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Fire behavior of polyamide 12 nanocomposites containing POSS and CNT

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Abstract

Nanocomposites of polyamide 12 with multiwall carbon nanotubes (CNT) and octaisobutyl polyhedral oligomeric silsesquioxanes (POSS) were studied to assess their flame retardancy properties. The fire behaviour was investigated with a cone calorimeter using 50kW/m² heat fluxes, by means of the oxygen index and the UL 94 H classification. The fire residue was characterized using FT-IR and SEM. The best overall performance was observed for the composites containing 3.3 wt% of POSS and 4 wt% of CNT. This composite achieved HB in UL 94, an oxygen index of 27 and a 74% reduction in the peak heat release rate. A synergistic effect was evidenced using POSS and CNT together whereas FT-IR and SEM analysis of the residue from fire experiments confirms the formation of SiO₂ shield on the surface of the burning sample.

Keywords:

Carbon nanotubes, Polyhedral Oligomeric Silsesquioxanes, Flame retardancy, Cone Calorimeter, Nylon 12

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1. Introduction

Fire safety is essential to our modern society. Nowadays the demand for flame retardants (FRs) in polymer is increasing in industry, as the development of fire resistant materials has become a key factor for the pursuit of safety. PA 12 is an important materials in the automotive field since is the most available material currently used for tank, fuel line and air brake tubing. All of those applications require being flame retarded without sacrificing mechanical properties as well barrier properties. Thermal degradation of PA 12 was firstly extensively studied by V. Mailhos-Lefievre et al. using thermal analysis methods and combined P-GC-MS [1]. They observed that lactam and nitriles are the most abundant products. Moreover, giving particular attention to the influence of a commercial halogenated flame retardant (decabromodiphenyl ether), they detected the participation of the flame retardant in condensed phase reactions. Since then, halogen compounds have long been used in polyamide, usually with a synergist such as antimony trioxide [2]. However, the United States government and the European Community expressed concern about the use of FRs, especially for those that can be harmful or can release toxic compound during fire, such as halogenated FR. Is a matter of fact that halogenated FRs are ubiquitous and persistent in the environment and pose potential health hazards to humans and wildlife [3]. Some of these chemicals, such as tetra-through heptabrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCD) have been included in the Stockholm Convention on Persistent Organic Pollutants for elimination [4].

Effective solutions have been found for derivatives containing nitrogen and phosphorus as reviewed by Weil et al. [2]. However, even phosphorus compounds can be considered dangerous for human health being capable of release phosphoric acid in case of combustion [5]. Metal hydroxides demonstrated to be effective FRs, however, the fire properties of polymers filled with aluminum trihydrate [6] or hydromagnesite [7] are only interesting at high loading levels that usually leads to the lowering of the mechanical properties, excluding them from automotive application of PA12.

Recently, in the effort to avoid the use of halogenated compound, much attention was given to the use of nanoparticles such as carbon nanotubes (CNT) [8–10], layered silicates [11,12], nanoscopic silica particles [13,14] and polyhedral oligomeric silsesquioxanes (POSS) [8,15,16]. Nanocomposites of PA12 and organoclay was firstly prepared by Reichart et al. [17] via in situ polymerization, but the effect of nanofillers on the fire behavior of PA12 and PA11 was firstly observed by Lao et el [18] on nanocomposites obtained via twin-screw extrusion, dispersing low concentrations of nanoparticles, namely nanoclays, carbon nanofibers, and nanosilicas. Only nanoclays demonstrated to be effective decreasing the peak of heat release rate (pHRR) of 24%

with a load of 5wt%. However, they needed to add 20 wt% of conventional intumescent flame retardant to obtain a V0 rating in UL94 test done on PA 11 samples. More recently Lecouvet et al. [19] studied the fire behavior of PA12/halloysite nanotubes nanocomposites prepared in a semi-industrial scale extruder using a non-traditional “one step” water-assisted extrusion process. During mass loss calorimeter experiments performed with a heat flux of 50 kW/m² they observed a reduction of 21% of the pHRR in nanocomposites containing 4 wt% of halloysite nanotubes. The mode of action of the halloysite nanotubes as flame retardant additives was explained as a combination of physical mechanisms including barrier, heat sink and fuel dilution effects.

