissions and gross energy requirements (GER), and extraordinary advantages in terms of costs and sustainability [11, 15–16].

Another characteristic of PVC resin is its inherent flame-retardant properties, providing good fire performance for PVC products. Indeed, PVC has low ignitability, is easily extinguishable, has low flammability and flame spread, and does not sustain combustion nor contribute to flame propagation [14]. It releases heat more slowly than other polymers, does not generate flaming droplets, and produces low smoke if well formulated [17]. Adding specific additives like plasticizers or some impact modifiers worsens fire performance. Still, they can be quickly recovered using specific flame retardants and smoke suppressants, sometimes reaching even higher levels than the PVC resin, which has an LOI of 45% O_2 [14].

PVC-P compounds are employed for the production of a variety of articles detailed elsewhere, [18] and their fire performance, enhanced through the use of flame retardants and smoke suppressants, makes them the material of choice for a broad range of applications where fire safety is critical. These include furnishings, electrical and electronic equipment (EEE), and articles used in transportation, energy, and infrastructure (E&I). PVC-P is particularly prominent in B&C, where it is widely used in permanently and not installed products such as roofing membranes, wall coverings, flooring, and most significantly, wires and cables. PVC-P compounds are used for manufacturing jackets, bedding, and insulation for various kinds, including energy, communication, control, signal, on- and off-shore, automotive, shipboard, submarine, and railway. They can be used for producing insulation up to a maximum voltage (Um) of 7.2 kV, according to IEC 60502-2 [19].

Specifically, wire and cable PVC compounds accounted for 39.5% of the market share in 2019 versus other materials, and it has been estimated that they achieved 35.0%–40.0% in 2023 [7, 20]. In 2021, 460.000 k tons of PVC compound for cables were produced in the EU [7, 9], and around 500.000 k tons in 2022 [21]. About 51% are used in B&C, where mainly low-voltage cables for energy, control, and communication are used, 25% in electrical and electronic equipment (EEE), and 24% in special applications such as Automotive [9]. PVC compounds for cables dominate other materials mainly because of durability, insulation properties, better price, recyclability, and fire performance. However, between 2000 and 2023, the market share of PVC compounds for cables decreased from 65% in 2000 to 35%–40% in 2023 [7, 16, 17, 22]. This decline was mainly due to national and new regulations demanding halogen-free status and smoke acidity assessment [16, 18].

PVC goods release hydrogen chloride (HCl) when they burn in fire, which is why they are intrinsically flame-retardant, being HCl a chemical capable of reducing the flame's energy. In the EU, the additional classification for acidity was initially introduced for cables (and only for cables) in 2006 through an amendment of

Council Directive 89/106/EEC (Construction Product Directive or CPD), [23] replaced by Regulation n. 305/2011 (Construction Product Regulation or CPR), [10] in 2017. CPR restricted the use of PVC cables in specific locations, such as public buildings, based on the additional classification for acidity. The acidity measure is considered an ancillary parameter in fire science by most fire scientists [13, 14]. In fact, the heat release rate is "The Single Most Important Variable in Fire Hazard." [13, 14, 24–26] The European Commission explored even the possibility of introducing the additional classification for smoke toxicity in all B&C products in 2017 [27]. All these aspects forced intense research in developing low-smoke acidity PVC compounds for cables and exploring the mechanism of scavenging of HCl at high temperatures to achieve the best classification for acidity [28–33].

1.2 | PVC Additives and Nano-Structured Additives for PVC

PVC compounds are currently formulated using additives such as thermal and light stabilizers, lubricants, plasticizers, processing aids, impact modifiers, fillers, flame retardants, smoke suppressants, and pigments to achieve the expected performance in the finished items. Furthermore, additives should also be preferably colorless, odorless, compatible with the polymeric matrix, non-migrating, and cost-effective [34]. The fundamentals of standard PVC additives and formulations by application are widely detailed in the literature [2–4, 35].

Since the end of the 90s of the last century, polymer compounding has been disrupted by the emergence of polymer-based nanocomposites science, with nanostructured additives able to achieve submicrometric dispersion.

Nanoadditives are employed not merely as substitutes for conventional fillers, but also to access a range of properties that traditional additives cannot deliver or can be achieved only at the cost of significant mechanical loss. Furthermore, the high surface-to-volume ratio of nano-structured materials, combined with their ability to interact with the polymer matrix at the intermolecular level, yields properties inaccessible to conventionally sized fillers, regardless of loading (e.g., gas barrier performance). Similarly, nanoadditives can modify char formation in ways that no conventional additive can replicate at comparable loading levels. In flame conditions, the homogeneous distribution of catalytically active nanosites promotes condensed-phase char formation, thereby improving fire performance. The research on these materials as polymer additives is continuously updated and, despite a very relevant increase of publications in the last decades, do not currently reach in general the depth of scientific knowledge that standard additives and formulations have reached.

This is even more true for PVC, as while several matrices have been thoroughly investigated in scientific publications for nanoadditives, a systematic work [36–38] on PVC is still lacking, providing knowledge and guidelines for industrial applications. The first publication on nanofillers for cable compounds based on PVC and TPU was published in 2008 by Beyer from the Belgian cable company Eupen AG [39].

This article reviews the fundamental concepts of thermal degradation, decomposition, and combustion of PVC compounds, exploring the physical and chemical modifications that enhance long-term thermal stability, color retention, and flame retardancy. Understanding these degradation/decomposition mechanisms is essential for rationalizing the use of nanostructured additives in PVC matrices, as reviewed in Section 3.

2 | Degradation, Decomposition, and Combustion

2.1 | Thermal Degradation, Decomposition, and Combustion: The Differences

Sometimes, misunderstandings can arise in the literature when this topic is addressed. It is essential to underline that a polymer's thermal degradation is not its thermal decomposition, and thermal decomposition does not mean combustion. ISO 13943 [40] defines thermal decomposition as a "process whereby the action of heat or elevated temperature on an item causes changes to the chemical composition," and also states that thermal degradation "causes a deterioration of one or more properties": for example, physical, mechanical, or electrical features are evidently (and irreversibly) perturbed. Thermal decomposition is a further step in which the stabilizer package, unlike during the degradation step, cannot withstand the disintegration of the matrix and the release of gases, including fuels. Combustion, actually the reaction of organics with oxygen, starts when fuels, composed of organics from the thermal decomposition of a polymer and its additives, burn in the air. If the released energy is sufficient to produce a thermal feedback loop, it feeds the process, and the combustion becomes self-sustaining [41].

PVC exhibits peculiarities in thermal degradation, decomposition, and combustion due to chlorine in its backbone.

The thermal degradation of PVC resin begins at 100°C [42] through a reaction called zip-elimination, yielding polyene sequences and releasing HCl (vide infra). Thermal and mechanical degradation of PVC during processing is delayed by specific additives such as lubricants and thermal stabilizers. Without them, or if they are not performant enough, molten PVC degrades rapidly due to shear and temperature in the machinery during production. So far, the items degrade quickly during their useful life. Significantly, additives such as thermal stabilizers delay degradation and shift it to higher temperatures. Their stabilizing action can also delay or slow the photodegradation of items exposed to outdoor conditions, decreasing the concentration of chromophores that absorb photons with wavelengths above 290 nm and reducing HCl emission. This factor drives photooxidation of the item surface [43, 44].

Thermal decomposition can begin during processing and continue during the item's useful life as the stabilizer is consumed. It is explained in detail in Ref [45]. In summary, the thermal decomposition of PVC compounds begins above 220°C, a temperature at which, despite thermal stabilizers, even well-stabilized PVC compounds release HCl rapidly. At such temperatures, additives commonly found in PVC compounds can have different fates: they can decompose in the condensed phase, evaporate, or decompose in the gas phase.

Here, the stabilizer package cannot withstand the decomposition processes involving the PVC resin because of the rate of this degradation.

In this stage, PVC resin releases massive amounts of HCl, rapidly changing its chemical nature, initially forming polyene sequences and subsequently a crosslinked framework, eventually originating char. In the presence of air, the aromatic and aliphatic moieties are released into the gas phase, together with components from additive decomposition, and they burn. Then the combustion process begins [37, 46]. The thermal decomposition of PVC compounds can be studied through hyphenated techniques such as TGA-FTIR-GC/MS, and combustion can be explored through micro combustion calorimetry (MCC). Those techniques provide fundamental insights into the mechanism of PVC matrix decomposition and how additives can influence it. In essence, they can drive the selection of flame retardants and smoke suppressants (or design new ones) to reduce flammability and smoke production from PVC products [27, 47–49].

2.2 | Thermal Degradation of PVC: An Overview of the Mechanism

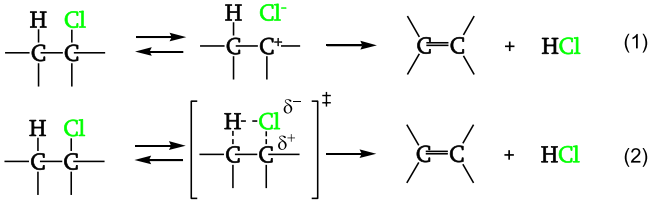
Thermal degradation begins at defects typically found in PVC resins, which are most prone to react as the temperature increases. These weak points are most likely tertiary and allylic chlorines, which are present in resin at low concentration and are formed during polymerization [38, 50–51]. From them, a localized degradation addressed as "cage reaction," the so-called self-accelerating zip-elimination, starts, bringing the growth and diffusion of the polyene sequences and the release of HCl. (Scheme 1).

Because of the formation of polyenic structures, mechanical changes and color variations follow the thermal degradation: the color of PVC compounds turns yellow, red, and, eventually, brown, and the polymer becomes brittle and fragile as thermal degradation continues [1–4]. Although the zip-elimination proceeds, secondary reactions form crosslinks within the PVC matrix, likely via an intermolecular Diels-Alder cyclization, and cause the emission of benzene from an intramolecular arrangement of conjugated polyene sequences.

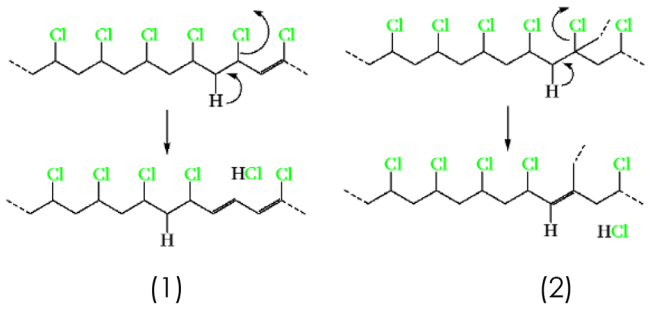
The mechanism of zip-elimination was a matter of debate for decades, involving radical [52–54], concerted six-center [55–63] and ionic/quasi-ionic [47, 64–67] mechanisms. The last one is the most convincing and the most thoroughly assessed mechanism; among the proofs, it has been shown that polar media significantly amplify the thermal degradation of PVC. This mechanism's validity is also supported by extensive research using low-molecular-weight PVC models. The proposed mechanism explains the catalytic effects of hydrogen chloride (HCl) or Lewis acids and highlights the crucial role in PVC degradation. It also makes clear, in remarkable detail, the chemistry behind some of the industry's unappealing issues, such as the thermal pinking of profiles or cables, which cannot be explained by Bacaloglu and Fish theory or radical-based models [68]. The complete description of the mechanism is detailed in Ref. [39]. The initiation from the defects in PVC resins is through the formation of an ion-pair (Scheme 1, ionic) or a four-center transition state (Scheme 2, quasi-ionic) [69].

In the ionic mechanism, Cl^- attacks the methylene hydrogens, and the expulsion of HCl follows. In the quasi-ionic mechanism, the HCl liberation occurs via a single-step concerted loss. The result is the creation of a new defect containing one additional conjugated double bond. Ionic initiation can explain the catalytic effect of HCl on dehydrochlorination and Lewis acids like $ZnCl_2$ [59, 70]. After initiation, the thermal degradation propagates, as in Scheme 3.

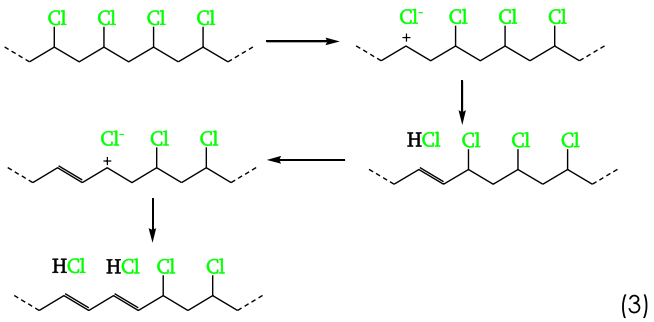
Once formed, one labile site can produce up to 30 double bonds, but the most common length ranges between 3 and 14 double bonds before it stops for thermodynamic reasons [38, 59, 71]. The formed conjugated polyene sequences remain inactive ("dead polyene sequences") until their concentration and that of HCl, are high enough to promote the formation of polyenyl cation diradicals. Here autocatalytic stage starts. These radicals (whose identity is unclear yet) attack the surrounding methylene hydrogens. Then, new radicals form in the PVC backbone, which rearranges fast into an allylic chloride structure through chlorine atom beta scission [62, 63]. Therefore, new allylic defects at other chain points or neighboring chains are generated, and degradation continues through the ionic mechanism [39]. This process causes



SCHEME 2 | (1) (ionic mechanism) and (2) (quasi-ionic mechanism)



SCHEME 1 | Zip-elimination from allylic (1) and tertiary chlorine (2).



SCHEME 3 | Zip-elimination and its propagation steps.

an autocatalytic degradation that, spreading throughout the matrix, leads to deterioration of the polymer's color and mechanical properties.

In addition, Lewis acids catalyze PVC degradation, promoting zip elimination and stimulating the crosslinking of polyene sequences through Diels-Alder reactions [59]. A Lewis Acid can be actual ($ZnCl_2$, $CdCl_2$, and others) or incipient (ZnO, Zn soaps, MoO_3); therefore, the additives within PVC compounds (as the ones described in the following section) can be the precursors of some strong Lewis acids and promote degradation itself. Some Lewis acids, such as $ZnCl_2$, are so effective at catalyzing PVC degradation that they can rapidly convert the matrix to a black, char-like mass. The phenomenon is called zinc burning.

The development of HCl and the presence or formation of Lewis acids should be considered when evaluating which substances can be used to stabilize the polymeric matrix.

