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The use of POSS-based nanoadditives for Cable-grade PVC: effects on the thermal stability

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Abstract

PVC for cables and insulation (plasticised PVC – P-PVC) is a very important applicative context of this polymeric material, considering the large commercial volume (around 70% of cables market share in EU), the variability of the required performances (ranging from outdoor to indoor to submarine contexts) and the requirements of reduction of noxious effects in case of thermal degradation or fire, mainly issued on the decomposition of the polymer with release of HCl-containing fumes.

In literature, the use of nanostructured additives in polymer-based nanocomposites and hybrids has operated a revolution in polymeric materials, but the study of PVC-based nanocomposites is not relevantly reported in scientific publication scenario.

In this work, an industry-compliant cable-grade PVC formulation was additivated with commercial nanostructured materials belonging to the family of Polyhedral Oligomeric Silsesquioxanes (POSS)* and studied in their effects of the thermal stability of P-PVC when used alone and in synergy with HCl scavenging agents as zeolites and hydrotalcites. Characterisation was carried on using Thermo Gravimetric Analysis (TGA) and reference methods for thermal stability and HCl evolution. Aside, other features as hardness and mechanical properties were considered in order to highlight the effects of these additives also in the perspective of final industrial uses.

Introduction

Polyvinylchloride (PVC) is a polymeric material, employed in a huge number of applications, ranging from medical devices, automotive, flooring, luxury goods, clothing, construction¹. The benefits of PVC as a commodity polymer rely in manifold aspects: in principle, the intrinsic features of the polymer, as the resistance to temperature (from -40°C to 125°C), to environmental ageing (i.e. UV light stability) and chemicals as oil and gasoline, the

* Hybrid Plastics

compatibility with biological fluids and the transparency. Under the technological point of view, PVC advantage is on the ease of processing, ranging from blending to moulding to extrusion, and the versatility of its formulation, providing easily a range of grades from rigid to flexible formulations in various colours. As material related with constructions and buildings, PVC uses are featured by particularly long lifetimes (from 10 to 100 years) with respect to other thermoplastics, as it is employed for building services both as rigid polymer (i.e. for water and sewage piping and for windows frames) and under semi-flexible and flexible formulations (i.e. for the insulation of electric cables or flooring). These two applications exploit over 60% of Western Europe's annual PVC production², and for electric and electronic applications specifically, PVC cables accounted for 46% of the European cable market in 2016, with market share in the low-voltage cables sector reaching 70%.³ Cable-grade P-PVC is used for sheathing and insulation of electrical and data transmission cables, houseware plugging, interconnection of audio and video appliances, domestic, commercial and industrial electric power distribution infrastructures, photovoltaic plants, conventional and electric/hybrid automotive wiring and industrial robotics. For electric and electronic field, aside the inherently high value of the electrical insulation coefficient, PVC key features are the self-extinguishing capability and the fire resistance. PVC in fact is difficult to ignite, does not sustain combustion nor contribute to flame propagation. Moreover, under heating, PVC does not generate flaming droplets and produce a low amount of smoke. Finally, in a life cycle analysis, most of the PVC cables is currently reused and recycled.⁴ **Errore. Il segnalibro non è definito.**

Considering the scenario of features and applications seen above, PVC products are developed by preparing formulations using a large number of additives. In a commercial PVC resin, a series of additional components are present, as stabilisers and lubricants operating during the production process, plasticisers, processing aids, impact modifiers and pigments. The fundamentals on standard PVC additives and formulations are reported in literature.⁴

Physical fillers such as calcium carbonate or other inorganics are also employed, used in amounts up to 60-80% wt., mainly to balance a reduction of amount of resin with acceptable mechanical features and a sustainable cost of the final formulation.

Inorganic fillers in the context of polymer compounding changed their role since the end of 90's of last century by the development of the polymer-based nanocomposites science⁵. The use of nanostructured additives able to reach a dispersion at submicrometric scale showed as striking innovation the possibility to achieve an unprecedented pool of mechanical and functional benefits due to occurrence of interactions at the intermolecular/interfacial level.

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 (as tensile strength and impact resistance, barrier effect to gas migration) was found.⁶

Furthermore, the homogeneous distribution of nanosized materials highlighted also relevant functional roles as the modification of the thermal behaviour 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 be stabilized by fire retardancy reactions⁷ due to physical effects⁸ and condensed phase catalysed mechanisms⁹. These manifold advantages given by polymer nanocomposites have been often observed at low percentage of addition (i.e. from 0.3 to 3% wt. in general)^{6,10} further promoting nanocomposites as effective and

lightweight high performance materials, counterbalancing also the generally higher cost of nanoadditives with respect to conventional fillers.

In the literature, studies on polymer nanocomposites have generated the wide 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 modelling of the behavior.

Usually, a winning strategy is combining 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 nanoscale level.

Up to now, while several matrices have been thoroughly investigated, a systematic work^{6,10}, also with the purpose of providing knowledge and guidelines for industrial applications, based on polyvinylchloride (PVC) is still lacking.

This work aims at filling this gap working on flexible cable-grade PVC formulations.

The main drawbacks of PVC for electric and electronic applications is the production of aggressive HCl-containing fumes in case of thermal degradation and combustion, and the main challenge is further improving the heat resistance, the thermal stability upon time and the reduction of noxious and toxic emission in case of heating and fire.

PVC thermal degradation occurs via the elimination of HCl from the polymer backbone that in turns self-accelerates the degradation process with the so-called unzipping reaction mechanism. It can be found that the onset of thermally induced dehydrochlorination unlocks an avalanche effect that is responsible of two main drawbacks in PVC. Firstly, dehydrochlorination causes the release of HCl, that is currently considered a critical fume component for the highly corrosive behaviour, while in the polymer, the loss of HCl produces a growing amount of double bonds and, conjugated unsaturated species with the loss of the chemical and physical features of the polymer and of the change of colour to brown/black¹¹.

Stabilisation of PVC upon heating can be promoted by the so called primary stabilisers, that reduce or hinder the unzipping reaction, or secondary stabilisers, that work on scavenging HCl or Cl radicals avoiding the chain propagation reaction.¹² Considering the thermal behaviour of a PVC formulation, the role of stabilisers was related to two main parameters: the induction time (i.e. the time lapse at a certain temperature before the HCl evolution starts taking place) and the rate (or the temperature) where the dehydrochlorination occurs massively.²¹

Though crucial for electrical and electronic applications, in a proper PVC suitable formulation the thermal stability, the amount and rate of HCl evolution upon heating and the resistance to ageing need to mandatory meet the preservation or improvement of rheology, mechanical resistance and flexibility. Furthermore, other desirable features for good additives are to be colourless, odourless and tasteless, compatible to the polymeric matrix, non migrating and cost effective.¹²

In this work, a series of nanostructured materials specifically designed for plasticised PVC (P-PVC) and matching several of the desirable features for additives¹³ was investigated, using basically innovative hybrid inorganic-organic 3D nanomaterials known as polyhedral

oligomeric silsesquioxanes (POSS)¹⁴, in combination with porous or layered inorganic fillers, to obtain a synergistic effect.