The FR nanocomposites developed so far revealed a good efficiency in reducing the heat release rate in the forced flaming combustion of cone calorimeter; however they don't allow the material to be self-extinguishing in other fire test such as UL 94 and OI. With this aim previous studies have focused on the synergistic effects between nanofillers and conventional flame retardant. Zanetti et al. observed synergy between organically modified montmorillonite and conventional vapor phase fire retardants, such as the combination of decabromodiphenyloxide and antimony oxide in PP nanocomposites [20]. Gallo et al. studied the flame-retardant synergism between phosphorus-based additives and metal oxides observing improvements in the UL 94 classification of poly(butylene terephthalate) [21] and polyhydroxyalkanoates [22]. Pappalardo et. al. demonstrated that the combination of 0.5 wt% of premodified sepiolite with 12 wt% of a commercial intumescent flame retardant showed a clear synergy in OI, UL-94 ranking and peak heat release rate of PP composites [23].

Despite the large amount of literature considering the fire behavior of polymers containing POSS and CNT either alone or as synergic additive with conventional FR, only Tang et. al consider the flammability of composites containing at the same time CNT and POSS [24]. They prepared thin sheets of MWCNT functionalized with POSS, containing about 25 wt.% of POSS. Those sheets, called buky-papers by the authors, were then impregnated with an unsaturated polyester resin subsequently cured in oven. The amount of MWCNT-g-POSS was evaluated to be around 7-10 wt% via TGA experiments. The flame-retardant performance of the bucky-paper composites was evaluated by the micro cone calorimetry test, where a significant reduction in pHRR by approximately 72% was observed for the MWCNT-g-POSS buckypaper/resin composite sample. The MWCNT-g-POSS buckypaper exhibited better efficiency in fire retardancy compared to the MWCNT buckypaper. SEM observation of the residue after the combustion revealed the formation of a more compact residue containing SiO₂ particles, suggesting that this structure could effectively act as barrier to limit the diffusion of flammable gases to the surface and slow down the combustion and degradation of the resin. No data are reported regarding a self-extinguish behavior in tests such

as UL 94 and OI. Despite these interesting results, the procedure reported by Tang require a prepreg approach not applicable to the most common thermoplastic polymers; further, the POSS and CNT require to be chemically bonded.

This paper makes a contribution by investigating the synergistic effect between multiwall CNT and octaisobutyl polyhedral oligomeric silsesquioxanes in fire behavior of polyamide 12 composites. A comprehensive characterization of fire behavior was performed with cone calorimeter, oxygen index and UL 94 test.

2. Materials and methods

An amine-terminated low-viscosity polyamide 12 ($M_n = 25500 \text{ g mol}^{-1}$, $M_w = 43800 \text{ g mol}^{-1}$, melt index MVR $230^\circ\text{C}/2.16\text{kg} = 25\text{-}70 \text{ ml}/10\text{min}$), characterized by high-flow extrusion grade, melting temperature of $178 \text{ }^\circ\text{C}$ and a tensile modulus of 1500 MPa , especially suitable for high speed extrusion of thin walled tube, was used as polymer matrix (PA 12). It was supplied by EMS-Grivory, under the trade name of Grilamid L 16 LM.

The nanocomposites were produced by melt compounding in a Thermo Prism Eurolab twin-screw extruder the PA 12 with masterbatch of the same polymer. Fillers have been dispersed mixing the PA 12 with a masterbatch containing 15 wt% of CNTs, which was supplied by Nanocyl under the trade name of PlasticylTM PA1502, and a masterbatch containing 10 wt% of POSS, which was supplied by Nova Res.

The CNTs was supplied by Nanocyl under the trade name of NanocylTM NC7000. The polyhedral oligomeric silsesquioxanes contained within the masterbatch was an octaisobutyl polyhedral oligomeric silsesquioxanes (POSS), characterized by a closed cage structure with octaisobutyl groups as substituents.

A first extrusion was carried out by melt mixing the pure polymer and the masterbatch, followed by pellettization, and then a second extrusion was carried out on the obtained material, in order to get an higher homogenization. Table 1 represents the composition of the prepared composites:

Table 1: Samples name and relative composition

Sample	PA 12 (wt%)	CNTs (wt%)	POSS (wt%)
PA 12	100		
PA 12-4CNT	96	4	
PA 12-POSS	96.7		3,3
PA 12-2CNT-POSS	94.7	2	3,3

PA 12-4CNT-POSS	92.7	4	3,3
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The specimens needed for the fire testing were manufactured, after a drying process at 80°C for 4 hours, through injection moulding machines as, the Babyplast 6/10 P and the Sandretto Serie Micro 65t, depending on the samples size.