2.3 | Heat Stabilizers: Primary and Co-Stabilizers: Types and Their Mechanism

Since PVC starts to degrade at about 100°C [38], to allow its processing as a thermoplastic material, it must be stabilized. The stabilization process slows down zip-elimination and, hence, the formation of conjugated polyene sequences and their consequent crosslinking. At the same time, it delays the color changes of the melt from yellow to red and eventually to brown, as well as the increase in its viscosity. The allylic chlorine displacement is the primary reaction in the PVC backbone for stabilizing PVC. The allylic chlorides are the weak points of the structure that lead to zip-elimination; they can be displaced by an entering group that forms a stronger bond, less prone to breaking. Substances that provide stabilization in this manner are known as primary stabilizers. These stabilizers can be further supported by the addition of other compounds, referred to as co-stabilizers or secondary stabilizers, which aid the stabilization process in several ways:

— Cooperating with the primary stabilizer in the displacement of allylic chlorine.

— Deactivating all species catalyzing the zip-elimination.

— Quenching all species that promote the formation of new defects.

— Shortening the polyene sequences through double bond addition.

In particular, primary stabilizers that prevent the formation of polyene sequences improve the color stability in processing. The species that cooperate with the primary stabilizers in the displacement reaction can improve the initial color and the color hold (Figure 1).

Primary stabilizers and species helping them in their activities have a "preventive" mechanism of action. The co-stabilizers, which deactivate the species catalyzing the zip elimination and promote the formation of new defects, can improve the long-term thermal stability by exerting a "suppressive" mechanism. Chemicals that shorten polyene sequences by adding double bonds provide better initial color and color hold and have a "curative" effect. Therefore, primary and secondary stabilizers are the fundamental ingredients of what we call thermal stabilizers. Zinc soaps and salts, and some organic substances, are today the main class of primary stabilizers. In contrast, other secondary stabilizers include metal soaps, beta-diketones, metal acetylacetonates, metal hydroxides, hydrotalcites, hydrocalumites, zeolites, organophosphites, epoxides, antioxidants, perchlorates, and polyols.

Industrially, additives used to promote stabilization are a blend of primary and co-stabilizers in appropriate proportions that enhance the initial color, color hold, and the prolonged thermal stability of PVC items. Hence, primary and co-stabilizers stand as crucial components of thermal stabilizers. When the stabilization package is combined with, among others, lubricants, processing aids, toner, and light stabilizers, the collective formulation is termed a "one pack" [72].

Today, various classes of stabilizers dominate the global market: [7].

- Solid Calcium Organic Stabilizers (COS), which include classical calcium zinc (CZS) with zinc soap/salt as the primary stabilizer and newer organic stabilizers (OS), where a zinc-free organic molecule displaces the allylic chlorine.
- Liquid Mix Metal Stabilizers (LMMS), featuring metal soaps/salts as primary stabilizers or an organic molecule blended with a range of liquid or solid co-stabilizers, all soluble in a solvent medium.

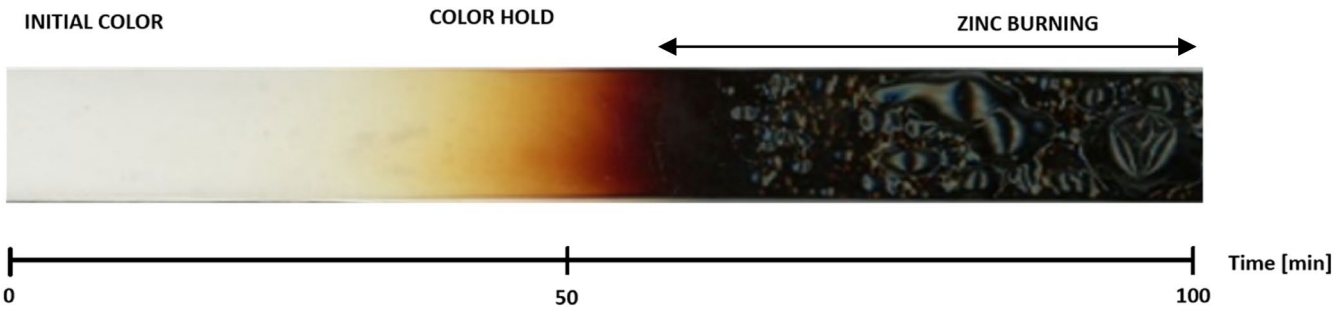


FIGURE 1 | Visualization of the point of initial color, color hold, and "zinc burning" decomposition. Mathis Oven at 180°C, moving at a speed of 0.5 cm/5 min (formulation: 100 parts of PVC K70, 0.8 parts Zeolite 4A, 0.4 parts Stearoyl benzoyl methane, 0.4 phr calcium stearate, 0.4 phr zinc stearate, 0.1 parts Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 2 parts Soybean oil, epoxidized).

- Lead-based stabilizers, relying on lead metal soaps or salts, cooperate with essential PbO salts as potent acid scavengers.
- Tin stabilizers, consisting of alkyltin molecules, impart notable characteristics to items in terms of thermal stability, clarity, initial color, and color retention.

These classes differ in the types of primary and co-stabilizers they use, each contributing distinct attributes to the processability and desired performance of the final product. Consequently, selecting an appropriate stabilizer class hinges on the specific requirements of the produced good, the manufacturing machinery employed, and custom practices. In particular, certain stabilizer classes have faced restrictions due to regulatory measures in certain countries or voluntary initiatives by PVC associations to enhance the safety of PVC products for both human health and the environment. In the EU market, thanks to the PVC industry's responsiveness to evolving regulations and proactive commitments, the phasing out of cadmium-based stabilizers and subsequently lead-based stabilizers has led to the emergence of COS as a prominent alternative. That happened between the mid-1990s and 2015 and shifted towards safer stabilizers in the EU. Today, this trend is continuing globally.

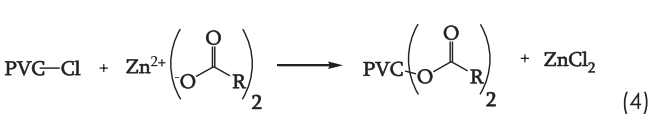
The allylic chlorine displacement and the "secondary" cooperation that helps stabilize the process can differ and depend on the specific stabilizer class. To better understand the interaction between primary and secondary stabilizers, the calcium-zinc stabilizer system, in which the primary stabilizers consist of zinc soaps/salts and the secondary stabilizers are calcium soaps/salts, can be considered.

The zinc compound can perform two labile chlorine displacements, as in Scheme 4, according to the Frye mechanism proposed in the 1960s [73, 74].

However, zinc soaps and salts can also act as HCl scavengers, another molecule capable of promoting zip elimination, through the reaction in Scheme 5.

As a byproduct, both reactions unfortunately yield $ZnCl_2$, a potent Lewis acid able to catalyze the zip elimination; therefore, it must be deactivated. The simplest method is to use calcium soaps or salts that act as shown in Scheme 6, capable of exchanging Zn with Ca in $ZnCl_2$, thereby restoring a Zn soap/salt and producing $CaCl_2$ as a byproduct, following the mechanism proposed for the first time by Onozuka and Asahina in 1967 [75].

Secondary stabilizers in calcium-zinc stabilizers also act as HCl scavengers, as in Scheme 7.



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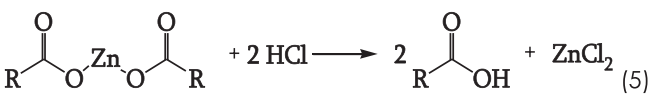
SCHEME 4 | Allylic substitution from zinc soaps/salts.



(5)

SCHEME 5 | Acid scavenging from zinc soaps/salts.

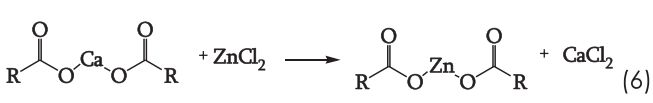
$CaCl_2$ is not a Lewis acid, and contrary to $ZnCl_2$, it does not promote zip elimination in the PVC matrix. Therefore, a mixture of zinc and calcium soaps or salts is the most straightforward calcium-zinc stabilizer system, in which zinc compounds, performing the allylic chloride displacement, improve the initial color and color hold, and calcium, one, deactivates $ZnCl_2$ and restores the zinc soap or salt, increasing the long-term thermal stability. In the same way, zinc compounds work with barium ones in barium-zinc stabilizers, whereas barium soaps or salts act as calcium compounds in calcium-zinc stabilizers. Cadmium salts or soaps act as primary stabilizers, and barium, lead, and calcium compounds were used to complete the stabilizer system. Cadmium stabilizers were phased out between the mid-1900s and 2007 through Council Directive 91/338/EEC [76], which applied to some specific articles, and Vinyl 2010, a voluntary commitment of the PVC Industry, which definitively banned their production and marketing in the EU [77]. Liquid and solid cadmium stabilizers were used in niche applications requiring extraordinary thermal stability and light resistance.

Lead soaps like neutral lead stearate (NLS) are the primary stabilizers in lead-based stabilizers. In contrast, dibasic lead stearate (DBLS), dibasic lead phosphite (DBLP), tri- and tetrabasic lead sulfate (TLS, TTLS), and dibasic lead phthalate (DBLPh) are the main co-stabilizers that help the primary stabilize. DBLP is a "multitasking" additive, an antioxidant, a light stabilizer, and an acid scavenger. Table 1 represents the lead stabilizers used in the EU until 2015.

The substances in Table 1 act as potent HCl scavengers, yielding $PbCl_2$, which is not a Lewis acid and is low in water solubility, neither promoting water uptake nor affecting the thermal stability of the PVC matrix. That is why this class of stabilizers imparts extremely high long-term thermal stability and remarkable insulation properties. In the EU, the RoHS Directive phased out lead-based stabilizers in electrical and electronic equipment (EEE) in 2006 [78], involving cables for internal wiring, cords, and plugs. Following that directive, the market itself substituted lead stabilizers in energy, automotive, and telecommunication cables. In 2015, lead stabilizers were phased out from the remaining PVC items, such as pipes and fittings, window and technical profiles, and foamed and compacted sheets, thanks to Vinyl 2010, a voluntary commitment of the PVC Industry [73].

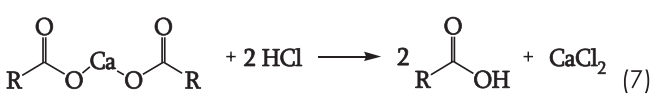
The organotin stabilizers are substances comprising mono or dialkyltin mercaptides or dialkyltin carboxylates.

These substances are all liquid (except for some maleates). Alkyltin mercaptide-based organo-tins are made up of a



(6)

SCHEME 6 | Exchange reaction between calcium and zinc soaps/salts, regenerating the primary stabilizer.



(7)

SCHEME 7 | Acid scavenging from calcium soaps/salts.

mixture of mono- and di-alkyltin mercaptides acting synergistically. The most widely used ones are thioglycolates. The monoalkyltin thioglycolates component (mono methyl, octyl, lauryl, or butyl) acts as a potent primary stabilizer since each molecule can displace up to two allylic chlorines, as in Scheme 8. The displacement reactions produce a substance (monoalkyltin chloride) that, although being a Lewis acid, is back-converted to monoalkyltin thioglycolates due to the high-speed exchange of the thioglycolate groups with the relevant dialkyl tin thioglycolate. Thus, the restored monoalkyltin thioglycolate continues its primary-stabilizing function [79, 80].

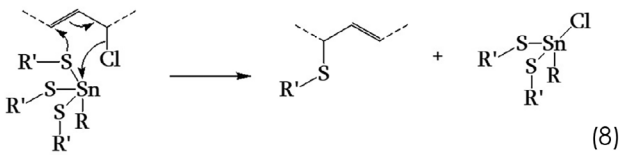
The displacement reactions produce a weak Lewis acid; [75, 76] therefore, they only slightly affect the thermal stability of the matrix, as COSs do. Moreover, their back-conversion to monoalkyltin thioglycolates by the relevant dialkyl tin thioglycolate prevents their Lewis acid effect even more. For this reason, they are stabilizers with a high intrinsic long-term thermal stability.

In addition, organotin compounds can deactivate species, catalyze the zip-elimination, act as an HCl scavenger through the reaction shown in Figure 2, and thereby boost long-term thermal stability.

Finally, shortening the polyene sequences, as in Schemes 9 and 10, they can repair the defect, saving the initial color and color hold.

TABLE 1 | Main lead stabilizers used in the EU before 2015.

Chemical name	Formula	Acronym
Basic lead carbonate	$2PbCO_3.\ Pb(OH)_2$	BLC
Tri basic lead sulphate	$3PbO.\ PbSO_4.\ H2O$	TBLS
Tetra basic lead sulphate	$4PbO.\ PbSO_4.\ H2O$	TTBLS
Di basic lead phosphite	$2PbO.\ PbHPO_3.\ 1/2\ H2O$	DBLP
Di basic lead stearate	$2PbO.\ Pb(COOC_{17}H_{35})_2$	DBLS
Neutral lead stearate	$Pb(COOC_{17}H_{35})_2$	NLS
Di basic lead phthalate	$2PbO.\ Pb(OOC)_2C_6H_4$	DBLPh



-R = -CH_3 (Methyl); -C_4H_9 (n-Butyl); -C_8H_{17} (n-Octyl); -$C_{12}H_{25}$ (Lauryl)

-R' = -CH_2-CO-O-Alkyl (I-Octyl or ethylhexyl thioglycolate); -CH_2-CH_2CO-O-Alkyl (β-mercapto propionate); -CH_2-CH_2O-CO-Alkyl (mercaptoethanoester or "reverse esters"); -Alkyl (alkilmercaptide)

SCHEME 8 | Allylic displacement by organotin stabilizers.

For these characteristics, organotin stabilizers impart unique and remarkable properties to many items, and the compounds stabilized with organotin can be processed in various production systems. Actually, there are also properties they do not impart to the compound; that is they do not exhibit any lubricating action. Therefore, when utilized, the formulations require the addition of internal and external lubricants and processing aids to facilitate processing in the article.