As a keystone to meet the industrial interests, both PVC formulation and nanoadditives were chosen to be ready for commercial applications. Hence, a P-PVC mix design composed of basically all the conventional co-formulants required for an industrial extrusion process was employed, and among the world of nanoadditives, a cutoff selection was targeted to use materials that can be purchased in tons scale on the market.

POSS are nowadays commercial grade hybrid inorganic-organic molecular nanomaterials with organosiliceous nature. They are composed of 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 in two main groups: the completely condensed POSS¹⁵ and the partially condensed POSS¹⁶⁻¹⁸ (Figure 1).

Close-cage POSS show a (usually cubic, often with higher number of vertex) 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 favour 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 propyl-glycidyl (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, as polarity, acidity, capability to interact with polar inorganic surfaces or free cations. In this work, open cage heptasilsequioxanes with isobutyl (IBuPOSS) and phenyl (PhPOSS) organic capping were used.

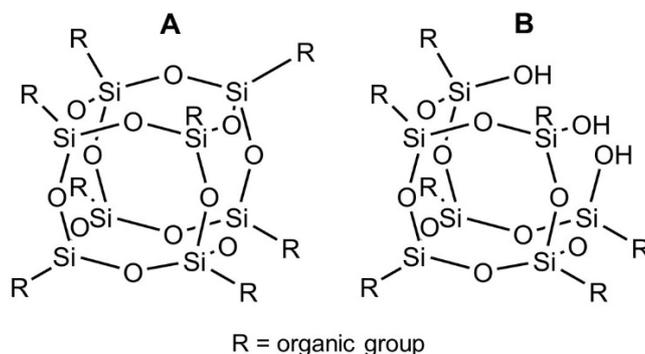


Figure 1. Completely (A) and partially condensed POSS (B).

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

[†] Commercial F9 X-type Zeolite Na⁺ exchanged n powder form (100 mesh) purchased from Tosoh Group (Tokyo, JPN)

[‡] Commercial carbonate Mg/Al hydrotalcite purchased by Purac Biochem B.V. (Gorinchem, NL)

Literature reports evidences of a good effectiveness of HTLC on PVC stabilisation¹⁹. Its role (in general referred to carbonate form) is claimed to be related both to the reactivity of the interlayer anions²⁰, but more convincingly to their acid-base surface reactivity²¹ and the electrostatic interactions between the positive layers of this hydroxide and the polymer chains, that weaken the ability of chlorine atoms to undergo dehydrochlorination¹². Regarding zeolites, their role in stabilizing PVC was basically related to the capability to entrap HCl in the porous structure²² by storing it in the polar porosities of the structure.

Processing of the polymers, made by dry blending, compounding and extrusion, were performed not on lab-scale equipment, but on tenth kilograms quantities using pilot scale machinery, fully compliant with the industrial specifications for production, to better meet the interests of compounders.

Finally, data related to the experimental activities couple the information given by standard Material Science characterization techniques (i.e. Thermogravimetric Analysis) with process parameters collected during the PVC preparation and reference methods for materials characterization according to cable- grade formulations.

The target is understanding how the molecular features of the nanoadditives, their amount and their nanometric dispersion can modify the P-PVC properties to better exploit the effects due to nanosized additives and reaching relevant final performances.

Materials and Methods

P-PVC ribbon preparation

The reference P-PVC for cable applications is a formulation containing a standard series of co-additives in order to tailor the properties for specific process conditions and final features. In order to conform the experimental activities to the applicative scale, a typical industrial formulation for cable-grade PVC was selected, whose composition (according to the common formulation procedure based on p.h.r. – parts for hundred resin -) is reported in table 1.[§]

Table 1: Composition of the P-PVC formulation

Component	Amount (phr)
PVC K.70	100
Coated CaCO ₃ (Atomfor S)	75
Non stab.diisonoyl Phtalate	50
Chloroparaffins (52%)	18
Calcium Stearate	1,5
Zinc Stearate	0,4
Epoxidised soybeans oil	4
Realube RL105	0,7
Stearic Acid	0,3
Irganox 1010	0,2
Sb ₂ O ₃	4

This reference resin formulation was additivated with POSS and other functional fillers at first alone to assess the best performing materials. Secondly, the best performing materials were used in combination. All the recipes are reported in table 2.1 and 2.2.

[§] The basic formulation was provided by the industrial pool of partners of PVCForumItalia – Milano - ITALY

Table 2.1: nanocomposite P-PVC formulations, single component

Coding	Component 1	phr	Component 2	phr
REF	-----		-----	
IBuPOSSOH_0.62	Trisilanol heptaisobutyl POSS	0.62	-----	
PhPOSSOH_0.62	Trisilanol heptaphenyl POSS	0.62	-----	
VyPOSS_0.62	Octvinyl POSS	0.62	-----	
GlyPOSS_0.62	Glycidyl POSS	0.62	-----	
Z-ZEO_0.31	X-type zeolite	0.31	-----	
Z-ZEO_0.62	X-type zeolite	0.62	-----	
HTLC_5	CO3-HTLC	5	-----	

Table 2.2: nanocomposite P-PVC formulations, double components

Coding	Component 1	phr	Component 2	phr
REF	-----		-----	
X-ZEO_0.31/GlyPOSS_0.62	X-type zeolite	0.31	Glycidyl POSS	0.62
X-ZEO_0.62/GlyPOSS_0.62	X-type zeolite	0.62	Glycidyl POSS	0.62
X-ZEO_1.25/GlyPOSS_0.62	X-type zeolite	1.25	Glycidyl POSS	0.62
HTLC_5/GlyPOSS_0.62	CO3-HTLC	5	Glycidyl POSS	0.62
HLTC_5/VyPOSS_0.62	CO3-HTLC	5	Vinyl POSS	0.62

Mixtures were treated with conventional industrial dry blending** for 2 minutes using a mixing profile varying the mixing speed from 1000 to 2900 rpm and then extruded on a Maris TM 20 HT – twin screw co-rotating extruder**, operated with a feed rate of 7 kg/h, with a l/d ratio of 40, D/d ratio of 1.5, screw profile of 3.5 mm. The temperature along the extrusion cylinder (over 13 temperature zones) were respectively set as 30, 100, 100, 100, 100, 100, 160, 160, 160, 140, 140, 160°C. The output, in form of 4 mm pellets were air cooled and collected.

Pellets were then processed in a single screw extruder with a shaped drawing to provide 40 x 4 mm ribbons.

A reference material, without any nanofiller, was processed and formed in the same way of the samples.

Characterization methods

The P-PVC ribbons were studied using thermogravimetric analysis (TGA), tensile test according to ASTM D638, Sh. A (15'') hardness according to ISO 868, HCl evolution

** Activities carried on as external service by a PVC machinery producer, Maris, Rosta (TO) - Italy

according to UNI EN ISO 182-3:2003 part 3 and CEI EN 50267-2-1/IEC 60754-1 and fire behavior following UL94/LOI directive ASTM D 2863.

All the measurements according to standard methods were carried on in certified laboratory structures. TGA analysis was performed on a Setaram SetSys Evolution instrument. As reported, samples were measured in ramp heating conditions (RT – 800°C) with a heating rate of 10°C/min and under an Ar flow of 20 mL/min. Isothermal measurement were performed with the same apparatus, setting the temperature using a fast heating to target temperature (> 30°C/min), using Ar flow at 20 mL/min.

