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Lecouvet, Benoît ; Sclavons, Michel ; Bourbigot, S. ; Bailly, Christian

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What is This?
Highly loaded nanocomposite films as fire protective coating for polymeric substrates

Benoît Lecouvet¹, Michel Sclavons¹, Serge Bourbigot² and Christian Bailly¹

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Abstract
The main fire retardancy mechanism of polymer–clay nanocomposites involves the progressive build-up of an inorganic-rich layer at the sample surface during combustion, by a combination of ablative reassembling and migration of the nanoparticles, reducing heat and mass transfer between gas and condensed phases. In this process, a non-negligible amount of polymer needs to be sacrificed before the entire surface of the residual material is shielded. This study aims to improve the fire behaviour of polymer–clay nanocomposites by accelerating the physical barrier formation through the development of new hybrid structures. For that purpose, a system based on polyamide 12 and halloysite nanotubes is chosen as reference and highly loaded nanocomposite films are coated on a virgin PA12 substrate. Both the influence of clay fraction in the nanocomposite film and its thickness on the flammability performance of the coated samples are evaluated by mass loss calorimetry and compared to that of homogeneous ‘bulk’ nanocomposites. Results show unambiguously that hybrid materials are more effective than conventional nanocomposites to flame retard polymers while substantially reducing the total filler loading, and so the cost of the final product. Moreover, a small amount of carbon nanotubes can be incorporated in the polymer substrate and/or in the nanocomposite film to suppress the vigorous bubbling of evolved degradation products as well as to reduce the flexibility of the thin protective skin, which can cause detrimental effects on its barrier properties.

Keywords
Halloysite, carbon nanotubes, polyamide 12, nanocomposite films, flame retardancy

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Introduction

Synthetic polymers exhibit limited thermal resistance and are easily flammable due to their organic nature, with some of them producing huge amounts of toxic gases and smoke during burning.\textsuperscript{1} For that reason, their flame retardancy becomes an important requirement to meet regulatory fire tests necessary for industrial applications. Different approaches have been considered for making fire-safe polymers,\textsuperscript{2} among which the direct incorporation of flame retardant additives in the organic matrix is usually preferred since this technique is straightforward and cost-effective.\textsuperscript{3}

In recent years, extensive research in the field of polymer nanocomposites has demonstrated that nanoparticles can contribute to the reduction of the flammability of polymeric materials in terms of heat release rate (HRR), and so could be a potential alternative to conventional flame retardants.\textsuperscript{4–8} In addition to enhanced fire performance, polymer nanocomposites usually exhibit substantial improvement in other physical properties such as mechanical, thermal and barrier properties at relatively low filler content (\(<5 \text{ wt.}\%\)).\textsuperscript{9–11} The outstanding performances of the final material can be ascribed to the high aspect ratio, specific surface area and intrinsic properties of the nanoscale particles, but also their good dispersion and chemical compatibility with the polymer matrix.

Among the wide variety of nanoparticles used for the preparation of polymer nanocomposites, nanoclay is undoubtedly the most extensively studied class of flame retardant nanofillers to date. Pioneering studies by Gilman et al. have reported large reductions in flame spread and prolonged burning times of polymer–clay nanocomposites in cone calorimetry.\textsuperscript{4,12,13} For instance, a decrease in the peak of HRR (pHRR) by 63\% can be achieved with only 5 wt.\% of nanodispersed montmorillonite in polyamide 6.\textsuperscript{4} Similarly, Bourbigot et al. have shown that the pHRR of poly(lactic acid) is lowered by about 40\% when adding 4 wt.\% layered silicates.\textsuperscript{14}

Beside clay platelets, other types of inorganic nanofillers with different shapes and chemical structures have also been examined as potential additives for the fire retardancy of polymers.\textsuperscript{15–17} In previous works, the flame retardant effect of halloysite nanotubes (HNTs) has been highlighted in different polymer matrices including polyamide 12 (PA12),\textsuperscript{18} polypropylene (PP)\textsuperscript{19} and polyethersulfone (PES).\textsuperscript{20} As an example, mass loss calorimetry has revealed that the incorporation of 16 wt.\% HNTs in PA12 leads to a 45\% decrease in the pHRR. Moreover, this parameter is further reduced up to 52\% when clay dispersion is optimized using a water-assisted extrusion process.\textsuperscript{18}