In the EU, organotin stabilizers are mainly used to produce PVC-U items such as packaging film (mainly blistering), foamed and compact sheets for indoor and outdoor use, including transparent corrugated sheets, and fittings for pressure pipelines, according to EN 1452-3 [81]. The main molecules used in the EU are di-octyl-tin ethyl-hexyl-mercapto-acetate (DOTE), mono-octyl tin ethyl-hexyl-mercapto-acetate (MOTE), mono-methyl tin ethyl-hexyl-mercapto-acetate (MMTE), and dimethyl tin ethyl-hexyl-mercapto-acetate (DMTE). The final products are octyl tin MOTE/DOTE and methyl tin MMTE/DMTE mixtures. To a lesser extent, the maleates and laurates are mainly used for outdoor applications. In the EU, organotin stabilizers have been under scrutiny by ECHA since 2022, when the authorization procedures started for DOTE and the reaction mass DOTE/MOTE [82] due to their toxicological profiles [9, 83]. Other substances in Figure 3 are under examination, including MMTE [85], DMTE, [86], and MOTE [87]. The last one appears to have a longer

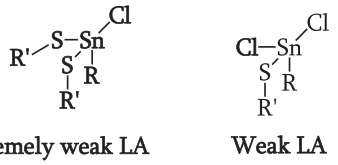
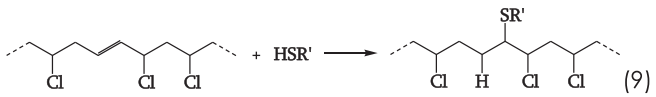
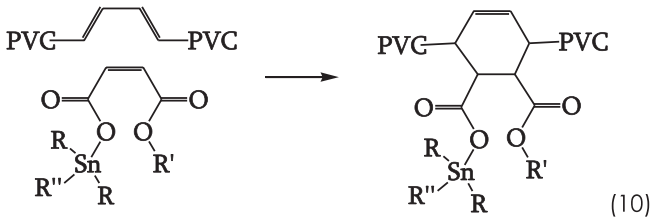


FIGURE 2 | Product forms allylic displacements.



SCHEME 9 | Addition reaction shortening the Polyene sequences.



SCHEME 10 | Addition reaction shortening the Polyene sequences.

lifespan due to its lower toxicological profile [7]. In any case, the risk is that the market could phase out all these substances before any regulatory action takes effect, regardless of whether they are more or less toxic or subject to regulatory measures. That has led to intense research on substituting tin stabilizers. The main alternatives are based on COS, but the high performance of organotin stabilizers in clarity, thermal stability, initial color, color hold, and processability has yet to be achieved. Failure to replace tin with COS stabilizers could lead to the penetration of other polymers, such as PO or PET, into markets where PVC is dominant.

In the U.S., organotins are the dominant stabilizers [6] They are predominantly used in various rigid PVC applications, including pipes, fittings, window profiles, siding, technical profiles, and sheets used in the building and construction industry. The primary organotin stabilizers utilized are methyltin, butyltin, and octyltin compounds, often in the form of mercaptides, carboxylates, and reverse esters.

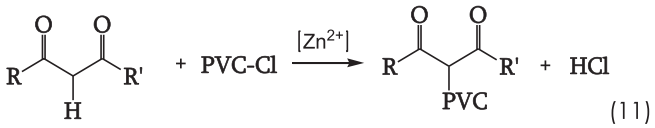
Methyltin stabilizers are known for their excellent performance in injection molding, complicated extrusion processes, and applications requiring high clarity, such as food packaging and medical uses. Butyltin stabilizers are widely used for various rigid PVC applications, including pipes, window profiles, and siding. In contrast, octyltin stabilizers, though less common, are also employed in specific applications that demand balanced stability and early color performance [6].

In the U.S., research and development on alternatives to organotin stabilizers are stalled due to several factors. These include the lack of regulatory action by authorities against organotin stabilizers, the reluctance of manufacturers to modify their facilities to handle solid stabilizers, the high costs of approving new stabilizers to meet specific standards, and the impact on formulation costs. However, it is noteworthy that in 2024, the first COS was listed in TR-02 Table 1 as a prequalified ingredient for the Plastic Pipes Institute (PPI) PVC Range Composition used to produce potable water pipes [88].

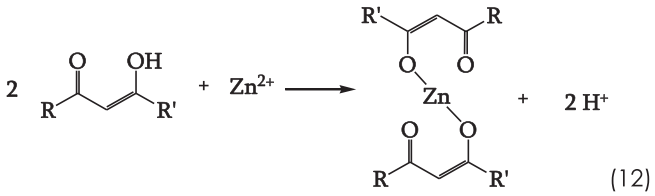
2.4 | Heat Stabilizers: Focus on COS. Secondary Stabilizers and Their Stabilization Mechanism

Calcium and zinc soaps and salts alone are not sufficiently performant to stabilize properly during processing and throughout the finished item's useful life. Therefore, additional substances are needed to impart the proper stability. Sometimes, the co-stabilizers have more than a mechanism of action, acting simultaneously as "preventive," "curative," and "suppressive." Some mechanisms can be predominant over subsidiary ones. The actual mechanism has not always been clarified [45].

Polyols such as pentaerythritol, sorbitol, and dipentaerithritol are currently used as co-stabilizers, [89] and some authors think that they act mainly as chelators of $ZnCl_2$ [90–95]. Other authors, on the other hand, believe that the predominant mechanism is an acid scavenging through an S_{N2} acid-catalyzed substitution of —OH groups by chlorine from HCl, whose efficiency would depend on the structure and position of the —OH in the molecule, where the primary hydroxyls are more prone to be substituted [96, 97]. In any case, both mechanisms suppress the



SCHEME 11 | Allylic displacement from beta-diketones.



SCHEME 12 | Chelation from beta-diketones.

species catalyzing the degradation of PVC, improving long-term thermal stability. It is worth noting that some polyols, such as mannitol, can caramelize [85] turning yellow. Some of these molecules are also prone to water uptake and, therefore, cannot be used in items that require good electrical insulation, such as cables [45].

Beta diketones and beta ketoesters, such as dibenzoylmethane, stearoylbenzoylmethane, metal acetylacetonates, dehydroacetic acid, and its salts, can act simultaneously through both preventive and suppressive mechanisms. They are thought to help zinc soaps and salts in the chlorine-displacement reaction, as shown in Scheme 11 [98–100].

Anyhow, they can also chelate $ZnCl_2$ as in Scheme 12 [101].

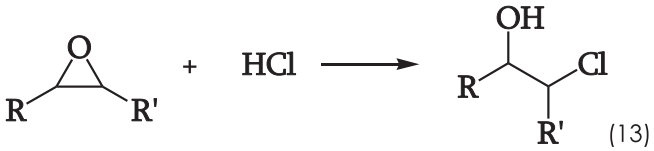
Therefore, they act on initial color and color hold, but also, to a lesser extent, on long-term thermal stability.

Epoxy compound co-stabilizers are epoxidized oils, such as soybean, castor, linseed, and sunflower. Less common co-stabilizers include epoxy resins, such as bisphenol A diglycidyl ether resins. The epoxy group is highly reactive with HCl, as shown in Scheme 13, and this reaction is well known and forms chlorhydrin. Therefore, it seems they act prevalently as acid scavengers, but some researchers also believe that they can deactivate $ZnCl_2$ with the mechanism mentioned in Ref. [102]. Both these phenomena are "suppressive" and increase long-term thermal stability.

Some other researchers also claim that the epoxy group can even replace the allylic chlorines in the backbone of the PVC chain in the presence of zinc, as in Scheme 14 [103–105].

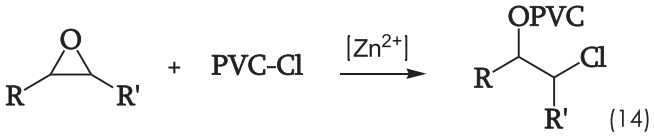
Commonly used epoxy compounds improve long-term thermal stability, and the "primary effect" of Scheme 14 appears to lack confirmation in everyday practice, as epoxy-based substances tend to affect the initial color of items profoundly. Therefore, the reaction in Scheme 13 is probably dominant.

Organic phosphites are another category of co-stabilizers in PVC. They are multipurpose additives with preventive, curative, and suppressive properties [106–109]. They boost long-term thermal stability by reacting with HCl, chelating $ZnCl_2$, and acting as hydroperoxide decomposers, deactivating the radical



(13)

SCHEME 13 | Acid scavenging from epoxides.



(14)

SCHEME 14 | Allylic displacement from epoxides.

species capable of creating new defects. They can even add double bonds and displace allylic chlorines, improving the initial and color hold. They can be liquid or solid and show this, and this is the main defect of this class of compounds: a tendency to hydrolyze (particularly the solid ones), which reduces their performance and leads to the production of byproducts that affect thermal stability, color, and volume resistivity [45, 110].

Phenolic antioxidants are the main antioxidants used in PVC. 2,6-di-tert-butyl-p-cresol, Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), and Octadecyl 3-(3,5-di-te rt-butyl-4-hydroxyphenyl)propionate are the most diffused. As proton donors, they suppress the radical species that generate new defects, thereby preventing the catastrophic propagation of diffused polyene sequences in the PVC matrix and the release of HCl. A detailed description of the used phenolic antioxidant can be found in Ref. [111].

Acid scavengers are probably one of the essential co-stabilizers. Designed to trap or react with HCl, zeolite 4A, hydrotalcites, hydrocalumites, metal oxides, and hydroxides are widely used to boost long-term thermal stability, especially in cable compound grades. Metal oxides and hydroxides are cheaper and commonly used in PVC [45]. Still, it must be highlighted that the products from the reaction with HCl are water-soluble and, hence, capable of impairing the insulation properties and the weatherability of finished articles. In particular, calcium and magnesium oxides and hydroxides are the most used.

Hydrotalcites and hydrocalumites are layered double hydroxides (LDH) designed to neutralize HCl as Cl^- through an acid–base reaction in their interlayers [107]. The hydrotalcites utilized in PVC comprise double-layered lamellar clays formed by brucite layers accommodating Al^{3+}. The positive charge within these layers is offset by a carbonate anion in the interlayer, which also accommodates two water molecules. The chemical formula of this Al/Mg hydrotalcite (HT) is typically represented as $Mg_4Al_2(OH)_{12}(CO_3)\cdot 3H_2O$. Other hydrotalcite forms employed in PVC may incorporate Zn, Mg, and Al in the layers and carbonate and water in the interlayer (HTZ). It is characterized by the chemical formula $Mg_3ZnAl_2(OH)_{12}(CO_3)\cdot 3H_2O$. While various hydrotalcite forms with different cations and interlayer anions have been developed in the past, the principal commercial forms of hydrotalcite for PVC today are HT and HTZ. Another notable subgroup within the LDHs family is hydrocalumite, which, in PVC applications, primarily includes hydrated calcium aluminate phosphates or carbonates. Historically, some of these compounds were commercially significant. The first example is $Ca_4Al_2(OH)_{12}HPO_3\cdot 3H_2O$ (Calcium Aluminum Hydroxide Phosphate, CAHP), and the second is $Ca_4Al_2(OH)_{12}CO_3\cdot 5H_2O$ (Calcium Aluminum Hydroxy Carbonate, CAHC) [112]. The scavenging mechanism of CAHP is similar to that of HT or HTZ, with CAHP being highly alkaline, exhibiting a pH of 10.5 [113]. Conversely, CAHC demonstrates higher hygroscopicity than HT or HTZ. Despite their initial commercial use, these compounds fell out of favor due to their above-mentioned disadvantages and higher production costs relative to cheaper acid scavengers. By 2021, the sole manufacturer of CAHP had ceased production, and CAHC production in the EU ended in 2016. Zeolites are crystalline aluminosilicates of AlO_4 and SiO_4 tetrahedra connected into three-dimensional frameworks. The presence of Al in the structure carries a negative charge, which is balanced by cations such as sodium or calcium. The structure features cages and pores of molecular dimensions that can adsorb gases such as HCl.

Chapter 3 will discuss Zeolites and LDHs (mainly hydrotalcites and hydrocalumites) built with various cations and ions as acid scavengers and flame retardants.

3 | Properties, the Role of Nanostructured Additive for PVC

3.1 | Introduction to Nanoadditives

As stated in the introduction, polymer-based nanocomposite science outcomes dramatically changed the polymeric materials approach. The use of nanostructured additives able to reach a dispersion at a submicrometric scale showed as a striking innovation, the possibility to achieve an unprecedented pool of mechanical and functional benefits due to the occurrence of interactions at the intermolecular/interfacial level [109].

By the perturbation of chain-chain and filler-chain forces and the filling of the polymer voids, nanoparticles originate a diffused and tough reinforcing effect with dramatic changes in several mechanical properties such as tensile strength and impact resistance, barrier effect to gas migration [114].

Furthermore, the homogeneous distribution of nanosized materials also highlighted relevant functional roles as the modification of the thermal behavior of the polymer, especially in flame conditions. In fact, due to the presence of evenly distributed catalytic active sites in the polymeric matrix, nanocomposites can show peculiar reaction pathways in flame conditions, resulting in an improved combustion behavior, particularly with char formation and reduced rate of heat release [115], due to physical effects [116] and condensed phase catalyzed mechanisms [117]. These manifold advantages given by polymer nanocomposites have often been observed at a low percentage of addition (i.e., from 0.3% wt. to 3% wt. in general) [118, 119], further promoting nanocomposites as effective and lightweight high-performance materials, but generally counterbalanced by the higher cost of nanoadditives with respect to conventional fillers.

In the literature, studies on polymer nanocomposites have generated a broad basic knowledge in the field of nanoscience and

nanotechnology, involving, for instance, the tailoring of proper nanostructured additives for a specific polymeric matrix and a target physical and functional role, the formulation of effective nanocomposites by achieving the distribution at nanoscale level, the technologies for the optimal dispersion of additives, the evaluation of the enhancement of the features and the modeling of the behavior [110].

Usually, a winning strategy combines molecular features of the nanoadditives (that need to match the chemical features of the hosting polymer) and the processing conditions to afford their distribution to maximize the interaction at the nanoscale level [110].

A fundamental discrimination of nanomaterials is related to the *number of nanosized dimensions* of the filler.

This produces three main categories of nanoadditives:

- 1D nanomaterials, which are materials with one nm-sized dimension, making these materials with a layered shape (i.e., lamellae)
- 2D nanomaterials, which are materials with two nm-sized dimensions, resulting in an elongated shape (i.e., tubes and fibers)
- 3D nanomaterials are materials with three nm-sized dimensions that identify nano-dimensional particles [114]

The physical form of nanomaterials can enhance the properties achieved through their chemistry. For example, various inorganic additives, such as metal oxides, hydroxides, chlorides, and carbonates, can affect the thermal decomposition of PVC, severely influencing the material's flame retardancy and smoke production. However, once they are in the form of nanoparticles or nanosheets, they can exploit a relevant chemical effect due to the high surface/volume ratio, often sided, for materials with a specific aspect ratio, such as layered materials or elongated nanostructures, with physical roles as barrier effect or surface ceramisation. A decrease in the temperature of the PVC dehydrochlorination step is noted at processing in the presence of chromium, iron, cobalt, copper, and molybdenum oxides. Aluminum, titanium, zirconium, cerium, and lead oxides do not change the temperature at the beginning of PVC dehydrochlorination, the first stage of the decomposition of PVC. In contrast, no effect was highlighted by the oxides in the second [120, 121].