Oxygen index (OI) testing was performed on the instrument Stenton Redcroft following the standard ASTM D2863-87, while the horizontal combusting testing was performed following the procedure of UL 94 H, but on reduced dimension specimens whose size were 67x13x3 mm.

Cone calorimeter tests were carried out to evaluate the fire behavior of the produced materials. The tests were performed with a Fire Testing Technology equipment, at a heat flow of 50 kW/m². The reported results are the average of 3 samples (dimension: 90x90x3 mm).

The residue from UL 94 test where studied in ATR and SEM. ATR infrared spectra were obtained with a Perkin-Elmer Spectrum 100 instrument equipped with a diamond single reflection ATR accessory. In the typical experiment, 32 scans were accumulated in the range of 4000-700 cm⁻¹ at 4cm⁻¹ resolution. The residue morphology was observed by SEM (Leica Stereo-Scan 410) applying the accelerating voltage during scanning was 20 kV. Samples were mounted on metallic stubs with double-sided conductive tape and ion coated with gold by a sputter coater (Bal-tec SCD 050) for 60 s under vacuum at a current intensity of 60 mA.

3 Results and discussion

3.1 Fire behavior under forced flaming conditions

Figure 1 display results obtained for the heat release rate of the PA 12 composites containing 4 wt% of CNT, 3wt % of POSS and both CNT and POSS, as compared to PA 12, with an external heat flux of 50 kW/m² applied in the cone calorimeter. In table 2 are reported the main parameter measured during the test. The total heat released and the peak of heat release rate are two of the most important fire behavior characteristics, corresponding to total fire load and fire growth, respectively.

Table 2: Cone calorimeter results (standard deviations in parentheses)

	pkHRR (kW/m ²)	THR (MJ/m ²)	Residual weight (%)	TTI (s)	CO yield (g/kg)	CO₂ yield (kg/kg)	TSR (m ² /m ²)	FPI (m ² s/kW)	FIGRA (kW/m ² s)
PA 12	1635 (28)	115.8 (0.9)	0.5 (0.6)	55 (6)	20 (2)	3.06 (0.05)	766 (38)	0,03	12.7 (0.5)
PA 12-4CNT	604 (22)	101.1 (0.5)	2,8 (0.5)	34 (9)	18 (1)	2.72 (0.01)	1232 (57)	0,05	6.0 (0.7)
PA 12-POSS	1521 (100)	112.4 (1.3)	0.0 (0.0)	36 (4)	16 (0)	2.80 (0.05)	610 (35)	0.02	11.5 (1.0)
PA 12-4CNT-POSS	425 (10)	94.9 (0.2)	5.1 (0.3)	21 (1)	19 (1)	2.63 (0.02)	1536 (69)	0.05	4.7 (0.2)

PA 12 shows a heat release rate (HRR) curve which is typical of many thermoplastic materials, where the heat release shows a sudden acceleration that causes a peak in the heat release rate. Subsequently, there is a fast decrease in the HRR, as a result of a gradual reduction of material amount in the sample holder. During combustion, PA 12 melts and leaves no residue. Adding 3,3 wt% of POSS the fire behavior of the PA 12 did not change, with the exception of the time to ignition that is decreased to 36 s. Octaisobutyl-POSS showed evaporation or sublimation in inert atmosphere, over a range of 250 °C to 300 °C [25]. This means that probably in the cone calorimeter experiment the POSS will evaporate earlier than the thermal degradation products of the polymer, increasing the ignitability. No significant change in total heat evolved (THR) was found.

The presence of 4wt% of CNT changed the fire behavior and the heat release rate curve typical for PA 12 was changed into a flattered curve shape similar to those observed in layered silicate polymer nanocomposites[26,27]. As observed before by other authors, the fire behavior of CNT composites was influenced by the consolidation of an interconnected network structure causing viscosity effects that hinder the release of pyrolysis products [28]. Indeed, during the experiment was not observed an apparent melting with bubbling on the sample surface. At the end of the cone experiment the PA 12-4CNT leaves a black/grey solid residue evidencing that not all the sample has been burned (Fig. 2 A). However, the residual weight for PA 12-4CNT is lower than the amount of CNTs contained in the composite, indicating that almost all the polymer has been pyrolyzed and even a part of CNTs may be burned. PA 12-4CNT showed a time to ignition of 34 s, which is lower than that of PA 12. Carbon nanoparticles are known to crucially change the thermal conductivity as well as the heat absorption and may thus have a significant influence on the TTI through these physical effects [29]. An increase in thermal conductivity is proposed as a factor increasing the thermal inertia and thus delaying TTI, whereas a concentration of heat absorption in the top layer, in which the pyrolysis

and thus mass loss occurs, is believed to enhance early ignition and it has been shown that for CNT a clear change in absorption can become the main parameter controlling ignition [30,31].