Results and Discussion

Addition of POSS: effects on rheology

The presence of POSS nanoadditives in the formulation showed a remarkable effect already during the extrusion process. In presence of POSS, during the melt processing the melt viscosity of PVC changes relevantly, as the homogeneous distribution up to the nanoscale level modifies the amount and strength of the interfacial interactions within the polymer chains. The most evident effect is on the process parameters, in particular on the torque measured during the extrusion.

In the formulation considered, relevant behaviours are found, that were used as guidelines for further experiments. Table 3 reports the process torque value recorded during extrusion of the formulations. A provisional test at 90 rpm with a high loading (1.25 phr) of Isobutyl POSS trisilanol (IBuPOSSOH_1.25) showed a dramatic change in the motor torque highlighting a relevant drop in viscosity: this result, already observed for the presence of POSS in other matrices²³, highlights that the effective dispersion has reached the molecular level and that POSS heavily interact with PVC chains. The final extrusion conditions, balancing at best the dispersion of fillers, was found at 150 rpm.

In these conditions, POSS nanofillers can be active in modifying the melt flow during extrusion when employed at high concentration (i.e. 1.25 phr or more), while formulations with reduced amounts of POSS (0.62 phr) provide torque values similar to the reference material, and POSS appear to reduce the viscosity also when coupled with other fillers (i.e. X-ZEO samples at 0.31 phr), counterbalancing the common effect of increase due to the addition of inorganic fillers.

Table 3: torque value during extrusion with different PVC nanocomposite formulations

Coding	Screw speed rpm	Motor Torque %
REF	90	35

IBuPOSSOH_1.25	90	17
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REF	150	24
IBuPOSSOH_1.25	148	20
PhPOSSOH_2.5	150	22
IBuPOSSOH_0.62	150	22
PhPOSSOH_0.62	151	22
VyPOSS_0.62	145	22
GlyPOSS_0.62	149	22
X-ZEO_0.31	153	24
X-ZEO_0.62	149	26
X-ZEO_0.31/GlyPOSS_0.62	152	20
X-ZEO_0.62/GlyPOSS_0.62	149	22
X-ZEO_1.25/GlyPOSS_0.62	150	25
HTLC_5	156	24
HTLC_5/GlyPOSS_0.62	150	23
HLTC_5/VyPOSS_0.62	151	24

On the basis of the process parameters, samples with high loading of POSS were dismissed, and only samples providing materials with features similar to the reference matrix were further characterized.

TGA analyses in ramp

For the complete understanding of the results of TGA analyses, a further focus on PVC degradation steps can be useful.

In the mechanism of PVC degradation, the presence of HCl causes an autocatalytic effect originating conjugated double bonds along the polymer chain in a first step, and a second step of condensation, where Diels Alder, cyclisation and cross-linking of polyene segments are responsible of the formation of aromatic fractions²⁴, and to the gradual darkening of the polymer²⁵. As causes of this behaviour, scientists have identified different factors, but the most relevant are the occurrence of tertiary chlorine containing sites, that play as “labile sites” promoting the degradation, allylic chlorine species siding a double bond occasionally present^{Errore. Il segnalibro non è definito.}, isotactic anomalies or in general defects due also to the processing, oxidation or ageing.

In literature a detailed kinetic study highlights that the dehydrochlorination process (expected to occur up to 350°C) is characterized by two steps with different mechanisms: the first degradation (occurring at lower temperature) is featured by a nucleation and growth model, hence degradation is promoted by discrete points (i.e. particularly labile sites, defects, irregularities) progressing in the rest of the material. The second dehydrochlorination step is instead diffusion controlled, giving rise to bubbles of HCl within the residual polymer structure, and sensitive, in the HCl evolution, to the degree of cross-linking of the degraded polymeric fraction.²⁶

The produced materials were tested using TGA under inert (Ar flow) condition both in temperature ramp (10°C/min) and in isothermal conditions.

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.

Hence, using both TGA and DTG profiles, the effects of the nanofillers on the degradation mechanism were evaluated in terms of different parameters. From TGA plots, the increase of the thermal stability was related to the temperature shift of the onset of degradation. The temperature shift (and also a plot shape modification) for the maximum rate of HCl evolution after the onset (highlighted by the DTG plot) was related to the stabilization of the primary dehydrochlorination, operated on the nucleation process by removing or avoiding the degradation of labile sites. Afterwards, at higher temperature, 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.

The TGA profiles of samples obtained with a single additive are reported in Figure 2, while TGA profiles of selected combinations of additives are reported in figure 3.

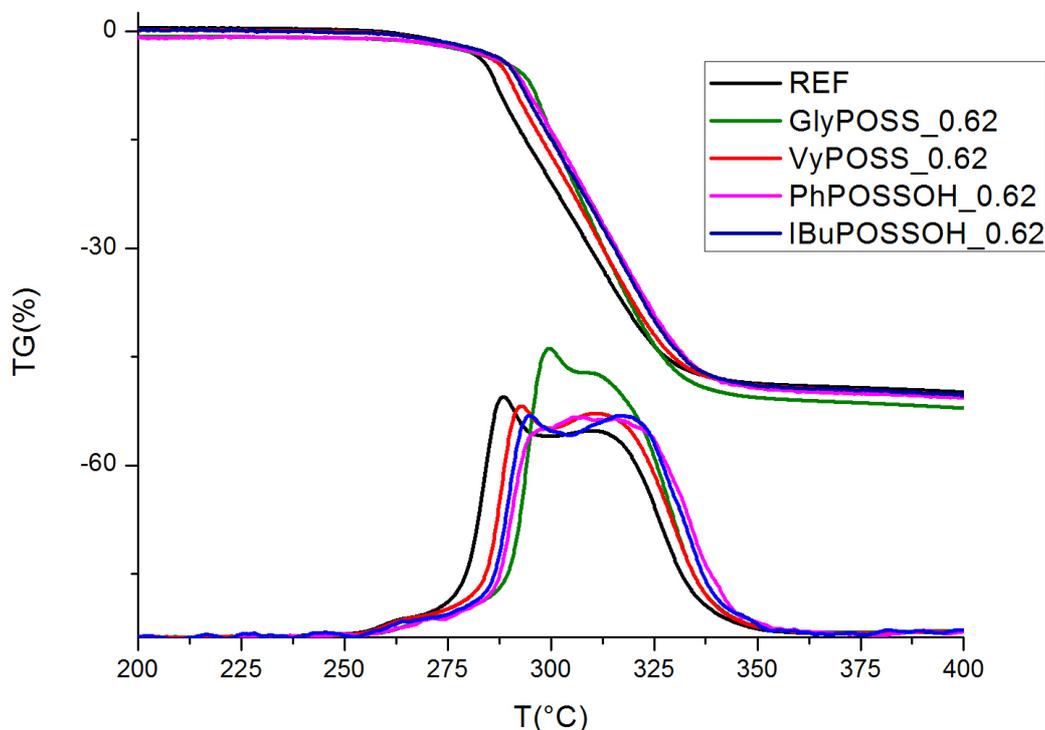


Figure 2: TGA/DTG analyses of reference P-PVC (REF, black) and POSS formulated PVC at 0.62 phr, respectively Glycidyl POSS (GlyPOSS_0.62, green), Octavinyl POSS (VyPOSS_0.62, orange), Trisilanol heptaisobuyl POSS (IBuPOSSOH_0.62, purple) and Trisilanol heptaphenyl POSS (PhPOSSOH_0.62, blue). Measurement are run at 10°C/min under Ar flow (20 mL/min) from RT to 800°C.