3.2 | Layered Materials

Layered materials are 1 D nanomaterials interestingly employed in polymer composites due to their aspect ratio, providing a significant difference between one dimension (the thickness) and the other. In general, layered inorganic structures suitable for the application in polymers are listed in the Table 2.

3.2.1 | Natural and Synthetic Clays Employed in Polymer-Based Nanocomposites

Most employed for the cost, performance, and availability aspects in polymer nanocomposites are purified or modified naturally occurring clays, such as montmorillonites (MMT) and synthetic layered double hydroxides (LDH), often addressed as hydrotalcites (HTLc).

Smectite clays, the most used mineral additives, are aluminosilicate materials with a layered structure based on two tetrahedral aluminosilicate layers (T), with an octahedral layer based on di/trivalent hexa-coordinated ions (O) in between. For this reason, the structure of these clays is often identified as TOT and represented in Figure 3.

The repetition of TOT layers in the xy plane carries out to the formation of the lamellar structure of the clays, and their packing gives rise to the interlayer space. Clays originate from different classes of materials depending on the composition of the T and O layers. In fact, the O layer can be homogeneously composed of Mg^{2+} or Al^{3+}, or vicariances of mono, divalent, and trivalent cations, as well as the T layer, which can be composed of Si with possible substitution with Al.

The occurrence of vicariances causes the presence of unbalanced negative charges on the layers, which induces the presence of the so-called exchangeable cations residing in the interlayer space. The total amount of "negative charge" exploited by the clay is the cation exchange capacity (CEC), and it is expressed as milliequivalents of cations for 100 g of clay. The interlayer space has a variable thickness depending on both the charge of the lamellae and the cationic species hosted in this region. Depending on the scale of observation (multi-scale structure), different levels of structural organization are present in the saponite structure. The lamella is a primary superstructure formed by repeating TOT structure units in the xy plane for a hundred nanometers. The dimensional anisotropy of the layers and the presence of negative charges on the faces and positive on the edges lead to the absence of rigid spatial organization of the lamellae. Hence, the lamellae can be randomly disposed and may assume different orientations from each other. Due to the face-edge electrostatic interaction, the structure called "house of cards" is formed (Figure 4).

Organo-modification of clays by exchanging the cationic species (namely, inorganic cations due to the mineral nature of these materials) with organic positively charged molecules makes these materials more compatible with polymeric matrices.

The most used modifiers are organo-substituted ammonium or quaternary ammonium species. Many studies in the literature refer to Altana (ex Rockwood) or Southern Clay products commonly named Cloisite. Other products with the same or similar organomodifiers are produced by companies such as Laviosa and Nanocor. These materials are montmorillonites (MMT) with platelets approximately 200 nm long and 1 nm thick, and are employed in three main forms.

i. Cloisite Na^+, purified natural clay fully exchanged with Na^+ ions
ii. Cloisite30B, organo-modified clay modified with MT_2EtOH (methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium, tallow is 65% wt. C_{18}; 30% wt. C_{16}; 5% wt. C_{14} hydrocarbon chains), Figure 5 left.

TABLE 2 | Layered nanostructured materials that can be employed in polymer nanocomposites [122].

Smectite clays	Montmorillonite (MMT), bentonite (BT), nontronite, beidellite, volkonskoite, hectorite (HT), saponite, sepiolite, stevensite, sauconite, sobockite, svinfordite, kenyaite
Synthetic clays	For example hectorite, $MgO(SiO_2)_s(Al_2O_3)_a(AB)_b(H_2O)_x$, (where AB is a ion pair, namely NaF)
Layered silicic acids	Kanemite, makatite, octosilicate, magadiite, kenyaite, layered organo-silicates
Other clays	Micas, vermiculite, illite, ledikite, tubular attapulgite, and so forth
Mineral layered hydroxides	For example brucite: $Mg(OH)_2$, or gibbsite: $Al(OH)_3$
Layered double hydroxides (LDHs)	$[M^{þ2}_{(1-X)}M^{þ3}{}_X(OH)_2]^{Yþ}(A^{n-Y/n})\ mH_2O$, for example $Mg_6Al_{3-4}(OH)_{18-8}(CO_3)_{1-7}H_2O$; or $Zn_6Al_2(OH)_{16}CO_3\ nH_2O$
Layered alumino-phosphates	For example mineral ALPO (berlinite), $Al_4(PO_4)_3(OH)_3 \cdot 9H_2O$ (vantasselite), or from hydrothermal synthesis of H_3PO_4 þ $Al(OH)_3$ with structure-directing agents
$M^{þ4}$ phosphates or phosphonates	$M^{þ4}$ ¼ Ti, Zr, or Sn; for example a-form: $Zr(HPO_4) \cdot 2H_2O$; g-form: $ZrPO_4O_2P(OH)_2{\cdot}2H_2O$; l-form; $ZrPO_4XY$ (X and Y are anionic or neutral ligands), and so forth
Chlorides	$FeCl_3$, FeOCl, CdI_2, $CdCl_2$
Chalcogenides	TiS_2, MoS_2, MoS_3, $(PbS)_{1.18}(TiS_2)_2$
Cyanides	$Ni(CN)_2$
Oxides	$H_2Si_2O_5$, V_6O_{13}, $HTiNbO_5$, $Cr_{0.5}V_{0.5}S_2$, $W_{0.2}V_{2.8}O_7$, Cr_3O_8, $MoO_3(OH)_2$, V_2O_5, $VOPO_4$-$2H_2O$, $CaPO_4CH_3$-H_2O, $MnHAsO_4$-H_2O, $Ag_8Mo_{10}O_{33}$, and so forth
Others	Graphite, graphite oxide, boron nitride (BN), and so forth

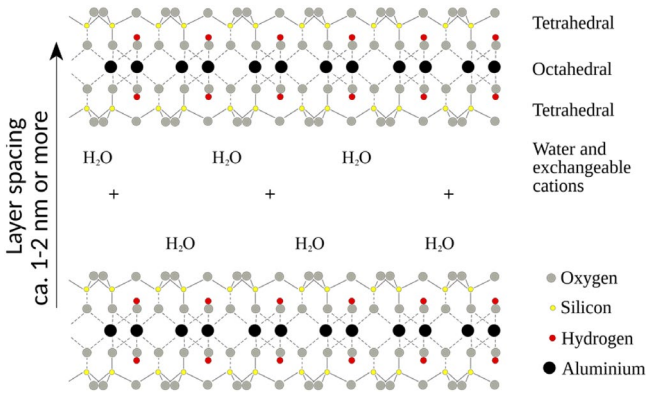


FIGURE 3 | TOT structure of a clay reported from Ref. [84].

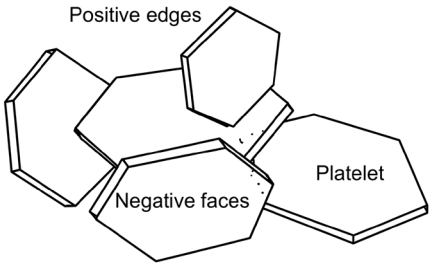


FIGURE 4 | House-of-cards structure of clays [123].

iii. Cloisite 93A, modified with M_2HT (methyl, dehydrogenated tallow ammonium, where hydrogenated tallow 65% wt. C_{18}; 30% wt. C_{16}; 5% wt. C_{14}), Figure 5 right [124].

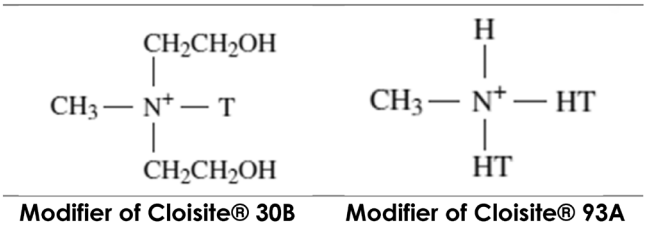


FIGURE 5 | Organo-modifiers of Cloisite clays [116].

Another clayey layered material deserving growing interest is Kaolinite. Kaolinite is a TO structure (hence based on a tetrahedral silicate layer and an octahedral Al-based layer) mainly contained in the mineral named kaolin. Compared with other fillers, this material finds application in areas demanding electrical resistivity and insulation.

Kaolinite, for its composition, has a low cationic exchange capacity from 5 to 15 meq/100 g, but much higher, up to about 100 meq/100 g due to the presence of other materials as impurities, compared with other clays; for example illite usually shows between 10 and 40, and smectites up to 150 meq/100 g. For halloysite, the CEC value varies significantly depending on structural variations, between 5 and 40 meq/100 g [125]. By contrast, the anion exchange capacity of kaolinite is greater than that for most clay minerals, due to the presence of replaceable (OH^-) ions on the outside of its structural layers [126].

Due to the low conductivity properties possessed by this layered material, composites show an improved electrical performance, making them suitable for the development of electronic components, electrical insulators, and circuit boards. Calcined kaolin

(namely, metakaolin, an amorphous material obtained by heating kaolin to temperatures between 650°C and 750°C) is generally used in wires and cable coverings as it provides excellent dielectric and water-resistant properties.

The tightness of the structure, given by the lack of hydrated cation-based interlayers due to the little isomorphic substitution present, can explain the occurrence of extreme particle failure and difficulties in separating kaolinite sheets [127]. To improve the compatibility and dispersion of kaolinite within the PVC matrix, additives are often modified. Common methods include the intercalation with Dimethyl sulfoxide (DMSO), which can be used to expand the interlayer spacing of kaolinite, facilitating better dispersion within the PVC [128].

Surface modification with stearic acid or chemical treatment with urea are also commonly employed. Stearic acid coating is claimed to improve the compatibility of kaolinite with the PVC matrix, whereas urea action is related to the increase in the surface area of kaolinite, enhancing its interaction with PVC [129].

3.2.2 | Layered Double Hydroxides (LDH)

Layered Double Hydroxides (LDHs) are inorganic anionic clays, both naturally occurring and synthetic. They are a unique class of layered materials that can exchange anions loosely retained in their structure. LDHs belong to the "Non-Silicate Oxides and Hydroxides" materials, but their features make them similar to the clay minerals. The similarities are their layered structure, the possibility of very different chemical composition (due to manifold possibilities of vicariance), the variable layer density of charges with the consequently ion-exchange capacity, the reactive interlayer space, the swelling in water, and their rheological properties. The unusually high anionic exchange capacity is the main difference from the clays, classifying them as "anionic clays" [130].

The general chemical formula is $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot mH_2O]$, where M^{II} and M^{III} are bivalent and trivalent cations, respectively, with x normally ranging from 0.1 to 0.33, octahedrally coordinated to six hydroxyl groups (Figure 6). The stability of LDH is correlated with the size of the cations in the layer. The minimum radius for bivalent metal is 0.06 nm, thus making LDH the typical structure of Mg^{2+}, Mn^{2+}, Ca^{2+} Co^{2+}, and Zn^{2+} hydroxides. Trivalent cations introduce a positive charge in the lamellar structure, compensated by the presence of organic or inorganic (CO_3^{2-}, Cl^-, NO_3^-) anions in the interlayer region ($[(A^{n-})_{x/n}\cdot mH_2O]$), in order to keep the electroneutrality. The stability of LDHs increases in the order $Mg^{2+} < Mn^{2+} < Co^{2+} < Zn^{2+}$ for divalent cations and $Al^{3+} < Fe^{3+}$ for trivalent cations. The thermal stability and the decomposition behavior are similar for all the LDHs since the stability is moderately affected by the nature of the interlayer anions, as reported in the literature [131]. The LDHs family is divided into subgroups, where hydrotalcite is the well-known representative of natural minerals.

Hydrotalcite is characterized by the brucite octahedral layer ($Mg(OH)_2$), in which some of the Mg^{2+} cations are replaced by Al^{3+}, with $Mg_6Al_2(OH)_{16}(CO_3)\cdot 4H_2O$ formula. The interlayer anion is usually the carbonate, exchangeable with different

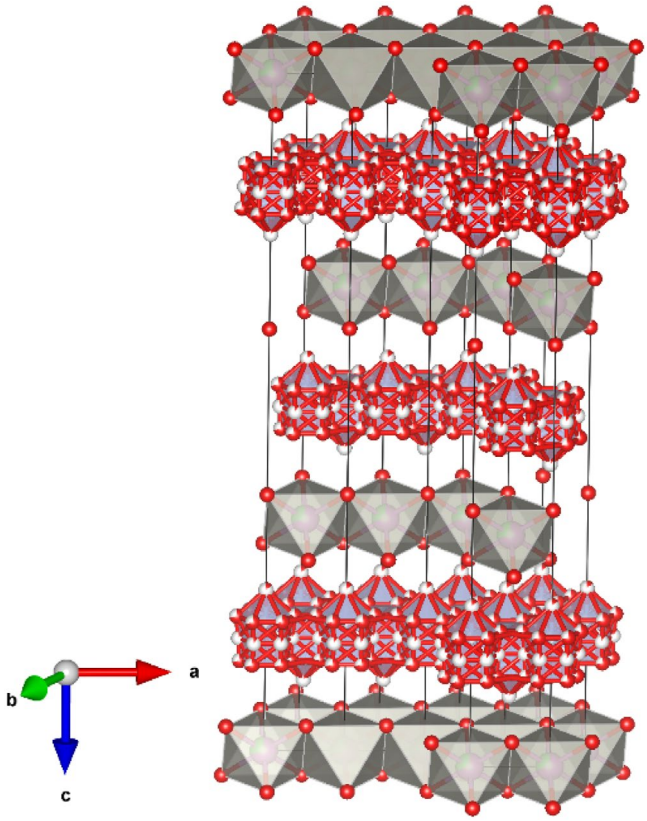


FIGURE 6 | LDH in nitrate form [119].

methods, such as nitrate, as in Figure 6, or others, such as Cl^-, SO_4^{2-}, and various organic carboxylates, sulfates, and sulfonates.