The simultaneous presence of POSS and CNT in the composites leads to a further diminishing in the HRR curve, with a peak of heat released of 425 kW/m^2 , and a longer time to stop flaming. As in the case of the sample containing the sole CNT there is no apparent melting and bubbling but the residue left by PA 12-4CNT-POSS has a different aspect as showed in figure 2 B. It seems more compact and presents a smoother surface with some dark grey area and other almost white. Previous studies on the thermal degradation of different POSS showed that during heating they can be subjected to two competing processes: evaporation/sublimation and the oxidation of organic substituents which leads to the formation of a silica residue [25,32–34]. As observed in the sample PA 12-POSS octaisobutyl POSS alone fails to produce a silica residue when exposed to heat: rather it undergoes volatilization. However, in the PA 12-4CNT-POSS, it seems that CNTs favor the formation of a silica residue. This event can explain the increase in the residual mass with respect to the composite PA 12-4CNT. This new barrier composed of silica and CNTs resulted more effective in the reducing the pkHRR. However, considering the time to ignition CNT-4CNT-POSS shows a major ignitability with the lowest TTI recorded in this set of experiments: 21 s. The increased heat absorption due to CNT affected not only the pyrolysis of the polymer, but even the earlier evaporation/sublimation of octaisobutyl POSS causing it earlier than in the PA 12-POSS sample.

Considering exhaust emissions, there are no significant differences in the CO yield during combustion. Instead, as for CO₂, it can be noticed that for all the composites the CO₂ yield is slightly lower with respect to PA 12. The total smoke released (TSR) of PA 12-POSS is similar to that of PA 12, while in the case of composites containing CNT the TSR is higher, indicating that the presence of CNT affects the smoke production.

A fire risk evaluation can be made by taking into consideration two parameters as the Fire Performance Index (FPI) and the Fire Growth Rate (FIGRA) (table 2). The FPI is defined as the ratio TTI/pkHRR and it is a parameter that balances fire risks due to ignition and fire growth [35]. An increase in the FPI parameter indicates an increase in the time to flashover, which corresponds to the moment when the fire becomes uncontrollable, allowing more time for firefighting. PA 12 showed a FPI of $0.03 \text{ m}^2\text{s/kW}$. Adding the sole POSS to the polymer leads to the higher fire risk lowering the FPI to $0.02 \text{ m}^2\text{s/kW}$. PA 12-4CNT and PA 12-4CNT-POSS have the higher FPI ($0.05 \text{ m}^2\text{s/Kw}$). This indicates that even with an increased ignitability due to a lower TTI, the fire risks are outbalanced by the reduction of HRR.

The FIGRA is defined as the growth rate of the burning intensity, HRR, during a test, and is calculated as the maximum value of the function (heat release rate)/ (elapsed test time) [36]. The lower is the FIGRA value the lower is the rate of fire growth. It can be noticed in table 2 that the composite PA 12-4CNT presents a FIGRA value which is lower than the PA 12's one, while the composite PA 12-4CNT-POSS shows the lowest FIGRA value among the analyzed materials. Again, the addition of the sole POSS did not lead to any improvement in the FIGRA as compared with the PA 12.

3.1 Flammability

The investigation of flammability was performed by OI and UL 94 test. Both tests generally are performed without an external heat flux, since the flame ignition source is removed after some seconds. The OI are reported in table 3.

Table 3: results of flammability tests

Sample	OI (O ₂ , Vol%)	UL94 H	Flaming Dripping
PA 12	23.0	-	Yes
PA 12-4CNT	22.0	-	No
PA 12-POSS	21.0	-	Yes
PA 12-2CNT-POSS	27.0	-	No
PA 12-4CNT-POSS	27.5	HB	No

The OI is the minimum concentration of oxygen, expressed as volume percent, in a mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature under the condition reported in the ASTM D 2863-87 standard. OI values above 27 normally indicate materials that are self-extinguishing in accordance with the V classification in UL 94. The OI of PA 12 is 23,0 while the composite PA 12-4CNT shows a higher flammability with an OI of 22. In the case of PA 12 large amounts of melt escaped the pyrolysis zone by dripping off, whereas the melt was stabilized by the interconnected network structure of the CNT, increasing the intensity of burning. This behavior has been seen before in nanocomposite, in particular for PA 6 and CNT nanocomposites [16]. Moreover, a charred residue is formed.