The main mode of action of the clay minerals as fire retardants is based on a physical mechanism (i.e. barrier effects) taking place in the condensed phase. The presence of a suitable amount of nanoclay in a polymer matrix enables the formation of a protective inorganic-rich layer at the sample surface during the combustion process.\textsuperscript{4,21} The insulating layer can shield the substrate from the heat source and/or the heat feedback from the flame. It can also impede the mass transfer between the flame zone and the underlying material (i.e. in-diffusion of oxygen and out-diffusion of flammable gases). As a consequence, both the thermal degradation of the polymer and the fuel supply are slowed down, which translates into reduced flame intensity (i.e. pHRR) and longer burning times.

Two mechanisms have been proposed to describe the barrier formation. One possible explanation for this phenomenon involves an ablative reassembling of the nanoparticles at the surface of the burning sample as a result of polymer pyrolysis, generating progressively an inorganic-rich residue.\textsuperscript{22} Another approach put forward by Lewin is based on the
migration of particles from the bulk towards the external surface of the sample at temperatures far below the pyrolysis temperature. This latter effect may have several origins, which are not mutually exclusive. Clay platelets can be propelled to the surface by rising gas bubbles from polymer decomposition. The transport mechanism can also be driven by the convection flow in the melt (i.e. temperature and viscosity gradients) in the heat source direction. Finally, the migration of nanoparticles towards the material surface can be thermodynamically controlled by the difference in the interfacial tension between polymer and filler. However, the contribution of this latter mechanism seems to be negligible compared to the other ones.

Beside the positive role played by the rising bubbles in the development of the physical barrier, Kashiwagi et al. have underlined an additional antagonistic effect. The burst of gas bubbles at the sample surface can propel nanoparticles outward from the bursting area, resulting in the development of ‘island-like’ floccules instead of a continuous net-like inorganic structure, especially at low filler loadings. Therefore, the surface of the burning material is only partially covered, and the protective layer is not efficient enough to provide mass and heat transfer limitations. This effect is less pronounced with increasing melt viscosity, and hence with increasing filler content, aspect ratio of nanoparticles and polymer molecular weight.

At the early stages of combustion, the flame retardant mechanism of polymer nanocomposites can thus be considered as a surface-controlled process, where the kinetics of the barrier formation depends on several parameters including filler fraction, initial morphology of the composite and viscosity of the melt. Indeed, thermal decomposition of the organic matrix starts at the external surface and then gradually moves towards the bulk polymer. At the same time, nanoparticles accumulate progressively near the sample surface by a combination of polymer recession and migration phenomena, increasing the surface coverage of the exposed material. Therefore, a non-negligible amount of polymer must be sacrificed to enable the build-up of a uniform protective layer shielding the entire surface of the residual material.

In this context, this study aims to improve the fire performance of polymer–clay nanocomposites by accelerating the barrier formation, and hence minimizing the amount of sacrificial organic material. For that purpose, new hybrid structures made of highly loaded PA12-HNTs nanocomposite films coated on the surface of a virgin polymer or nanocomposite substrate are designed and tested. This paper is organized in three main sections. First, the influence of the clay concentration in the nanocomposite films is evaluated with respect to flame retardancy under forced flaming conditions, and surface-coated PA12 specimens are compared to conventional PA12-HNTs nanocomposites. In the second part, the flammability of the hybrid structures is examined as a function of surface film thickness. Finally, different formulations are elaborated by combining halloysite with multiwalled carbon nanotubes (CNTs) in order to improve the mechanical properties of the protective layer during cone calorimeter experiments.

**Experimental**

**Materials**

The PA12 used is Vestamid L2101F produced by Evonik Degussa AG (Germany). A commercial grade of pristine halloysite has been supplied by Sigma–Aldrich (Germany). The
average length and outer diameter of HNTs are about 1 μm and 70 nm, respectively, according to a distribution analysis of the tube dimensions. The specific surface area of the aluminosilicate is 64 m$^2$/g, cation exchange capacity is 8 meq/g, pore volume is 1.25 ml/g and specific gravity is 2.53 g/cm$^3$. CNTs are Nanocyl®-7000 kindly provided by Nanocyl S.A. (Belgium). They are produced via catalytic carbon vapour deposition (CCVD) process and display 7 graphene shells. The average dimensions provided by the supplier are 1.5 μm length and 9.5 nm outer diameter. The carbon purity is 90% and specific surface area is 250–300 m$^2$/g.