Another important subgroup of LDHs is the hydrocalumite, a hydrated calcium aluminate with a general formula: $[Ca_2M^{III}(OH)_6]^{x+}[(A^{n-})_{x/n}\cdot mH_2O]$ [132].

Hydrotalcite is present in nature, but in limited quantities and variable chemical compositions. To avoid such limitations, the synthetic way is a mandatory route. Large amounts of hydrotalcite can be easily synthesized with elementary and cheap methods, allowing the tailoring for several applications. The experimental conditions can influence the purity, dimensions, shape, surface area, and anionic exchange capacity (AEC) of the hydrotalcite, that is, the number of anionic equivalents that can be exchanged by 100 g of material (meq/100 g).

3.2.3 | Clay-Based PVC Nanocomposites

PVC clay-based nanocomposites are usually prepared to contain up to 5 phr of montmorillonite clay, treated with different organic intercalants. All cationic intercalants (ammonium and –onium quaternary salts, phosphonium and imidazolium salts) were found to accelerate the dehydrochlorination of PVC with a negative effect in the order phosphonium ion, imidazolium ion > alkyl ammonium ion > ethoxy/alkyl ammonium ion, whereas the non-ionic (i.e., glycol stearates) did not affect thermal degradation. On the other hand, some non-ionic intercalants showed poor dispersion.

Most organically modified montmorillonite (OMMTs) commonly reported in state-of-the-art literature are commercially available in the market. They contain alkyl ammonium salts as modifiers, and although they are effective in producing exfoliated nanocomposites for several different polymers, the catalytic effect on the dehydrochlorination of PVC makes most of them unsuitable as intercalants for PVC nanocomposites. However, some of them, such as tallow triethanol ammonium cation, are much less detrimental to PVC thermal stability because the thermal decomposition products from this tallow are less basic [133].

It was demonstrated that problems with thermal stability of these nanocomposites during compounding were largely eliminated by pre-treatment of the organoclay with plasticizer (dioctyl phthalate), which created a barrier between polymer and quaternary amine in the preparation by melt intercalation using a single screw extruder.

This approach ensures better dispersion of the organo-modified clay within the PVC matrix in the extrusion process, as confirmed by Transmission Electron Microscopy (TEM), Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), and X-Ray Diffraction (XRD) techniques [134].

Similar studies were carried out by Awad et al., preparing PVC-based nanocomposites using both hectorite- and bentonite-based organically-modified clays with tallow-triethanol-ammonium ion as a modifier. PVC organo-modified clay nanocomposites can be prepared using either the direct mix or the pregel methods. In the pregel method, the organo-modified clay is first incorporated into the plasticizer before being mixed with PVC. Actual nanocomposites, showing intercalation and exfoliation of the layered materials, were produced, and an increase in modulus of about 17% without a significant decrease in tensile strength or elongation at break was found., The classic HCl evolution method specific for PVC (EN 60811-405 [135])showed no clear effects of the clay on this parameter, but PVC composite smoke release is 50%–60% lowered for the nanoclay composites compared to appropriate control formulations. TGA shows that the composite's thermal decomposition is affected by nanoclays: the temperature at which a 10% mass loss occurs is slightly lower, but the temperature for a 50% mass loss is slightly higher compared to unfilled PVC. The authors also proved that well-dispersed nanoclays significantly decrease smoke production at low dosage levels (2%–3%). Smoke production starts earlier, for a longer time, but with lower intensity than the control. The authors suggest that nanoclays can interfere with the mechanism of smoke generation during burning. According to the current and more solid theory on smoke generation from PVC compound in combustion, the intramolecular reaction of polyene sequences from dehydrochlorination generates volatile aromatic species that burn and produce soot. This reaction competes with the intermolecular reaction that yields condensation products from polyene sequences [136–141].

The explanation of the effect of organo-modifiers and acceleration of the polymer decomposition in the initial step was addressed to the thermal destruction of ammonium via the Hoffman mechanism and the related basicity of the residue [142] with the formation of some H^+ and HCl, catalyzing the reaction of splitting off hydrogen chloride from the PVC chain. Therefore, the introduction of ammonium salt at the modification of the PVC matrix with MMT accelerates the process of polymer dehydrochlorination and diminishes the temperature at the beginning of its decomposition.

Other consistent results derive from the study by Peprnicek et al. [116], also featuring a novel way to prepare the composite by mixing PVC plasticizer with clay, both natural and organophilic, and the suspension in the form of a paste was then compounded with the other components. In the study, variable but, in general, worse results depending on the type of modifier (13–24 min vs. 19–29 for neat PVC) were obtained on the thermal stability (congo red test) [131]. This decrease is addressed to the thermal decomposition of the quaternary ammonium salts used as modifiers that make acid environments under elevated temperatures, further facilitating PVC decomposition [116].

A similar method was used to preexfoliate clays in a hot diisodecylphthalate (DIDP)/epoxidized soybean oil (ESO) mixture. Then, the resin, thermal stabilizer, calcium carbonate, stearic acid, and, according to the experiments, metallic oxides were mixed at room temperature, and after they were subjected to shear up to 80°C, DIDP/ESO exfoliated clay was added. An intercalated/partially exfoliated microstructure was found. Combustion and smoke-release properties revealed that the metallic oxides significantly affected the combustion and smoke-suppression properties, reducing the absolute quantities of heat rate and smoke release. The presence of organoclays only discretely affected these properties. The results are consistent with the role of metal oxides in anticipating dehydrochlorination, reductive coupling, and benzene suppression, which resulted from the presence of copper, molybdenum, and zinc metals [143].

Beyer also showed that the flame behavior of PVC-containing clays might be related to roles provided by the layered structure. He observed that peak heat release reduction is lower for plasticized PVC composites containing modified montmorillonite than neats PVC. One possible explanation is that the char of the modified montmorillonite sample is less cracked. Though organoclays initiate accelerated HCl release from PVC, resulting in unwanted color changes of the compounds. He proposed a simple method to measure the basic character of the organoclays simply by pH measurement of organoclay suspensions to rank organoclays to be used in PVC with low HCl release and low coloring [144].

The thermal behavior of PVC/nanoclay composites was studied with X-ray photoelectron spectroscopy (XPS) by Du et al. [145], both with and without plasticizer dioctylphthalate (DOP). Upon heating, approximately 50% of the chlorine remains at 230°C, and 8% remains at 460°C. Nanocomposites that contain 2% and 30% clay, PVC-2-0 and PVC-30-0, show a higher resistance to thermal degradation. The presence of the clay stabilizes the allylic species, which are formed during the degradation, and leads to an enhanced stability for PVC relative to that in the absence of the clay. XPS can show the variation of the amounts of covalent vs. ionic components of Cl for the nanocomposites. All the chlorine is covalent up to about 200°C, when the covalent component begins to decrease and the ionic (actually thought as allylic chlorine) increases. This change occurs for both virgin PVC and the nanocomposites, but more covalent chlorine

is converted to ionic in the presence of clay than in its absence, and the amount of clay, whether 2% or 30%, has no effect on the course of the reaction. The presence of the clay enhances the formation of this allylic chlorine, which yields more defects and, therefore, the PVC degrades faster. Clay's role seems to act as a cross-linker, as 30% wt. of clay gives an extent of crosslinking at 460°C of 52%, 32% when 2% wt. is present, and 24% for virgin PVC. The greater the amount of clay, the earlier the crosslinking manifested. The presence of clay in combination with DOP has an enormous effect on the chlorine release. In system with 2% wt of clay and 35% wt. of DOP, clay particles may act as physical crosslinking sites and stabilize the dimensional changes (the polymer is less swollen) and lower the rate at which DOP can migrate to the surface, leading to a decreased surface enrichment of chlorine, In the presence of clay, covalent chlorine is more easily lost. The allylic chlorine concentration is higher in the clay-containing system than in virgin PVC. Thus, the presence of the clay enhances the resistance to thermal decomposition by delaying the loss of the allylic species [141].

Combining clays and plasticizers was applied to different layered materials with different interlayer compositions. Poly (vinyl chloride) (PVC) and dioctyl phthalate (DOP) were mixed with 5 and 10 wt % of Cloisite Na^+, Cloisite 30B, or Cloisite 93A. Adding 5 wt % of nanoclay to PVC increased its stability to the thermal decomposition for Cloisite Na^+ < Cloisite 93A < Cloisite 30B. The authors claimed that the organic modifier for 30B and 93A could lower the surface energy of the silicate layers and enhance the miscibility between the silicate layers and the polymer matrix. The tensile strength, elongation (%), and Young's modulus were considerably enhanced upon increasing the clay content to 5 wt % in the Cloisite Na + <Cloisite 93A < Cloisite 30B sequence [146].

Recent studies dealt with Na MMT treated with solvents to make it compatible with PVC using tributyl citrate (TBC). TBC modifier was extracted from the OMMT and was dispersed in the PVC/DINP matrix.

The compatibility between TBC and DINP is much better than between TBC and MMT, and during the melt processing of DINP plasticized PVC and TBC-modified MMT, the TBC leaves the MMT, which then reaggregates. When TBC-modified MMT in PVC plasticized with TBC instead of DINP was used, good performance was obtained (a significant increase in the E-modulus and a significant decrease in the oxygen permeability) as regions of intercalated and exfoliated nanostructures were obtained. In the achievement of a nanocomposite based on plasticized PVC, both the organo-modification of the MMT and the formulation of the matrix require careful consideration for this matrix [147].

Recent results on the role of plasticizers can be found in Bohn et al. [148]. Here, the effects of different plasticizers as dioctyl adipate (DOA), dioctyl phthalate (DOP), and a green plasticizer (as it can be derived from renewable resources), such as poly-E-caprolactone (PCL), and mixture methods on clay dispersion Cloisite 30B, a clay modified with MT_2EtOH (methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium) in PVC as well as a dispersion with sonication and mechanical mixture were studied. Pre-dispersion decreased the clay agglomerates size, and some intercalated/exfoliated regions were also found. Using sonication methods for PVC/DOP resulted in a further increase of 10% in Young's modulus, whereas for PVC/PCL led to a decrease in Young's modulus of 8%. Furthermore, in the case of PVC/DOA, the addition of clays both without and using predispersion resulted in a decrease in the mechanical features.

Interesting perspectives on the functional roles of nanoadditives were provided by Yin et al. [149]. PVC was added with anionic-surfactant-modified lanthanum organic montmorillonite, obtaining exfoliated nanocomposites. The effects of the La-organoclay on the mechanical properties, flame retardancy, and smoke suppression of PVC were studied. The incorporation of the La-OMMTs enhanced the mechanical properties of the nanocomposites. Cone calorimetry and gas chromatography–mass spectrometry (GC–MS) analyses indicated that incorporating the La-OMMTs enhanced the flame retardancy and smoke suppression of the PVC nanocomposites. Overall, La-OMMT/PVC nanocomposites achieved higher mechanical properties, flame retardancy, and smoke suppression. GC–MS revealed fewer aromatic compounds (benzene and toluene) in the gas phase at 550°C, confirming that intermolecular reactions of polyene sequences are more probable. This results in less smoke production and more consistent char formation. The authors attribute this to the replacement of allylic chlorine with La-OMMT, whose hindrance impedes intramolecular reactions that produce aromatic fuels and smoke. However, cyclizations producing aromatic fuels seem to happen at higher temperatures.

These results were confirmed in another paper. Lanthanum organic montmorillonites (La-OMMTs) were obtained from Na-MMT with anionic surfactants and lanthanum chloride and used with polyvinyl chloride (PVC) at 3% wt. From TGA/DTG, La-OMMTs could significantly enhance the resistance to the thermal decomposition of PVC. The onset decomposition temperature increased to 132.4°C, more than the reference materials [150].

Another interesting solution to avoid harmful effects due to common organo-modification with ammonium salts is the covalent organic functionalization by silanizing sodium and organo-modified clay. However, even after the incorporation of reinforcing clay into the PVC matrix, many complications remain, such as decolorization during its melt compounding process, attributed to its unsolved thermal instability [151, 152]. The partial effectiveness in the reduction of the degradation of the polymer promoted by the clay can be related to different aspects. Actually, the silanisation is based on spray technology, and it is applied to the filler powder, whose aggregation state exposes only the outer-layered particles. Once dispersed in the polymer, the platelet dispersion allows a relevant increase in the interfacial interactions, involving the inner surface of the platelets, to be exposed. The surface of the clay, containing several active sites for Brönsted acidic sites or redox impurities, can promote a solid-state catalysis able to favor the polymer degradation.

3.2.4 | LDH-Based PVC Nanocomposites

Layered double hydroxides (LDH) can be considered remarkable additives for increasing the thermal stability of PVC and were

studied intensively to understand the mechanistic aspects of HCl scavenging and how to improve long-term thermal stability with different cations in the layers and anions in the interlayer [153, 154]. Particularly, Refs [140, 155] claim that HCl scavenging by LDHs occurs in two stages. In the first stage, HCl reacts with the counter anions in the interlayers and the second with the —OH groups in the layers. For example, in Mg-Al-OH-CO_3^{2-} LDHs, carbonate anions can react with HCl, releasing water and CO_2, whereas 2 chlorines remain trapped in the interlayer [156]. The second stage starts when CO_3^{2-} is no longer available.

Then, HCl begins to react with the hydroxides in the layers. Initially, the layers remain intact, but as the dehydrochlorination proceeds, the layers eventually break down completely, forming metal chlorides. Furthermore, Du also highlights that when the ratio of Mg/Al is 2, Mg-Al-OH-CO_3^{2-} LDH has a higher number of CO_3^{2-} in the interlayers, the thermal stability of the PVC compounds is higher [141]. Therefore, thermal stability is primarily influenced by the efficiency of the reaction between HCl and the anions in the interlayers rather than by the overall capacity of LDHs to react with HCl. This is evident because while the reaction of HCl with the —OH groups in the layers neutralizes one of the main actors of thermal degradation, it also produces metal chlorides, which can be potent Lewis acids, severely affecting the thermal stability of PVC. However, the good thermal stability of a PVC compound is not just based on the efficiency in HCl scavenging from LDHs but also depends on the presence of other ingredients, such as primary and other co-stabilizers, as explained in Section 2.3, which give a compromise between initial color, color hold, and long-term thermal stability. Gupta shows how to adjust the thermal stability of PVC compounds using LDHs and metal stearates [157]. Metal chlorides also play a crucial role in thermal decomposition. Xu clarifies this aspect further. It was found that 4 wt % of a Zn_2-Al-CO_3 LDH promotes the process of dehydrochlorination in the temperature range 270°C—300°C, the initial part of the first decomposition stage of PVC, and decreases the release of volatile fuels (alkyl hydrocarbons) in the second stage (400°C—550°C) [158]. This LDH can accelerate PVC decomposition because HCl evolves rapidly and first reacts with the hydroxides in the layers, which are more accessible than the interlayer anions.