Figure 2 reports the mass loss percent upon thermal decomposition in inert environment of the different P-PVC nanocomposites to be compared with the reference formulation in black; in the lower part of the figure, the derivative of weight loss upon time (DTG) is reported as usual in classic thermograms.

The thermal profile of REF highlights the onset of the decomposition process, that, after a preliminary weight loss starting at 250°C (probably due to additives in the formulation) begins at 258°C and reaches a degradation rate of 0.5% wt./°min at 265°C, a subsequent thermal degradation process reaching the maximum rate of decomposition (i.e. the maximum of the DTG curve) around 288°C, and a second degradation process, with a peak rate at 311°C rate and distributed in temperature up to 350°C, causing the loss of about 50% of weight of the polymer.

When POSS are added, it is interesting to note that the effects on the thermal behaviour are due to relevantly low amounts (0.6 phr) of POSS differing in the chemical features (i.e. close vs. open cage, different R pendant groups).

PVC containing close cage Vinyl POSS (VyPOSS_0.62, red curve in figure 2) shows a delay of the thermal processes (+1°C for the onset), with a shift of both the first degradation path and second decomposition process of about +7°C. The use of open cage POSS with different R groups (Isobutyl or Phenyl), the blue and purple curves labelled IBoPOSSOH_0.62 and PhPOSSOH_0.62 respectively, highlights some further difference in behaviour. Phenyl POSS causes the reduction of the decomposition rate of the first process, that appears mixed with the second degradation effect, while glycidyl substituted POSS (GlyPOSS_0.62, green curve) shifts relevantly the occurrence of the first degradation of about +11°C with a significative effect on the static thermal stability of the formulation.

These evidences underline an active role for POSS with potentially reactive R groups (i.e. OH on silanols, vinyl and glycidyl pendant groups) that, despite the low concentration, being homogeneously distributed in the polymer, can interact either during the extrusion process or upon the thermal treatment with the PVC matrix (in particular with the already claimed labile sites that are responsible of the preliminary formation of degradation “nucleation centers”²⁶).

Further relevant results are obtained when POSS are combined with other inorganic additives. Figure 3 shows the thermal behavior of P-PVC additivated with glycidyl POSS at 0.62 phr with the presence of X-type zeolite at 0.31 phr (X-ZEO_0.31/GlyPOSS_0.62).

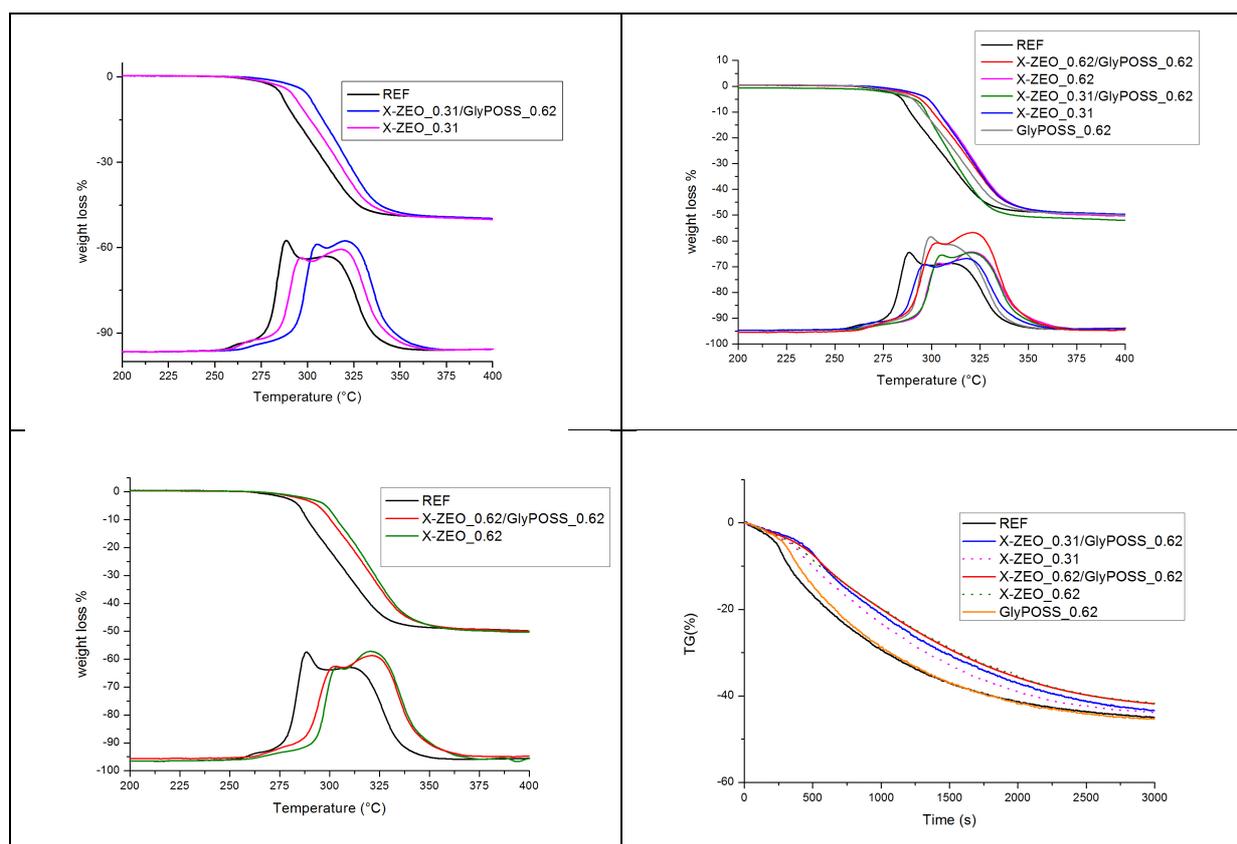


Figure 3: TGA analyses of (top left): reference P-PVC (REF, black), X-type zeolite and X-type zeolite/GlyPOSS formulated PVC (X-ZEO_0.31 and X-ZEO_0.31/GlyPOSS_0.62 purple and blue curves) - ramp heating 10°C/min, Ar flow (20 mL/min) from RT to 800°C; (top right): reference P-PVC (REF, black), Gly POSS and X-type zeolite/GlyPOSS formulated PVC (GlyPOSS_0.62, X-ZEO_0.31/GlyPOSS_0.62, X-ZEO_0.62/GlyPOSS_0.62, X-ZEO_0.31 and X-ZEO_0.62 green, blue, red, grey and purple curves) - ramp heating 10°C/min, Ar flow (20 mL/min) from RT to 800°C; (bottom left): reference P-PVC (REF, black), X-type zeolite and X-type zeolite/GlyPOSS formulated PVC (X-ZEO_0.62 and X-ZEO_0.62/GlyPOSS_0.62 green and red curves) - ramp heating 10°C/min, Ar flow (20 mL/min) from RT to 800°C; (bottom right) isothermal measurements (Ar, 265°C) of reference P-PVC (REF, black), X-type zeolite and X-type zeolite/GlyPOSS formulated PVC (X-ZEO_0.31/GlyPOSS_0.62 and X-ZEO_0.62/GlyPOSS_0.62 blue and red curves). Dotted curves are formulations without GlyPOSS (X-ZEO_0.31 and X-ZEO_0.62); curve in orange is GlyPOSS_0.62 formulation for comparison.