Even in the case of PA 12-POSS it has been detected an OI lower than that of the PA 12 alone, being 21. During the combustion the formation of a black layer in the pyrolysis zone of the sample can be observed, however, this layer escapes together with the molten polymer.

Surprisingly, using at the same time POSS and CNT, the OI of PA 12 is increased to 27,0% for PA 12-2CNT-POSS and 27,5% for PA 12-4CNT-POSS. During the combustion, the samples burned leaving a solid black residue with a specimen like shape.

In the horizontal burning test, UL94 H, the HB classification is reached when the burning of a specimen, clamped horizontally, stops before 100 mm. PA 12, PA 12-4CNT and PA 12-POSS resulted not classifiable. PA 12 resulted as non-classifiable, because the flame arrived to the sample end, producing a remarkable amount of flaming dripping material. Even being not classifiable, PA 12-4CNT showed a totally different behavior compared to the unfilled PA 12: there was no dripping and the flame transit induced the formation of a self-supporting residue, whose shape and size corresponded to those of the specimen, as can be observed in figure 3.

The fire behavior of PA 12-POSS is similar to those observed in OI test. The sample produced a thin carbon layer not sufficient to hinder the polymer dripping and leaved no residue.

On the other hand, the composites containing both POSS and CNT (PA 12-4CNT-POSS) cease to burn before the 100mm mark, reaching the HB classification. Indeed, the flame has extinguished at 27 mm from the sample's tip, with an average time of burning of 108 seconds. The flame front transit induced the formation of a self-supporting residue, whose shape and size correspond to that of the specimen. As can be seen in figure 3 the residue appear to be composed of a mix of charred material and inorganic compound showing white/grey zones. This residue has been characterized in FTIR-ATR and the spectrum is reported in figure 4. Being mainly composed of carbon the spectra do not possess absorption peaks with the exception of a characteristic absorption peak at 1070 cm^{-1} , typical of Si-O-Si stretching of silica, belonging from POSS thermal decomposition. The specimen was then burned over a Bunsen flame in order to eliminate completely the carbonaceous phase. The ATR spectra of the remaining white residue correspond to those of amorphous silica and is reported in figure 4. The residue from UL 94 was also observed by SEM and the picture of a portion of the specimen corresponding to a surface crack is reported in figure 5. As can be seen the surface is covered by micro particles of silica, while the bulk of the specimen is composed by a multicellular structure. The walls of these cells appear to be rather smooth and containing micro particles similar to those observed on the surface but in a less amount.

PA 12-2CNT-POSS, even if its OI value is very similar to the composite PA 12-4CNT-POSS's, did not reach the HB classification showing a slightly different burning behavior. Indeed, during the test

the sample withstands a heavy deformation, losing its original size and shape and the flame reaches the specimen end.

These data indicate that both POSS and CNT used alone are not sufficient to achieve a flame retardant effect, even worsening the fire performance in OI test. However, the simultaneous use of the two nanofillers shows the possibility of obtaining a self-extinguishing composite thanks to a synergistic effect between the fillers. CNTs are able to produce a network during the combustion but are not able to produce an effective protective shield. The POSS alone is not able to produce a layer of silica to make effectively flame retarded the polymer. In these condition POSS undergoes to volatilization. On the other hand the action of the POSS supported by the network of CNT is able to produce an effective shield capable to reduce the flammability.

4. Conclusions

In this paper, a study on fire behaviour of composites based on polyamide 12 containing CNTs, POSS or both of them, was carried out.

In the forced flame condition of the cone calorimeter experiment the PA 12 composites containing both CNT and POSS showed the best performances in term of HRR, FPI and FIGRA. Even showing the lower TTI, the reduction of fire growth balanced the fired risks. On the other hand, adding the sole POSS to the polymer worsen the fire properties increasing both the fire risks and the fire growth. However, the addition of POSS to the composite containing CNT improves the fire performance strengthening the CNT effect.