Additionally, when metal chlorides, such as $ZnCl_2$, are formed, they act as potent Lewis acids. Consequently, Zn_2-Al-CO_3 LDHs, which eventually produce $ZnCl_2$, catalyze zip-elimination, promoting early HCl release, lowering the onset temperature of thermal decomposition, and causing the reaction to proceed within a narrow temperature range. This promotes the formation of a consistent char, enhancing flame retardancy and reducing smoke production, according to Starnes, Montaudo, O'Mara, Pike [133–137].

In LDHs, the composition of the layers and the counteranions in the interlayer can have a substantial effect on thermal stability. Gupta explored the effect of Mg and Ca in the cationic layers and Cl^- and CO_3^{2-} in the interlayer on the thermal degradation of PVC compounds [159]. Thermal degradation was explored at a 2 phr dosage of LDH, monitoring HCl evolution in the N_2 stream, using the static thermal stability test in the oven (ASTM D2115) [160] and following the polyene sequences formation through the UV–visible spectroscopy after the dissolution of degraded test specimens in THF. The cations in the hydrotalcite structure have a pronounced role in long-term thermal stability. Formulations containing Mg-Al-OH-CO_3^{2-} exhibit a dehydrochlorination time (2 mmol HCl evolution) more than 9 times that of neat PVC and more than 1.4 times that of PVC with Ca-Al-OH-CO_3^{2-}. The substitution of Mg by Ca diminishes the HCl stability behavior. The effect of cations in hydrotalcites on thermal stability can be explained based on the ionic radius of Mg^{2+} and Ca^{2+}, as Mg^{2+} is 0.072 nm and Ca^{2+} is 0.100 nm. The smaller radius of Mg^{2+} causes an increased attraction on Cl of HCl gas, which reacts in the interlayer of hydrotalcite where anions $CO_3^{2-}$are found: in general, hydrotalcites at 2% provided significant improvement in thermal stability compared to virgin polymer. The kind of interlayer anions affects long-term thermal stability as well. If Mg-Al-OH-CO_3 has an induction time of 497 min, Mg-Al-OH-Cl is only 371 min. Cl brings the same drop in Ca-Al-OH-CO_3, which has 349 min, while Mg-Al-OH-Cl only has 141 min. The paper suggests that the reason can be that Cl anions in the interlayers cannot be exchanged with Cl from HCl, and HCl can be only adsorbed with less efficiency in the surface "including pores" of LDH.

In Ref. [161], the effects on thermal stability were studied by preparing Sb-LDH by intercalating SbS33 into LDH layers. PVC composites with Sb-LDH (15% wt, 2% wt, and 5% wt) show enhanced transparency but very poor thermal stability, making its role useless.

In Ref. [162], Sn-containing LDHs have been prepared and compounded into poly (vinyl chloride) (PVC), and their fire performance has been evaluated using limited oxygen index and cone calorimeter techniques. The peak rate of heat release and smoke parameter were reduced by 64% and 81%, respectively, when replacing 10 wt % of the primary ATH fire-retardant filler by the synthesized Sn-LDHs while keeping the total fire-retardant loading at 100 phr. Thermogravimetric analysis indicates that Sn-LDH is an effective char promoter for PVC.

Stearic acid coated LDH with carbonate anion and Mg/Al, MgCu/Al, or MgZn/Al layer (30 phr) was added to emulsion-grade PVC with 100 phr diisononyl phthalate. Heat stabilities at 200°C and dynamic heat stability tests show that conventional LDH provided the best dynamic heat stability. Partial replacement of the magnesium with copper significantly delayed the release of volatile HCl, while zinc replacement of Mg provided better color retention; in general, different metal substitutions affect performance differently in different heat stability tests [148, 163].

New hints for a functional LDH stabilizer were developed by Zhang et al. They prepared 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid (BP) anion-intercalated Mg/Al-carbonated layered double hydroxide (LDH) (LDH-BP) and studied the accelerated weathering and thermal stability of PVC/LDH-BP composites by color change, oxidation products, surface morphology, and thermal stability time. The addition of LDH-BP can improve the static thermal stability time of PVC. PVC's dynamic thermal stability behavior in both open and closed processing environments is also enhanced after the addition of LDH-BP [164].

Thermal aging tests of polyvinyl chloride (PVC) mixed with Zn-Al-LDHs, calcium stearate ($CaSt_2$), and β-diketone showed that Zn-Al-LDHs can not only enhance the stability of PVC

significantly due to the improved capacity of HCl-adsorption but also increase the initial stability and ensure good initial coloring due to the presence of the Zn element. The optimum composition was determined to be 0.1 g Zn-Al-LDHs, 0.15 g $CaSt_2$, and 0.25 g β-diketone in 5 g PVC.5 g PVC, 2.5 g DOP, and various amounts of Zn-Al-LDHs [165].

3.3 | Carbon-Based Materials

Carbon-based nanostructured materials are mainly the so-called 2D nanomaterials (i.e., nanotubes and nanofibers) and 1D nanomaterials (i.e., graphene and graphite sheets).

Carbon nanotubes are a finite carbon structure consisting of needle-like tubes consisting of graphitic sp^2 carbon arranged in a single rolled sheet (single wall carbon nanotubes—SWNT) or coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50 (multi-walled carbon nanotubes—MWNT). Nanotubes can range in diameter from a few to 10 of nanometers in diameter, reaching up to 1 μm in length [166].

Graphene is an isolated single layer of sp^2 carbon with the same bonding and electronic features as graphite and a thickness of 0.335 nm. Graphene flakes may consist of a few layers of carbon atoms, up to mono-layer graphene.

The features of this material are relevant for structural and physical characteristics [167]. The strong σ bonds in the graphene lattice give the high mechanical properties of graphene. At the same time, the presence of a delocalized π structure constitutes a delocalized electrons network, resulting in excellent electrical conductivity [168].

PVC flooring can incorporate carbon nanotubes to enhance its properties, particularly for electrostatic discharge (ESD) control and other applications. Single-walled carbon nanotubes (SWCNTs) are commonly used to improve conductivity and surface finish, allowing for thinner, more durable, and colorable flooring [169].

3.3.1 | Carbon PVC Nanocomposites

Multiwalled carbon nanotubes (CNT), as prepared, ball-milled, and acid-treated, were mixed with poly(vinyl chloride) (PVC). All three types of CNT in small amounts (0.1 or 0.3 phr) could stabilize PVC against thermal degradation by retarding the rate of formation of a conjugated polyene structure, with the stabilizing efficacy in the order of ball-milled CNT > CNT > acid-treated CNT.

All three types of CNT promoted thermal degradations of PVC to HCl in the initial 30 min of aging but were clearly stabilized against degradation over prolonged aging (for instance, 120 min) by ball-milled and acid-treated CNT with optimal stabilizing efficacy at 1 phr [170].

Thin films of PVC/multiwalled carbon nanotubes (MWCNT) and PVC/graphene (GN) nanocomposites were prepared, but MWNT were poorly dispersed. PVC/GN nanocomposites were thermos-mechanically more stable than the PVC films [171].

In another paper, a good dispersion of CNT in PVC increased the conductivity with growing CNT's content in the PVC matrix [172].

The PVC/CNT nanocomposite was prepared with commercial poly(vinyl chloride) (PVC) and multiwall carbon nanotube (CNT). Electromagnetic interference shielding effectiveness (EMI SE) and electrical conductivity of PVC/CNT nanocomposite showed that the PVC/CNT nanocomposite had increased properties for both [173].

3.4 | Halloysite Nanotubes (HNT)

Halloysite nanotubes (HNTs) [174] are tubular 2 D nanomaterials and are a type of natural aluminosilicate nanotubes that can be used as a nanofiller for polymers, such as polypropylene, epoxy resin, polyethylene, polyamide, and rubber. Due to their unique structure, HNTs show a promising reinforcing effect for polymers. For example, the strength and modulus of polymers can be significantly improved by HNTs. HNTs can also enhance the thermal stability of polymers.

3.4.1 | HNT / PVC Nanocomposites

Recently, HNTs were found to potentially increase the elongation of PVC, indicating their toughening effect on PVC. However, poor compatibility between HNTs and plasticised-PVC highlighted the need for surface treatment of HNTs to improve compatibility [175].

For this reason, PVC/PMMA-grafted HNTs nanocomposites were prepared by melt compounding.

The grafted HNTs were uniformly dispersed in PVC. PMMA-grafted HNTs can effectively improve PVC's toughness, strength, and modulus. The glass transition T_g of PVC increases to 66 from 73°C by adding 5 phr of PMMA-grafted HNTs, and thermal decomposition temperatures (T50%), and fastest degradation (Tmax, which is defined as the peak on the derivation of the TG curve) of PVC phase in PVC/PMMA-grafted HNTs nanocomposites are shifted towards slightly higher temperatures than that of pristine PVC.

3.5 | Zeolites

Zeolites (Figure 7) are naturally occurring and synthetic aluminosilicate minerals featuring the critical property of microporosity. According to IUPAC recommendations [177], pores with free diameters of less than 2 nm are called micropores [178]. Due to the high porosity and affinity towards water, they produce large amounts of steam due to the adsorbtion when put in contact with water after drying. Axel Fredrik Cronstedt called the material zeolite from the Greek ζέω (zéō), meaning "to boil," and λίθος (líthos), meaning "stone". From December 2018, 245 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known. The current IMA-approved nomenclature is reported in Coombs et al. [173]. Their definition is: "A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting

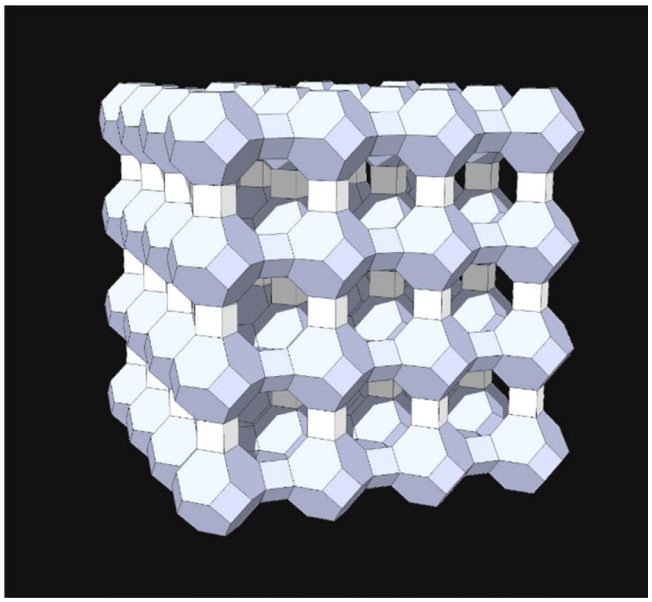


FIGURE 7 | Zeolitic structure showing the microporosity [176].

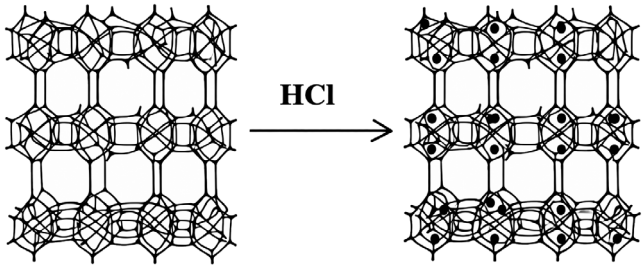


FIGURE 8 | Adsorption of HCl in zeolite pores (small black spheres indicate HCl molecules) [153].

of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H_2O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400°C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra."

3.5.1 | Zeolite/PVC Nanocomposites

Zeolites are cation exchangers, but when subjected to HCl evolution and color stability testing, the zeolite used in the paper by Gupta et al. [153] exhibited a stability time of 337 min versus 50 min for the blank sample. Zeolites can only exchange Na^+ ions with H^+ ions. They cannot exchange Cl^- ions. Thus, the improved thermal stability of zeolites cannot be explained based only on ion exchange. Zeolites contain pores that can adsorb HCl [47], acting as long-term stabilizers similar to hydrotalcites (see Figure 8).

According to the authors, zeolites feature short induction periods, i.e., when no detectable amount of hydrogen chloride gas could be observed, and a higher rate of dehydrochlorination.

3.6 | Other Relevant Features of Nanoadditives

The effects of plasticized poly(vinyl chloride) (PVC) nanocomposites (formulated as PVC powder (100 phr), DOP (60 phr), and Ba–Cd heat stabilizer (0.2 phr) with the addition of 5 phr of organoclay, TiO_2 and ZnO nanoparticles, and SWCNT respectively) on plasticizer migration (DOP) was studied, according to ASTM D 1203-94. Migration and exudation tests upon ASTM D 2199-82 showed that all of the nanofillers (at low contents) decreased the degree and rate of migration. Carbon nanotubes were the best antimigration agent in the plasticized system, followed by TiO_2 and ZnO nanoparticles. Incorporating the nanofillers improved the thermal stability of the PVC studied with TGA [179].

3.6.1 | Polyhedral Oligomeric Silsesquioxanes

POSS are relevant novel nanomaterials in the field of polymer additives. Thanks to their fully synthetic nature and the possibility to control the composition and the purity, they can be considered homogenously and reproducibly 3D nanomaterials. Nowadays, POSS are available at commercial grade and represent a family of hybrid inorganic–organic molecular nanomaterials with organosiliceous nature. They comprise an inorganic Si-based cage framework (the most common cage structure is cubic, with 8 Si units), involving three bonds per Si-unit and an organic pendant group (namely R in the standard nomenclature) on each silicon atom.

POSS can be divided into two main groups: the completely condensed POSS [180] and the partially condensed POSS [181, 182] (Figure 9).

Close-cage POSS show a (usually cubic, often with a higher number of vertices) cage structure with the silicon atoms localized on the apices and a large variety of pendant groups that can promote chemical compatibility with solvents and hosting polymeric systems or instead favor some chemical reactivity by the presence of reactive organic groups. In this study, two commercial close-cage POSS (with cage mixture with 8–12 Si atoms) were employed, with unsaturated vinyl (VyPOSS) and propylglycidyl (GlyPOSS) functional pendant groups.