A relevant effect given by a very little amount of zeolite (0.31 to 0.62 phr), operating as HCl physical scavenger, can be already seen, with a temperature shift of +3-+8°C on the onset of thermal induced processes for X-ZEO_0.31 and X-ZEO_0.62 samples respectively. A significant synergistic effect can be seen by the coupling of zeolite with glycidyl POSS at 0.62 phr (X-ZEO_0.31/GlyPOSS_0.62). In fact, the effect of stabilization is far more evident (with a shift of temperature of +10°C for the onset, +17°C and +10°C of shift for the two degradation steps with respect to reference PVC). It is noteworthy that glycidyl POSS, for its chemical composition, has no direct capability to perform HCl storage effect, though epoxidized oils are considered secondary stabilizers used to enhance the effectiveness of conventional additives²⁷, but in this case it clearly promotes and enhances the effect due to the presence of the zeolite. Data on thermal stabilisation are summarized below (figure 5).

TGA analyses in isothermal conditions

TGA isothermal experiments are interesting for the mechanistic information they can provide; in fact, if temperature is set at the beginning of the degradation process (i.e. just after the onset of the phenomenon, at a temperature where the degradation 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.²⁸ In these measurements, if the role of the additive is basically 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 play also an active chemical role able to change the degradation mechanism, a different profile and increased residual mass with respect to the reference material can be found.

Figure 4 shows on the left Ramp TGA experiments run with the combination of zeolite X and glycidyl POSS with increasing concentration of zeolite from 0.31 to 1.25 phr (X-ZEO_0.31/GlyPOSS_0.62, X-ZEO_0.62/GlyPOSS_0.62 and X-ZEO_1.25/GlyPOSS_0.62, green, red and purple curves respectively in figure 5). Notably, the effects of stabilization (i.e. the shift of the onset temperature) are consistent for all the three formulation, while the rate and the relative rate of the first vs. second degradation path are influenced by the concentration of X-type zeolite. This behavior, that confirms the role of zeolites as HCl retainers²² when degradation is diffusion controlled,²⁶ is emphasized by the isothermal experiments reported on the right in figure 5. For all the experiments, the isothermal temperature was set at 265°C (selected on the basis of the onset of neat PVC, intended as a weight loss rate greater than 0.5% wt./°C) and an inert gas flow (Ar) was chosen. As clearly shown by the plots, all the composite formulations gain stability versus neat PVC over the first 600 seconds and after this time the composition of the three additivated samples differentiate them, showing a growing stability along time and at the end of the experiment (after 3000 sec.) with the increase of the amount of zeolite.

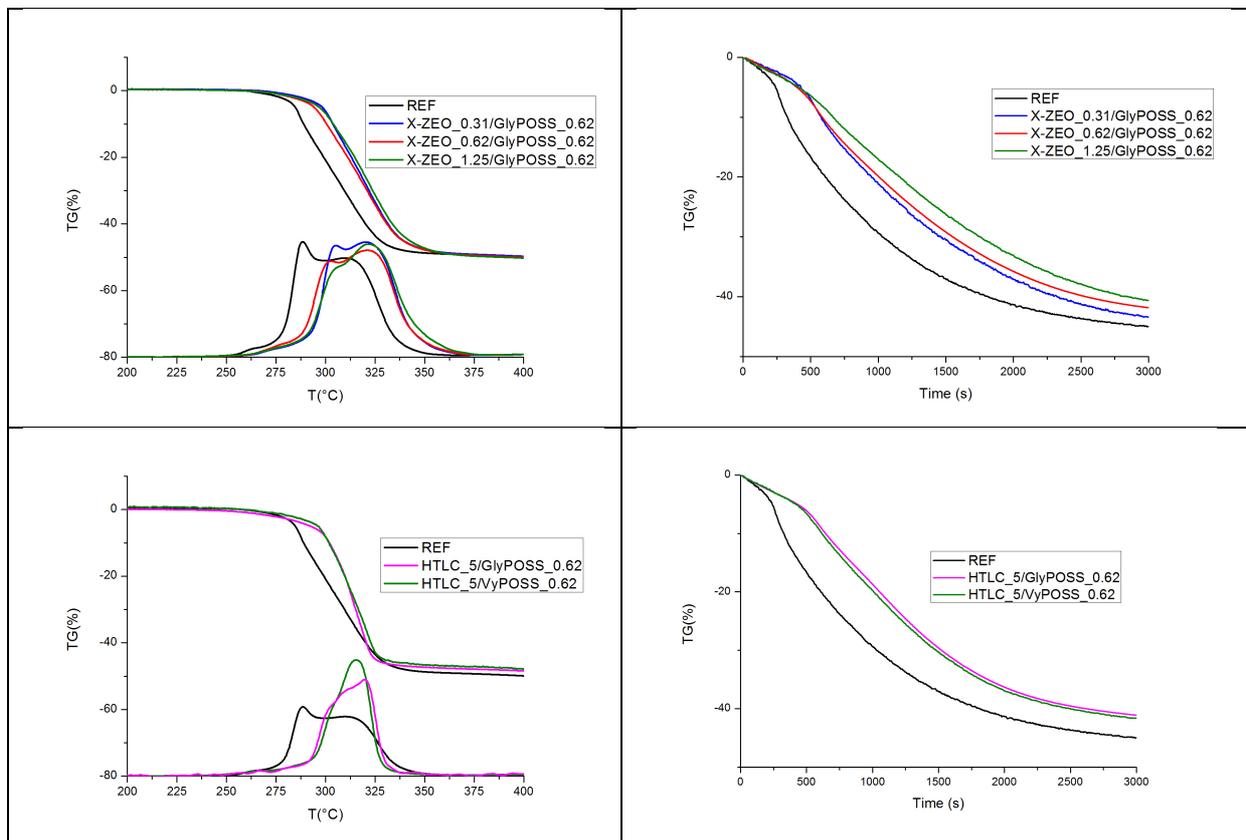


Figure 4: Upper left: TGA analyses of reference P-PVC (REF, black) and X-type zeolite/POSS formulated PVC with different compositions (X-ZEO_0.31/GlyPOSS_0.62, X-ZEO_0.62/GlyPOSS_0.62 and X-ZEO_1.25/GlyPOSS_0.62, blue, red and green curves) - ramp heating 10°C/min, Ar flow (20 mL/min) from RT to 800°C; Upper right: TGA analyses of the same samples in isothermal conditions (265°C, Ar flow); (lower left): TGA analyses of reference P-PVC (REF, black) and HTLC/POSS formulated PVC with different compositions (HTLC_5/GlyPOSS_0.62 and HTLC_5/VyPOSS_0.62, purple and green) - ramp heating 10°C/min, Ar flow (20 mL/min) from RT to 800°C; (lower right): TGA analyses of the same samples in isothermal conditions (265°C, Ar flow).