**Sample preparation**

All PA12 samples coated with nanocomposite films have been elaborated following a three-step process, and the complete manufacturing route is presented in Figure 1. First, two types of PA12 nanocomposites have been prepared by melt compounding. The extrusion of PA12-HNTs nanocomposites has been carried out in a semi-industrial scale extruder using water injection during melt blending. The experimental procedure has been fully described in a previous paper where it has been demonstrated that the water-assisted extrusion process enables to obtain a more uniform dispersion of pristine halloysite in PA12. Extruded strands have been immediately quenched into cold water and pelletized. PA12-CNTs

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**Figure 1.** Flow diagram of the manufacturing procedure for the elaboration of surface-coated specimens.
nanocomposites have been melt-mixed in a co-rotating twin-screw mini-compounder (DSM Xplore Microextruder 15 cm$^3$) equipped with two stainless steel screws and a bypass allowing continuous recycling of the material. The melt compounding process has been conducted at 240°C for 8 min with a screw speed of 250 r/min.

In the second step, nanocomposite films have been extruded from pellets in continuous mode using a cast film line (DSM Xplore Microfilm device, inset (a) of Figure 1) connected to the mini-compounder equipped with a slit die of 0.2 mm thickness and working at the following temperature profile: $T_{\text{hopper}}/T_{\text{middle}}/T_{\text{die}} = 235/240/245°C$. The screw speed (100–200 r/min) and the speed of the collecting rollers have been adjusted to reach the desired film thickness. Extruded films have been cooled down at the exit of the die using an air flow to avoid necking. Two different types of films have been prepared: (i) PA12-HNTs nanocomposites with various clay fractions and thicknesses and (ii) PA12-HNTs-CNTs nanocomposites by mixing together pellets of PA12-HNTs and PA12-CNTs.

Finally, nanocomposite films have been cut and positioned on the surface of 3 mm thick PA12 or PA12-CNTs hot-pressed plates previously prepared by compression moulding (inset (b) of Figure 1). Next, the hybrid structure has been inserted in a hydraulic press and the plates have been placed just in contact with the mould without applying any additional pressure. Samples have been kept for about 3 min at a temperature just below the melting temperature of PA12 ($\pm 180°C$) in order to prevent the loss of the laminated structure, but still allowing polymer chain diffusion at the interface between film and substrate. An example of nanocomposite film surface-coated sample is shown in the inset (c) of Figure 1.

Prior to being processed by extrusion or compression moulding, all components have been dried in a vacuum oven at 80°C for 48 h. All compositions elaborated in this study are given in Table 1, where PA, H, C and W are used as identification labels for PA12, HNTs, CNTs and water, respectively. For each formulation, the mass fractions of HNTs and CNTs in the bulk matrix ($m$), in the film ($f$), as well as the total filler content ($tot$) are detailed.

### Table 1. Composition of the classical nanocomposites and hybrid systems (polyamide 12 (PA), HNTs (H), CNTs (C) and water injection (W)).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$H_m$ (wt%)</th>
<th>$H_f$ (wt%)</th>
<th>$H_{tot}$ (wt%)</th>
<th>$C_m$ (wt%)</th>
<th>$C_f$ (wt%)</th>
<th>$C_{tot}$ (wt%)</th>
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</thead>
<tbody>
<tr>
<td>PA</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>PA-H4-W</td>
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<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA-H16-W</td>
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<td>16</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA/(PA-H16 200 $\mu$m)</td>
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<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>30</td>
<td>1.9</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA/(PA-H30 350 $\mu$m)</td>
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<td>30</td>
<td>3.1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA/(PA-H30 500 $\mu$m)</td>
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<td>30</td>
<td>4.3</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PA-C2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>PA-C2/(PA-H30 350 $\mu$m)</td>
<td>0</td>
<td>30</td>
<td>3.1</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>PA-C2/(PA-H30-C2 350 $\mu$m)</td>
<td>0</td>
<td>30</td>
<td>3.1</td>
<td>2</td>
<td>2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

HNT: halloysite nanotube; CNT: carbon nanotube; PA: polyamide.