Partially condensed POSS show an opened-cage structure with dangling Si-OH groups; in this case, the open corner originates peculiar features similar (but not identical) to those of a silica surface, such as polarity, acidity, capability to interact with polar inorganic surfaces or free cations. This work used open-cage heptasilsequioxanes with isobutyl (IBuPOSS) and phenyl (PhPOSS) organic capping.

3.6.2 | POSS/PVC Nanocomposites [184]

POSS additives were used alone and also studied in combined formulations in synergy with other functional additives such as HCl scavengers. They proved to be interesting for their effects on PVC thermal degradation. In particular, formulations included commercial X-type zeolite (X-ZEO [185]) and carbonate-substituted hydrotalcite (HTLC [186]).

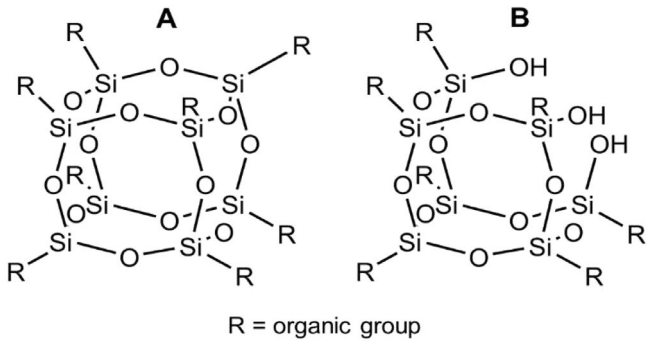


FIGURE 9 | Open and close cage POSS [183].

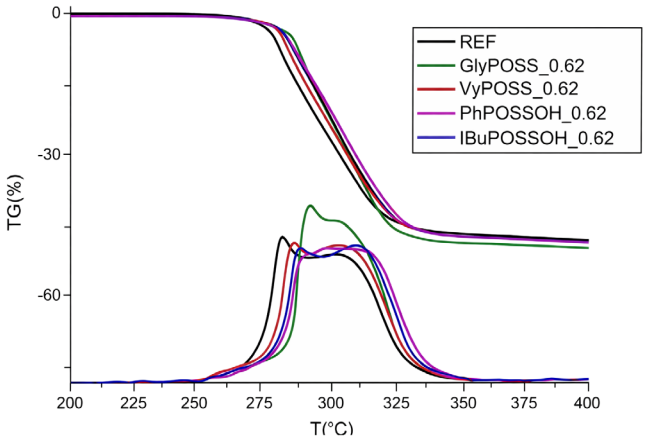


FIGURE 10 | TGA/DTG analyses of reference P-PVC (REF, black) and POSS formulated P-PVC [184].

Powdered PVC-P and nanoadditive(s) were treated with conventional industrial dry blending and then extruded into pellets on an industrial twin screw co-rotating extruder (Maris TM 20 HT, operated with a feed rate of 7 kg/h, with a l/d ratio of 40, gentle screw profile, Temperature profile from 100°C to 160°C), and then processed in a conventional single screw extruder with a shaped drawing to provide 40 × 4 mm ribbons, followed by a roll calender and air cooling.

TGA ramp heating (10°C/min) under nitrogen shows (Figure 10) evident effects on the thermal behavior even when POSS are added at 0.6 phr, and results differ based on the chemical features (i.e., close vs. open cage, different R pendant groups) of the POSS. Actually, POSS with potentially reactive R groups (i.e., OH on silanols, vinyl, and glycidyl pendant groups), despite the low concentration, seem to reduce the amount and/or the reactivity of the already claimed labile sites. They are responsible for the preliminary formation of degradation "nucleation centers" [187], probably due to their homogeneous distribution in the polymer and their interactions with the PVC-P matrix during the extrusion or upon thermal treatment.

Close cage Vinyl POSS in PVC shows a delay of the thermal processes (+1°C for the onset), with a shift of the first and second decomposition processes (from the maxima in the DTG profile) of about +7°C. Open cage (identified in general as POSSOH) Phenyl POSS causes the reduction of the decomposition rate of the first process, which appears mixed with the second thermal effect. At the same time, glycidyl-substituted POSS shifts relevantly to the first decomposition of about +11°C.

3.6.3 | Synergistic Effects on Thermal Degradation of PVC

POSS were also studied with other (nano)additives (Figure 11, top). Glicidyl POSS (0.62 phr) was added in synergy to X-Zeolite (0.31 to 1.25 phr) as the onset degradation temperature was increased to +10°C, and degradation of PVC up to +17°C, and the rate and the relative rate of the first versus second degradation path are influenced by the concentration of X-type zeolite [171].

At the same time, the isothermal decomposition at the onset temperature for neat P-PVC (stated at 265°C under inert gas) showed that the presence of the zeolite delayed GlyPOSS/X-ZEO formulations. This behavior, confirming the role of zeolites as HCl retainers [188] when the degradation is diffusion controlled, [189] can be seen in Figure 11. All the composite formulations gain stability versus neat PVC-P over the first 600 s, and, after this time, the composition of the three additive-containing samples differentiates them, with an increase in the stability over time and at the end of the experiment (after 3000 s.) related to the increase in the amount of zeolite. On the contrary, GlyPOSS alone has only some stabilization role in the 0–1000 s range. The combination of the two additives has evident gains depending on the zeolite concentration, with a distributed stabilization effect over the whole time of the experiment.

The combination of POSS with layered inorganic nanofillers as LDH is still more relevant (Figure 11, bottom), as, aside from the chemical role reported above, some concurrent effects can occur due to the layered aspect. In particular, a physical role for the presence of inorganic platelets, driven to the surface due to the ablation of the polymer upon degradation, can side with the possible chemical role in promoting different chemical degradation paths by massive HCl adsorption. The TGA plots (both in ramp heating and isothermal conditions at 265°C) show that the presence of glycidyl and vinyl POSS (always at 0.62 phr) together with 5 phr of HTLC have dramatically modified thermal stability and degradation. As evident in the DTG profile, with both POSS but in particular when vinyl POSS is present, the mechanism is no longer featured by two steps but a single, delayed one. The isothermal measurements confirm this evidence: HTLC-containing formulations, with the presence of POSS, have a relevant gain in decomposition temperature and residual mass amount.

3.6.4 | Effect of POSS and Other (Nano) Fillers on the Static Thermostability Analyzed With TGA

Using different nanoadditives and/or their combination can modify the whole decomposition behavior of PVC-P. The first evidence can be found in the static thermostability (according to CEI 20-34/3-2), which shows that the presence of glycidyl POSS at 0-62 phr increases the time of stability by about 50%. A

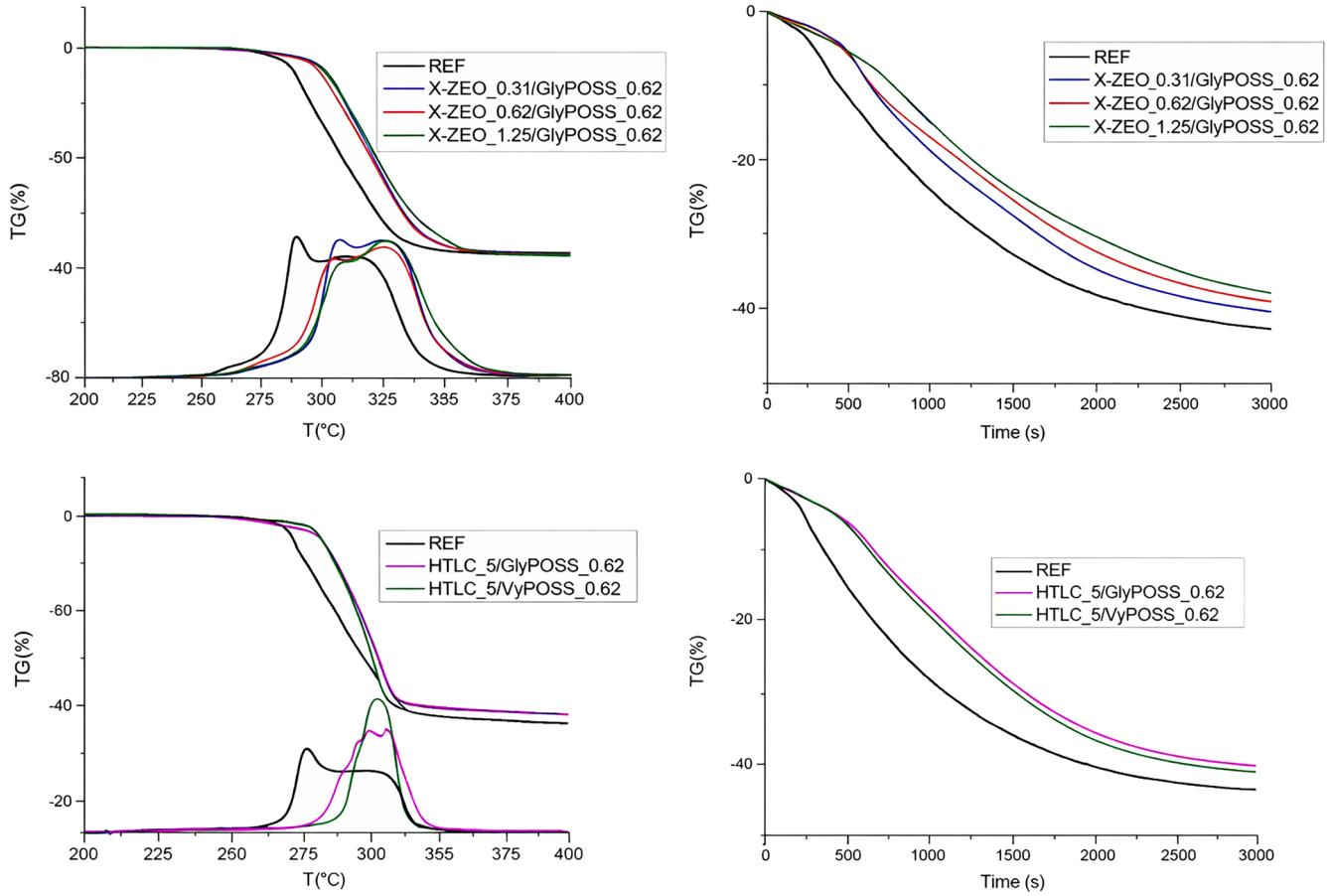


FIGURE 11 | TGA analyses of reference PVC and X-type zeolite/POSS (0.31–1.25 phr) P-PVC (top) and REF and HTLC/POSS P-PVC (bottom) formulations in the compositional range 0.62–5 phr in ramp (left) and isothermal conditions (right) [184].

relevant further improvement was obtained with the combined addition of GlyPOSS at 0-62 phr and 5 phr of HTLC, which increases of three times the time of stability (unpublished results). Figure 12, top, summarizes changes in the main aspects of thermal degradation, considering the onset of thermal degradation (red bar). The maximum decomposition rate for primary dehydrochlorination (green bar) or the maximum degradation rate for the secondary dehydrochlorination process (gray bar). Chemical effects within the degradation process are evident from the graph in Figure 12, bottom, where the weight loss and the delay time concerning the REF during isothermal experiments at 265°C are compared. Samples containing only POSS may have relevantly different behavior; POSS alone can provide a preliminary stabilization; when PVC-P contains zeolite or HTLC HCl scavengers, an evident protection effect is detected, causing an increasing delay of decomposition. Combining these HCl retainers and glycidyl and vinyl POSS makes the delay even more effective.

4 | Additive Sustainability, PVC Recycling, Environmental Impact, and Concluding Remarks

Over the past decades, significant progress has been made in the development of PVC formulations, particularly in the transition towards more sustainable and less toxic stabilizers. European regulatory frameworks have driven formulation changes to replace additives with lower toxicological profiles, a trend that is spreading worldwide. Historically, PVC relied on additives such as lead and cadmium, which posed environmental and health concerns. In the EU, regulations such as RoHS and REACH [190–192], as well as voluntary industry commitments of the PVC value chain [193], drove towards safer alternatives that replaced the problematic substances. The industry now offers a broad portfolio of modern stabilizers that meet stringent safety and performance standards.

At the same time, recycling has become a cornerstone of PVC sustainability, with over 9.5 million tons of PVC recycled since 2000 [194], resulting in substantial reductions in both gross energy requirements and CO_2 emissions. In most cases, the original stabilization of items ensures that recycled PVC retains sufficient residual thermal stability to withstand further processing. Still, for the most severe processes, an additional stabilizer quantity can be added to provide greater stabilization. On the other hand, recycling can be more complex due to the presence of legacy additives, for example those of toxicological concern found in older PVC formulations. Although it has been demonstrated that stabilizers, such as lead-based systems, do not leach out of the PVC matrix [8, 195], these legacy additives have limitations in recycled compounds as of REACH regulation [10], for the reasons discussed in Section 2.3.