The combination of POSS with layered nanostructured additives, in particular a commercial carbonate-substituted hydrotalcite (HTLC) is still more relevant. When layered materials are involved in thermal degradation of polymeric matrices, some concurrent effects can be present. In particular, the physical role of the presence of inorganic platelets, driven to the surface due to the ablation of the polymer upon degradation, can side the possible presence of a chemical role of the material in promoting in general some different chemical path of degradation⁸ and in this case, in particular, a 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) sided by the presence of 5 phr of HTLC (HTLC_5/GlyPOSS_0.62 and HTLC_5/VyPOSS_0.62, purple and green curves respectively) have a further dramatic capability of modifying the thermal stability and degradation. As evident in 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. This evidence is confirmed by the isothermal measurements: HTLC containing formulations, with the presence of POSS, have a relevant gain in thermal stability and in residual mass amount.

The effects of stabilization of the onset of degradation, shift of decomposition temperature for step 1 and 2 of degradation of PVC, as well as the effects of stabilization in isothermal conditions for several modified P-PVC formulations are reported in figure 5 - top. As can be noted, the use of different nanoadditives and/or a combination of them can modify the whole decomposition behavior of PVC changing relevantly the onset of thermal degradation (red bar), the maximum rate of decomposition for primary dehydrochlorination (green bar) or the maximum rate of degradation for secondary dehydrochlorination process (grey bar). Chemical effects within the degradation process are evident from the graph in figure 5 - bottom, where the weight loss and the delay time with respect to the reference during isothermal experiments at 265°C are compared. The plots show well that samples containing only POSS may have relevantly different behavior; for instance, vinyl POSS at 0.62 phr reduces the isothermal stability vs. the reference, while glycidyl POSS at the same concentration provide a preliminary stabilization that vanishes during time with a straight linear trend.

When PVC is additivated with zeolite or HTLC HCl scavengers, an evident effect of protection is detected, causing an increasing delay of decomposition. However, the combination of these HCl retainers and glycidyl and vinyl POSS make the isothermal stability even more effective. The convex profile of this curve suggest that the efficacy of the additives increases during the first part of the experiment.

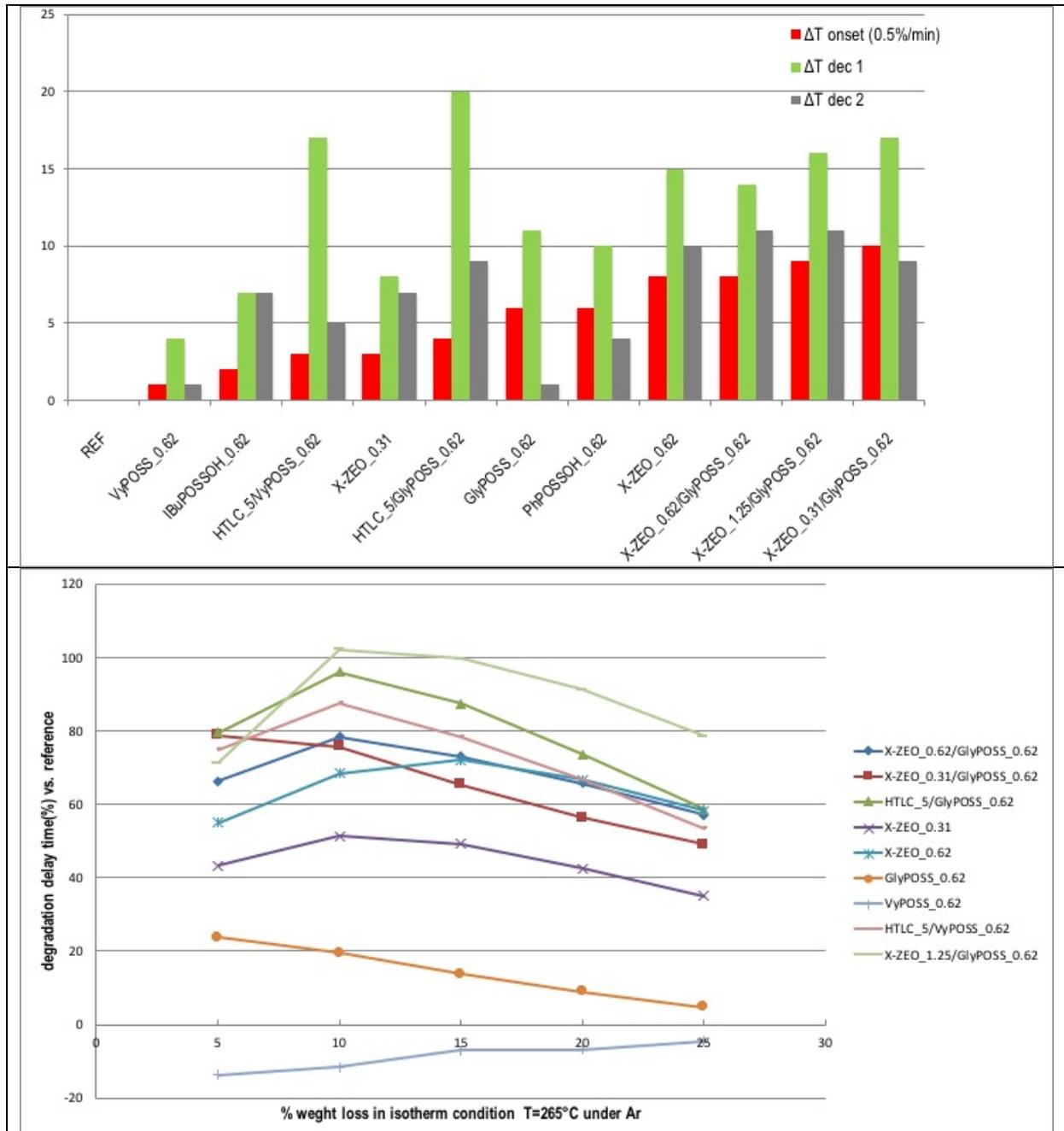


Figure 5: top, graphical representation of temperature shifts ($^{\circ}\text{C}$) of the degradation onset, the first and second decomposition process derived from ramp TGA ($10^{\circ}\text{C}/\text{min}$, Ar flow) for nanocomposite P-PVC formulations vs. reference; bottom: degradation time shift derived from isothermal TGA (265°C , Ar flow) with for nanocomposite P-PVC formulations vs. reference.

HCl evolution

The thermal stability measured according to UNI EN ISO 182-3:2003 part 3^{††} reported in table 4 evaluates the time occurring before the beginning of release of HCl upon heating at 180°C and requires also a preliminary thermal ageing (thermal stability after 168 hours at 80°C) that often makes the testing methodology very demanding for the materials properties.