The investigation of flammability was performed by OI and UL 94 H tests. PA 12-CNT and PA 12-POSS showed a higher flammability than PA 12 showing lower OI, 22 and 21 respectively. However, the simultaneous presence of both additives in the composite reduced the flammability increasing the OI to 27. The same trend was observed the UL 94 H test where all the samples were unclassifiable, with the exception of PA 12-4CNT-POSS that showed a self-extinguishing behaviour. In this latter case the residue from UL 94 H contains silica, as observed in ATR, accumulated on the surface, as observed in SEM. These results indicated a synergistic effect between POSS and CNT during fire experiments since octaisobutyl POSS alone is prone to evaporate/sublimate. Then, the formation of silica contribute to produce a shield together with the CNT network acting in a similar manner as observed for layered silicate.

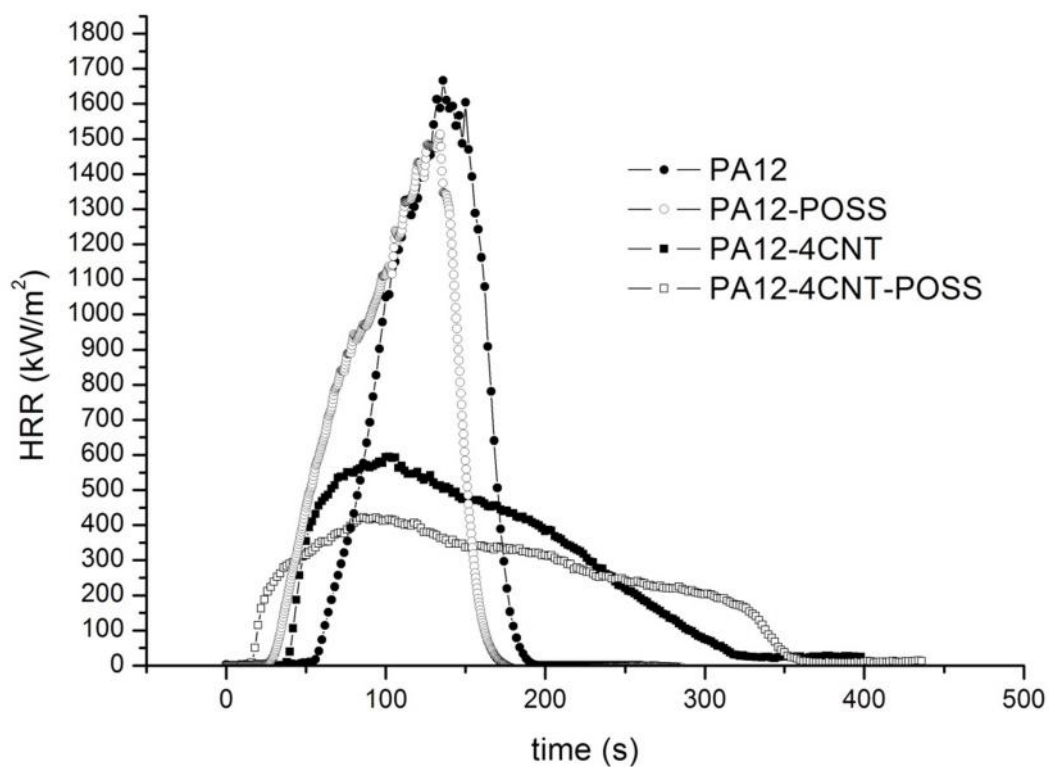


Figure 1. Heat release rate of the PA12 and PA12 composites containing 4 wt% of CNT, 3.3 wt% of POSS and both CNT and POSS, with an external heat flux of 50 kW/m².