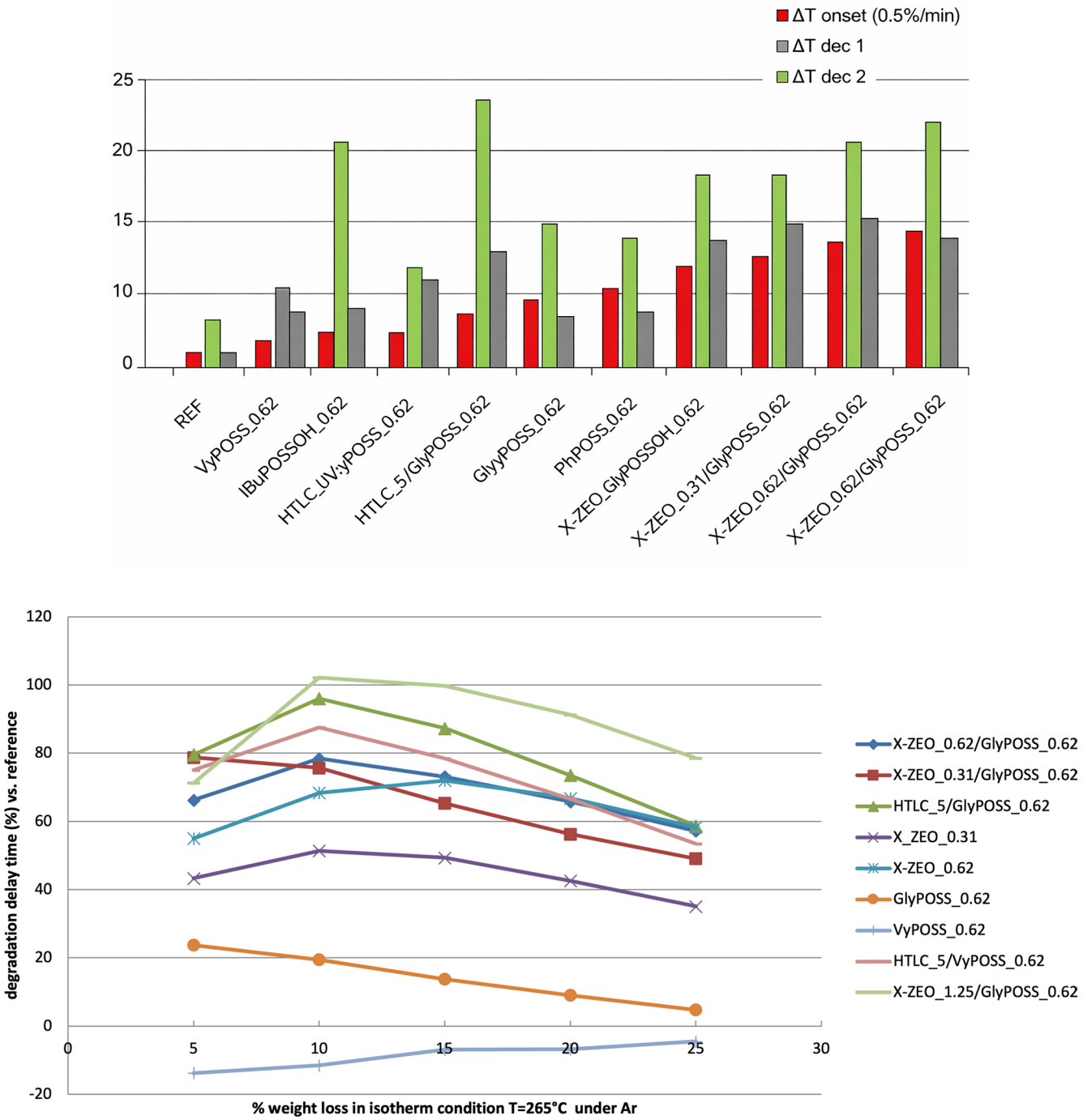


FIGURE 12 | Graphical representation of temperature shifts (°C) of the degradation onset, the first and second decomposition processes derived from ramp TGA (top), and degradation time shift derived from isothermal TGA (bottom) for nanocomposite P-PVC formulations vs. reference PVC [184].

The shift from legacy lead and cadmium stabilizers to calcium organic stabilizers (COS) has overcome this issue, making new PVC items recyclable without any limitations. PVC is predominantly used in building and construction applications, pipes, fittings, profiles, and cables, all of which are now stabilized with COS [196]. In addition, VinylPlus has developed a technology capable of detecting the presence of toxic substances in PVC destined for recycling [197]. Rather than being a barrier, the industry has demonstrated that legacy additives can be effectively controlled within recycling processes, enabling the detection and sorting of them [198, 199], and thus ensuring that recycled PVC is both safe and sustainable. Beyond safer stabilizers and recycling, PVC's use in durable applications further supports its sustainability, as it contributes minimally to mismanaged plastic waste [192]. The use of recycled materials not only conserves resources but also supports the goals of a circular economy. However, legacy additives remain in recycled materials, making their responsible management essential. In this perspective, the new outcomes related to innovative additives, in particular regarding nanostructured materials, could potentially dovetail new perspectives for the

processing and production processes not only in the field of PVC, but in general in the context of polymeric materials.

For instance, considering POSS use as industrial additives, the available data suggests that plasticized PVC/POSS formulations can be relevant for flexible PVC products processed by extrusion and/or calendering, especially cable insulation and jacketing, followed by flexible films/sheets, membranes, flooring, and tubes/hoses, thanks to the improved thermal stability, delayed dehydrochlorination, and lower HCl release at very low POSS loadings. In particular, POSS additives appear especially useful in formulations with a narrow processing/stability window, where exposure to compounding and shaping temperatures can initiate early degradation. Under these conditions, POSS alone provides moderate stabilization, whereas the most significant gains are obtained when reactive POSS species are combined with HCl scavengers such as X-zeolite or hydrotalcite, making these systems particularly attractive for cable-grade flexible PVC and, more cautiously, for other extruded/calendered flexible products where process robustness and thermal issues are critical.

In addition to this suggestion, important considerations can be done in the field of circular economy. Nanoadditives can be employed in recycled PVC, as their addition at very low percentages can improve and restore market-required performance and provide second-life materials with enhanced quality and properties.

In general, recycled PVC fractions have very low or even negligible costs and, as nanostructured and innovative additives are employed in very low amounts, there could be some economic margin to introduce these more expensive materials, particularly in applications where the use of a minimum recycled content is mandatory by regulation and environmental aspects.

Altogether, these integrated advancements position PVC as a leading example of how plastics can evolve towards greater environmental responsibility.

Author Contributions

Stefano Gardi: conceptualization, methodology, formal analysis, writing – original draft, writing – review and editing. **Gianluca Sarti:** conceptualization, methodology, writing – review and editing, supervision. **Luca Palin:** formal analysis, writing – original draft. **Enrico Boccaleri:** conceptualization, writing – original draft, methodology, visualization, data curation, supervision. **Alberto Frache:** methodology, validation, formal analysis, writing – review and editing, data curation.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Appendix A

Methods for the Assessment of Thermal Stability of PVC

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is part of thermal analysis techniques used to characterize various materials. TGA provides complementary and supplementary characterization information to the most commonly used thermal technique, DSC. TGA measures the amount and rate (velocity) of change in the mass of a sample as a function of temperature or time in a controlled atmosphere. The measurements are used primarily to determine materials' thermal and/or oxidative stabilities and compositional properties. The technique can analyze materials that exhibit mass loss or gain due to decomposition, oxidation, or loss of volatiles (such as moisture). It is beneficial for studying polymeric materials, including thermoplastics, thermosets, elastomers, composites, films, fibers, coatings, and paints. TGA measurements provide valuable information that can be used to select materials for specific end-use applications, predict product performance, and improve product quality. The technique is beneficial for the following types of measurements:

Compositional analysis of multi-component materials or blends

- Thermal stabilities
- Oxidative stabilities
- Estimation of product lifetimes
- Decomposition kinetics
- Effects of reactive atmospheres on materials
- Filler content of materials
- Moisture and volatiles content [200]

In the thermal profiles recorded under ramp heating on PVC nanocomposites, alone or in synergy with HCl scavengers, the calculation and graphical representation of the DTG derivative (differential mass loss—% wt/min) highlight the presence of the two steps described above.

Experiments in TGA analysis are essentially based on the monitoring of the mass of the sample (i) during a constant rate heating/cooling (ramp experiments) and (ii) during time at a defined temperature (isothermal experiments). Aside, the environmental conditions of the experiments (i.e., atmosphere and, in some cases, relative humidity) are controlled.

For TGA experiments, the following parameters must be set:

	Ramp experiment	Isothermal experiments
Temperature	Range (beginning/end)	Fixed
Heating rate	Constant rate (°C/min)	Flash to target T.
Measured variables	Weight or weight loss (%) versus T	Weight or weight loss (%) versus time
Atmosphere	Oxidative, Inert, reducing, vacuum	Oxidative, Inert, reducing, vacuum

TGA plots show the percent of weight loss at different temperatures. The main parameters regarding materials stability on the TG plot are the onset point, defined as the temperature where the decomposition rate reaches 0.5% wt./°C or a fixed reference amount of weight loss per °C, and the determination of the % amount of weight loss related to a given decomposition step (evaluated on the y-axis of the plot). A useful add-on is the calculation and graphical representation of the DTG derivative (differential mass loss–% wt/°C); this plot highlights, at best, the presence of different decomposition steps using peaked profiles. For the mathematical meaning of the DTG plot, the peaks of this plot are related to the maximum rate of a given process. Using both TGA and DTG profiles, the effects of the nanofillers on the decomposition mechanism were evaluated in terms of different parameters. From TGA plots, the shift in temperature of the onset of degradation vs. the reference material without additives indicates a better resistance to decomposition. The temperature shift in DTG accounts for the maximum rate of a process after the onset and (together with a plot shape change) evidences the effects of stabilization against the decomposition. Applied to PVC, the increase in thermal stability against decomposition was related to the temperature shift of the onset of degradation. In contrast, the enhancement of the temperature of HCl evolution highlighted by the DTG plot just after the onset was related to the stabilization of the primary dehydrochlorination, which operated on the nucleation process by removing or avoiding the degradation of labile sites. Afterward, at higher temperatures, changes in the DTG profiles were related to the impact of nanofiller(s) on secondary processes (secondary dehydrochlorination and conjugation) due to stabilization or hindering its evolution or absorbing it without release in the gas phase.

TGA isothermal experiments are interesting for the mechanistic information they can provide; in fact, if the temperature is set at the beginning of the decomposition process (i.e., just after the onset of the phenomenon, at a temperature where the decomposition rate reaches 0.5% wt./min), it can allow the discrimination of a physical effect due to the presence of additives from a chemically active filler, that changing the pathway of degradation reactions towards final different products with a different profile in time and final residual mass [201]. In these measurements, if the role of the additive is physical, a reduction of the rate of the degradation process due to a different kinetic is usually observed, with a slower convergence to the same residual mass of the reference material. Conversely, when additives also play an active chemical role, able to change the degradation mechanism, a different profile and increased residual mass for the reference material can be found.

Static Thermostability

Thermal stability in static conditions identifies the different experimental setups where only heat acts on the samples.

Two main different methods are commonly used:

— Discoloration of the sample due to the occurrence of the formation of polyenic structures
— Time until hydrochloric acid is evolved

All tests require a significant statistically representative number of specimens identical in terms of features and physical history.

Dehydrochlorination (DHC) Test

This procedure evaluates the thermal stability, evaluating the time occurring before the beginning of release of HCl upon heating at 180°C according to *UNI EN ISO 182–3:2003 part 3* [202].

Sample pieces are placed in close vessels and heated at 180°C under a gas flow (air, nitrogen, or argon), and it is bubbled in deionized water where conductivity and/or pH monitoring is performed.

Once the target temperature is reached, the conductivity and/or pH values over time are collected.

The test result is given in minutes, representing the time when pH begins dropping for the dissolution of gaseous HCl carried by the gas flow, or instead conductivity of water increases. This value is referred to as *induction time*. Another critical value the method provides is the *stability time*, the time lapse from the beginning of heating, where conductivity increased by 50 μS.

This method can also be applied to evaluate the residual thermal stability, which performs the same dehydrochlorination test after a preliminary thermal aging of 168 h at 80°C, often making the testing methodology very demanding for the material's properties.

The DHC test is currently carried out using automated equipment to control the temperature, gas flow, and electrochemical parameters.

A less automated procedure is the Congo Red test, according to IEC 60811-405, [131] which uses small pieces of PVC samples in closed test tubes with a moist pH-sensitive paper piece. Tubes are submitted to heating (up to 200°C), and the time from the start of the thermal exposure to the visible color change of the indicator paper is determined.

In the literature, some modifications of the method can be found: that is upon heating at 180°C under a steady flow of nitrogen (60 mL/min), induction period noted as T_1 and stated as the period during which no detectable amount of hydrogen chloride gas could be observed can be found sided by HCl evolution time T_2, considered as the total time during which 2 mmol of HCl is evolved [203].

Oven Heat Stability Test

The procedure follows the ASTM D 2115 [204]. The samples are placed in an oven at 180°C (this value may reach 200°C) and visually examined every 10, 20, and 40 min during the first, second, and third hours, respectively. An automated method to control the exposition to the heat of samples is a moving-tray oven, where PVC cut in stripes is inserted completely and extracted from a narrow opening by the regular movement of the tray, which guarantees that a gradual increase of permanence time of samples takes place. Color change can be evaluated visually (see Figure A1 below) or measured using a colorimeter.

Dynamic Thermostability

Dynamic thermostability is considered when PVC is subjected to heat and shear forces, as typically experienced during processing.

Four main methods can be used:

— Discoloration on a two-roll mill
— Time until crosslinking occurs in a laboratory kneader
— Discoloration of PVC melt in a kneader
— Multiple extrusions

Discoloration on a Two-Roll Mill

This method, often called the long-term milling test, works on the plasticization of PVC on a two-roll mill where the two rolls have the same temperature but different rotation speeds, thus applying a shear stress on the material. Samples are collected at different intervals, and the end of the test (related to the time recorded) is given by sticking the polymer to the rolls or the occurrence of a browning effect.

FIGURE A1 | Change of color of sheets with time at 180°C [105].

Crosslinking in Laboratory Kneader

The test is performed by kneading the polymer and tracking the torque value. PVC has a typical curve involving a first range where plastification and gelation occur. In an equilibrium region where torque remains almost steady or has a slow drift, a sudden increase of torque is found due to crosslinking and/or decomposition. The onset of this phenomenon is the dynamic thermostability; this value is (erroneously) inferred also by the emission of HCl, tested with moist pH paper.

Discoloration of the melt in a kneader.

A laboratory kneader can track the discoloration to brown/black of PVC, by extracting specimens from the sample at different intervals. This method avoids the crosslinking in the kneader chamber and the emission of HCl, preventing the work of cleanup and potential corrosion of the equipment. It must be taken, however, into account that taking amounts of samples from the kneading chamber reduces the filling of it and, hence, the shearing stress.

Multiple extrusions.

This method is very time-consuming, as it requires the extrusion of a dry blend of PVC, producing a sample or granules that are ground up again and resubmitted to extrusion recursively.

The thermal stability of PVC is evaluated using parameters such as torque and back pressure during the extrusion process, or evaluation of the color change, or the evaluation of the static thermal stability of samples taken before every cycle using the DHC test, oven test, or Congo red test.

Combustion Tests

Reference Method for HCl Emission

The tests are performed at 800°C or over 935°C. The test at 800°C is performed by weighing a gram of the sample and burning it in a tube furnace through a normalized airflow. It is based on thermal heating of the sample with a heating rate from room temperature to 800°C in 40 min and for a further 20 min at 800°C in isothermal conditions. The effluents are collected in bubblers containing a basic standard solution, where the chlorine dosage is performed through a back titration. The final result is given in mg HCl/g of sample. The method is described in IEC 60754-1 [205] and detailed in Refs [27, 29].

In the test over 935°C, the sample is introduced in the tube furnace in isothermal conditions at a temperature ranging from 935°C to 965°C for 30 min. The effluents are collected in the bubblers containing double-deionized water, and pH and Conductivity are measured. The test is described in IEC 60754-2 [206] and detailed in Refs [27, 29].