The reference material has a time of 40 minutes, and the addition of POSS alone changes this results in the range between 45 and 60 minutes (i.e. from 12.5 to 50% of increase). The case of GlyPOSS_0.62 is interesting as there is a residual evident effect also after thermal ageing, where the induction time (though reduced to 87.5% of the pristine value) can be still observed. When POSS are coupled with zeolite or HTLC, the effects are relevant; formulations containing X-type zeolite and POSS gain between 20 – 25% of induction time increase. The formulations of P-PVC with POSS and HTLC reach the best performances both in direct DHC test and after thermal ageing. In these tests, the role and effect of POSS is not evident, but, as shown before, the dynamic thermal behavior under ramp heating highlights some differences.

Table 4: HCl evolution according to UNI EN ISO 182-3:2003 test method for P-PVC and nanocomposite formulations, Limiting Oxygen Index (LOI) according to ASTM D 2863

Formulation	Thermal stability [min]	Residual th. stab. [min] after 168h at 80°C	LOI [% O_2]
REF	40	-	24.5
X-ZEO_0.31	40	-	25.5
X-ZEO_0.62	45	-	25.5
X-ZEO_0.31/GlyPOSS_0.62	55	-	25.5
X-ZEO_0.62/GlyPOSS_0.62	55	-	25.0
IBuPOSSOH_0.62	45	-	25.0
PhPOSSOH_0.62	40	-	25.5
VyPOSS_0.62	40	-	25.0
GlyPOSS_0.62	60	35	25.5
HTLC_5/GlyPOSS_0.62	165	140	25.5
X-ZEO_1.25/GlyPOSS_0.62	40	35	25.0
HTLC_5/VyPOSS_0.62	165	140	25.5
HTLC_5	165	140	26.0

^{††} Measures conducted using a Metrohm 895 Professional PVC Thermomat

Limiting Oxygen Index (LOI) measured according to ASTM D 2863 on the samples further underline the efficacy of POSS formulations, in particular for Z_ZEO_0.31, PhPOSSOH_0.62 and GlyPOSS_0.62, hence used alone in the formulation. For these samples, though the best performance was reached by HTLC_5 (hydrotalcite alone at 5 phr addition) with a result of 26%, the results of these formulations (all at 25.5% of LOI) reveal the high efficiency of the co-formulated materials as this result was obtained with amounts of fillers around 1/10 – 1/20 of that of HTLC.

Considering the results obtained in controlled thermal conditions, a comparison of best performing samples with a reference method (CEI EN 50267-2-1/IEC 60754-1) was carried on. This test allowed to better highlight the synergistic role of POSS with HCl scavengers as HTLC (table 5).

In this test, that is based on thermal heating of the sample up to 800°C along 30 minutes and on the collection of HCl released by the sample, the presence of 5 phr of HTLC or 0.6 phr of glycidyl POSS alone respectively give a reduction of HCl evolution of 10.7 and 7.1% with respect to the reference sample. When they are combined, however, despite the result is not the direct sum of the two, it is clear that HCl amount is far more increased (up to 14.3%).

Table 5: HCl evolution according to CEI EN 50267-2-1/IEC 60754-1 method for P-PVC and nanocomposite formulations

Sample	HCl evolution (mg/g)	Variation %
REF	140	
HTLC_5	125	-10.7
GlyPOSS_0.62	130	-7.1
HTLC_5/GlyPOSS_0.62	120	-14.3

Other properties

With the aim of focusing not only on the thermal stability and HCl evolution, a comprehensive analysis of several other features of the nanoreinforced P-PVC were considered. When possible, standard methods were employed in order to provide useful information for potential industrial end-users. Results of mechanical tensile test ASTM D638 on standard dogbone samples obtained by cutting the ribbons, and Sh.A (15'') hardness test according to ISO 868 are collected in table 6.

Table 6: mechanical properties for tensile test and hardness test

	Tensile Modulus (MPa)	error	Stress at break (MPa)	error	Strain at break (%)	error	Hardness Sh. A, 15''
REF	10	0.33	13.8	0.13	320	3.5	80
X-ZEO_0.31	9.57	0.13	13.2	0.9	310	15	77.5

X-ZEO_0.62	9.69	0.56	13.2	1.26	310	12	77.5
X-ZEO_0.31/GlyPOSS_0.62	8.81	0.18	13.2	0.16	330	6.3	77
X-ZEO_0.62/GlyPOSS_0.62	8.44	0.27	12.4	0.77	310	6.8	78
IBuPOSSOH_0.62	8.93	0.127	13.6	0.32	320	2.1	77.5
PhPOSSOH_0.62	8.95	0.18	13	0.13	320	1.6	78
VyPOSSOH_0.62	8.91	0.138	13	0.01	310	1.4	81
GlyPOSS_0.62	8.87	0.104	13.5	0.32	320	6.6	79.5
HTLC_5/GlyPOSS_0.62	9.35	0.178	12.54	0.14	310	0.92	80
X-ZEO_1.25/GlyPOSS_0.62	9.12	0.002	12.3	0.05	300	2.3	77
HTLC_5/VyPOSS_0.62	9.44	0	12.7	0	310	0	81.5

The physical properties like hardness are modified by the presence of nanoadditives, and in several cases (highlighted in orange in the table) the materials are softened by the presence of the POSS, being them alone or in co-presence of dispersed X-type zeolite. When layered materials are present, an increase of hardness was found, despite, in the case of HTLC_5/GlyPOSS_0.62, the co-presence of GlyPOSS leads to a hardness value identical to the reference sample.

Other relevant results can be observed using tensile mechanical properties. Considering the functional role in stabilizing P-PVC upon thermal degradation, a good evidence from all the formulations tested is that the elastic modulus and stress at break remain basically unchanged for all the materials. Notably, a feature often suffering the presence of additives, the elongation at break is often similar to the reference material, and in a formulation based on two additives (i.e. X-ZEO_0.31/GlyPOSS_0.62) the presence of POSS completely reverses the effect of the addition of the X-zeolite, that alone (X-ZEO 0.31) results in a lower elongation. Also the acceptable reduction of elongation found for formulations with 5 phr of HTLC in presence of POSS is relevant.

Conclusions

Cable grade formulations based on P-PVC have good chance to see the improvement of their performances, in particular those related to thermal stability and HCl release, by the use of nanostructured additives in amounts relevantly lower than usually employed fillers for polymer compounding.

POSS with different chemical features were molecularly distributed as unique nanoadditive within P-PVC proving their ability to promote a relevantly different thermal behavior for the unzipping reactions of PVC towards conjugated polyaromatic systems, and their efficacy was demonstrated with amounts between 0.3 to 1 phr.

Among all the POSS, very interesting results, balancing the thermal behaviour under the different perspective considered, the mechanical features and the overall results is GlyPOSS.

This material introduces a ceramic cage surrounded by epoxy terminated organic arms. The explanation of its relevant efficacy can be related to the role, known in literature, of epoxidized oils as secondary stabilizers used to enhance the effectiveness of conventional additives as metal soaps, as acceptors for the free hydrogen chloride²⁹ and retardants for the change in colour³⁰.

The use of POSS together with active inorganic materials able to interact with evolved HCl (X type zeolite and carbonate-substituted HTLC) proved that in presence of amounts of inorganics between 1.25 and 5 phr, the decomposition profile is dramatically modified and a synergistic effect can be highlighted.

The effect evaluated using TGA information are consistently confirmed by the measures of thermal stability and HCl release using standard reference methods.