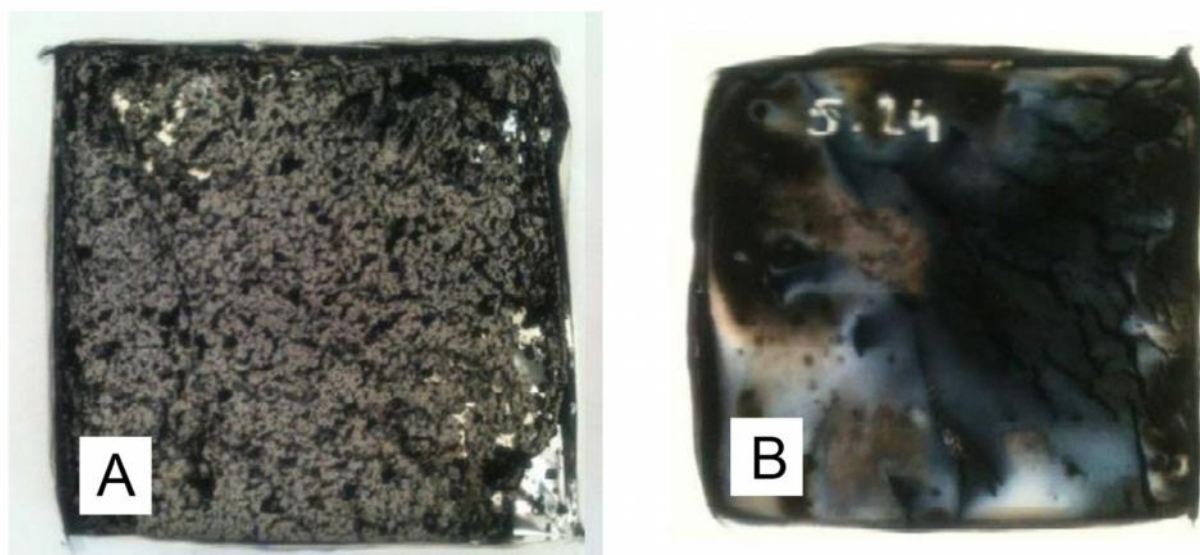


Figure 2. Residues of PA12-4CNT (A) and PA12-4CNT-POSS (B)

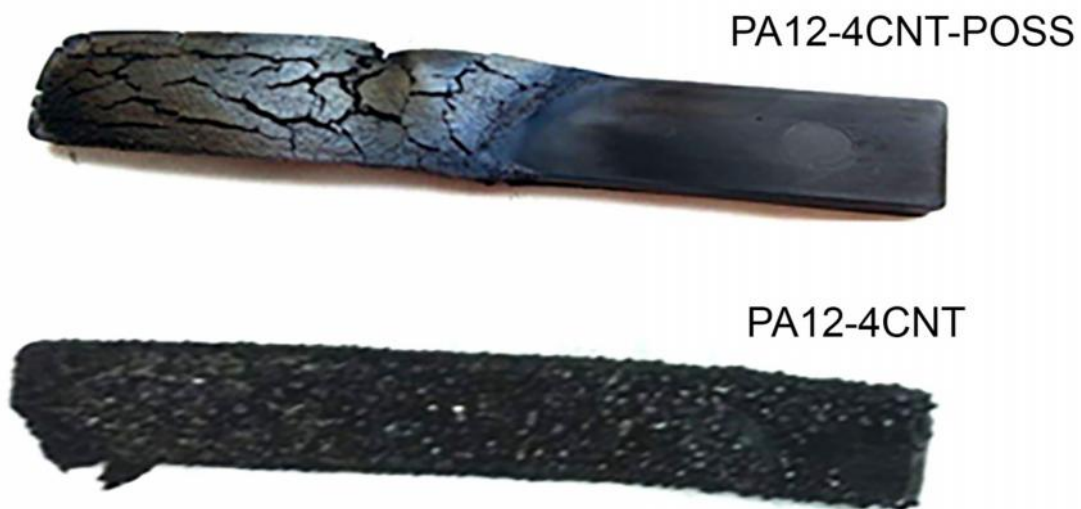


Figure 3. Specimens from UL 94 H test after fire test.