The improvement of the thermal stability, sided by the preservation of features like the processability, mechanical features and a good performance under UV and thermal ageing makes the use of POSS-based nanoadditives promising in widening the applications of P-PVC formulations, both in the field of cables where stability in temperature and HCl are critical issues, and for contexts where resistance to temperature is required during the production process.

In the field of additives, POSS, POSS/Zeolite and POSS/HTLC systems have several beneficial aspects being colourless, odourless, tasteless and non migrating.¹² Under the cost issue, the efficacy and the added amount (up to 0.62 phr for the more expensive POSS fraction) can balance the cost issues.

These results provide an overview on the role of nanoadditives in P-PVC matrices, identifying the possibility to use the extrusion process to involve and promote strong interactions with nanofillers, in some cases also favoring covalent interactions and formation of hybrid systems. In addition, optimal range of composition was found, that, based on the evidences of the effects on the final features, for some specific additives or combination of them can go down to 0.3 phr.

Data Availability

Data regarding experiments and results are fully reported in graphical form in the paper.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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- ¹ W. V. Titow, *PVC Plastics - Properties, Processing, and Applications*, Springer Netherlands, 1990
- ² www.pvc.org
- ³ www.pvc4cables.org – AMI consulting
- ⁴ W.V. Titow, *PVC technology*, Elsevier Applied Science Publishers, London & New York, 1985
- ⁵ A. Usuki, M. Kawasumi, Y. Kojima, A. Okada, T. Kurauchi, O.J. Kamigaito, “Swelling Behavior of Montmorillonite Cation Exchanged for V-amino Acids by E-caprolactam”, *Mater. Res.*, 1993, vol. 8, no.5, p. 1174.
- ⁶ F. Hussain, M. Hojjati, M. Okamoto, R. E. Gorga, “Review article: Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview”, *Journal of Composite Materials*, vol. 40, no. 17, pp. 1511-1575, 2006
- ⁷ “Flame Retardant Polymer Nanocomposites, A. Morgan and C. Wilkie (editors)”, John Wiley & Sons, Inc., Hoboken, New Jersey, 2007,
- ⁸ H. O. Pastore, A. Frache, E. Boccaleri, L. Marchese, G. Camino, Heat Induced Structure Modifications in Polymer-Layered Silicate Nanocomposites, *Macromol. Mater. Eng.*, vol.289, pp. 783–786, 2004
- ⁹ F. Carniato, E. Boccaleri, L. Marchese, A. Fina, D. Tabuani, G. Camino, Synthesis and Characterisation of Metal Isobutylsilsesquioxanes and Their Role as Inorganic–Organic Nanoadditives for Enhancing Polymer Thermal Stability”, *Eur. J. Inorg. Chem.*, pp. 585–591, 2007
- ¹⁰ F. Gao, *Advances in Polymer Nanocomposites: Types and Applications*, Woodhead Publishing, 2012; Yiu-Wing Mai and Zhong-Zhen Yu ed. *Polymer Nanocomposites*, Woodhead Publishing 2006,
- ¹¹ M.W, Sabaa, R.R. Mohamed, “Organic thermal stabilizers for rigid poly(vinyl chloride). Part XIII. Eugenol (4-allyl-2-methoxy-phenol)”, *Polym. Degrad. Stab.*, vol. 92, pp. 587-595, 2007
- ¹² O.M. Folarin, E. R. Sadiku, *Int. J. Phys. Sci.*, vol. 6, no. 18, pp. 4323-4330, 2011
- ¹³ W. Zhang, G. Camino, R. Yang, “Polymer/polyhedral oligomeric silsesquioxane (POSS) nanocomposites: An overview of fire retardance”, *Progress in Polymer Science*, vol. 67, pp. 77–125, 2017
- ¹⁴ POSS are 3D nanostructured materials developed by Hybrid Plastics, Hattiesburg (MS) - USA
- ¹⁵ F.J. Feher, D. Soulivong, G.T. Lewis, *J. Am. Chem. Soc.*, vol. 119, p. 11323, 1997
- ¹⁶ F.J. Feher, T.A. Budzichowski, R. L. Blanski, K.J. Weller, J.W. Ziller, *Organometallics*, vol. 10, pp. 2526, 1991
- ¹⁷ F.J. Feher, D. Soulivong, A.G. Eklund, *Chem. Commun.*, p.399, 1998
- ¹⁸ F.J. Feher, R.Terroba, J.W. Ziller, *Chem. Commun.*, p. 2309, 1999.
- ¹⁹ R.F. Grossmann, *J Vinyl. Addit. Technol.*, 2000, 6,4 – 6, L. Pesic, S. Salipurovic, V. Markovic, D. Vucelic, W. Kagunya, and W. Jones, *J. Mater. Chem.* vol. 2, pp. 1069, 1992
- ²⁰ R. Kalouskova, M. Novotna, and Z. Vymazal, *Polym. Degrad. Stab.*, vol. 85, pp. 903, 2004
- ²¹ S. Gupta, D.D. Agarwal, S. Banerjee, *J Vinyl. Addit. Technol.*, 2009, vol. 15, no. 3, pp. 164 - 170
- ²² A.C. Lepilleur, M.A. Mazany, L.D. Milenius, and A.L. Backman, U.S. Patent 6,306,945 (2001).
- ²³ POSS User Guide by Hybrid Plastics - <https://hybridplastics.com/wp-content/uploads/2015/04/user-v2.06.pdf>
- ²⁴ A. Marongiu, R. Favarelli, G. Bozzano, M. Dente, E. Ranzi, *J. Anal. Appl. Pyrolysis*, 2003, 70, 519 - 553
- ²⁵ W. H. Starnes Jr, “Structural and mechanistic aspects of the thermal degradation of poly(vinyl chloride)”, *Prog. Polym. Sci.*, vol. 27, pp. 2133-2170, 2002
- ²⁶ P.E. Sánchez-Jiménez, A. Pewrejón, J. M. Criado, M. J. Diánez, L. A. Pérez-Maqueda, *Polymer*, vol. 51 pp. 3998-4007, 2010
- ²⁷ J. Stepek , H. Daoust, “Additives for plastics”, New York: Springer; 1983.
- ²⁸ O. Monticelli, E. Zunino, F. Carniato, E. Boccaleri, L. Marchese, A. Chincarini, “Novel polymer nanocomposites based on polystyrene and Ti-functionalized polyhedral silsesquioxanes”, *Polym. Adv. Technol.* vol. 21, pp. 848–853, 2010
- ²⁹ F. E. Okieimen, C.E. Sogbaike, *Eur Polym J*, vol. 32, no. 12, pp. 1457, 1996
- M.T. Benaniba, N. Belhaneche-Bensemra, G. Gelbard, “Stabilization of PVC by epoxidized sunflower oil in the presence of zinc and calcium stearates”, *Polymer Degradation and Stability*, vol. 82, pp. 245–249, 1990
- ³⁰ D.F. Anderson, D.A. McKenzie, *J Polym Sci* 1970, A1(18), 2905, T. Iida , J. Kawato, K. Maruyama, K. Goto, *J Appl Polym Sci*, vol. 34, pp. 2355, 1987