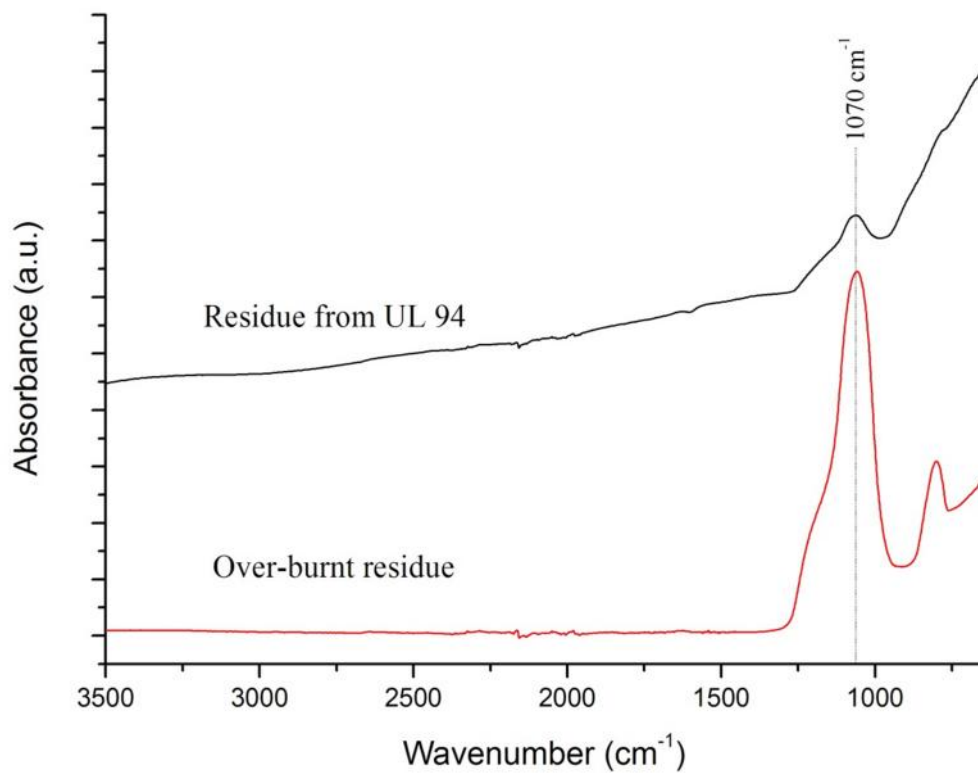


Figure 4. FTIR-ATR spectrum of the residue obtained in the UL 94 H test of PA12-4CNT-POSS and after over-burning it on a Bunsen flame.

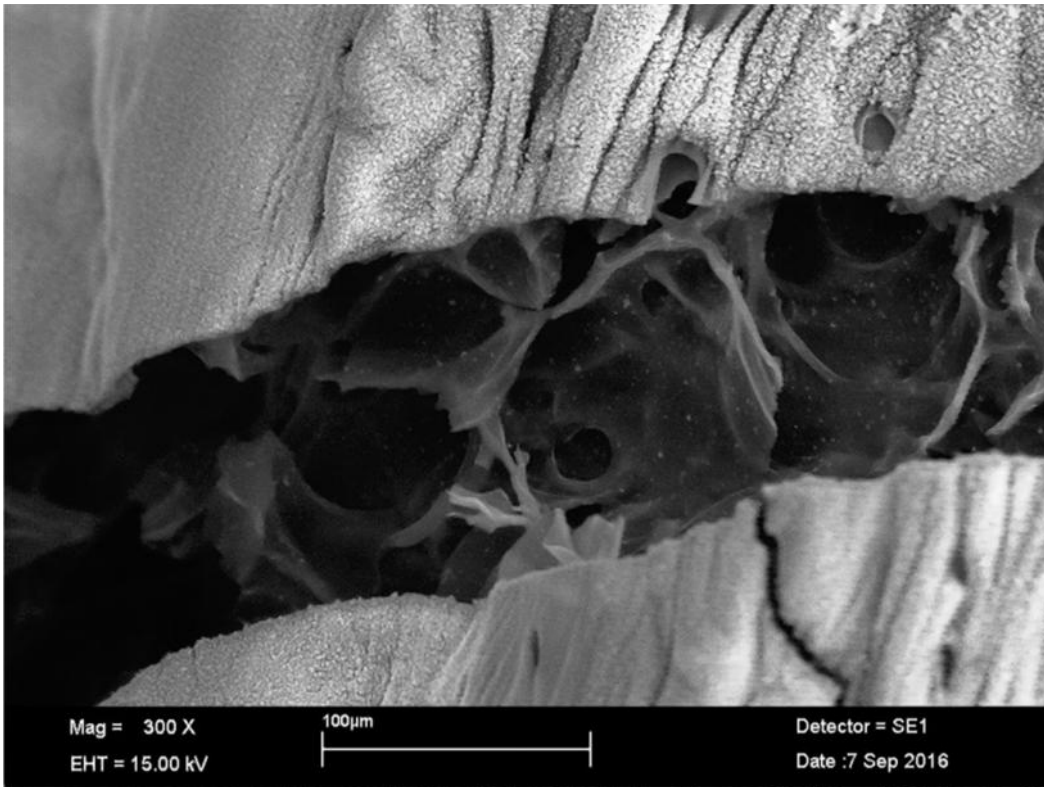


Figure 5. SEM image of a portion of the specimen from UL 94 H test corresponding to a surface crack.

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