**Scanning electron microscopy**

The structural characterization of the coated PA samples has been performed using a LEO 982 (Zeiss) scanning electron microscope operating at 1 kV.
Transmission electron microscopy
A transmission electron microscope LEO 922 (Zeiss) with a 200 kV acceleration voltage has been used to study the morphology of PA-H nanocomposite films as well as the dispersion state of CNTs in the polyamide matrix. Specimens for transmission electron microscopy (TEM) analysis are cut from bulk compounds at room temperature using a Reichert Microtome. Ultrathin sections of approximately 95 nm in thickness are cut using a cryodiamond knife with a cut angle of 35° (Diatome, Switzerland) and transferred to 400 mesh copper grids.

Mass loss calorimetry
Forced combustion experiments have been carried out using a FFT (Fire Testing Technology) Mass Loss Calorimeter following the procedure defined in ISO/DIS 13927. The equipment is similar to that used in oxygen consumption cone calorimetry. The only difference is the use of a thermopile at the top of the chimney to measure the HRR instead of employing the oxygen consumption principle.

Specimens (100 x 100 x 3 mm³) are horizontally placed under the cone heater and irradiated at an incident heat flux of 50 kW/m². This flux has been chosen because it corresponds to the common heat flux in a mild fire scenario. Ignition is triggered using a standard spark ignition system. The flammability parameters monitored in this study are as follows: the time to ignition (TTI), heat release rate (HRR), peak of heat release rate (pHRR), total heat released (THR) and char residue. The cone data are based on the average of three replicated experiments with a standard deviation on HRR measurements of less than 10%.

Results and discussion
Morphological characterization
Scanning electron microscopy (SEM) has been used to determine the final structure of the hybrid samples. Figure 2 shows a micrograph of a virgin PA plate coated with a PA-H30 nanocomposite film of 350 μm thickness. The dash line indicates the interface between unfilled matrix and nanocomposite film. The aluminosilicate nanotubes (white spots) are homogeneously dispersed in the polyamide film, as revealed by the presence of only few micron-sized aggregates. The clay dispersion is quite acceptable since partial aggregation of the nanotubes is almost unavoidable for highly loaded systems. A well-defined interface is also observed on this image with HNTs selectively localized in the PA film. Such observation confirms that the nanocomposite films can be effectively welded on the sample surface by compression moulding (T≤Tm) while maintaining the laminated structure.

TEM analyses have been carried out to further investigate the dispersion state of HNTs in the nanocomposite films and also the morphology of PA-C2 hot-pressed plates. Figure 3(a) presents TEM micrographs of the PA-H30 film of 350 μm at low and high (inset) magnifications. In agreement with SEM observations, most of the nanotubes are evenly dispersed at the nanoscale and surrounded by some aggregates of a few microns. It is noteworthy that HNTs are preferentially oriented in the extrusion direction, parallel to the film plane. As shown in Figure 3(b), CNTs are mainly individualized in the PA matrix, even if some aggregates still remain after melt compounding.
Flame retardancy

Influence of halloysite loading. In this first part of the flammability results, cone calorimeter tests have been performed on PA plates coated with a nanocomposite film of 200 μm containing different clay concentrations (16 and 30 wt.% HNTs). HRR profiles are presented in Figure 3.

Figure 2. SEM micrograph of PA/(PA-H30 350 μm) at a magnification of 2000×.
SEM: scanning electron microscopy; H: halloysite nanotubes; PA: polyamide.
The dashed line indicates the boundary between virgin PA matrix and PA-H30 nanocomposite film. Red circles underline HNTs aggregates.

Figure 3. TEM micrographs of (a) PA-H30 nanocomposite film of 350 μm at a magnification of 2300× and 10,000× (inset); (b) PA-C2 nanocomposite at a magnification of 16,000×.
TEM: transmission electron microscopy; PA: polyamide.

Flame retardancy

Influence of halloysite loading. In this first part of the flammability results, cone calorimeter tests have been performed on PA plates coated with a nanocomposite film of 200 μm containing different clay concentrations (16 and 30 wt.% HNTs). HRR profiles are presented in
Figure 4. Heat release rate as a function of time for neat PA, PA-H4-W nanocomposite and PA/(PA-H 200 μm) samples with various halloysite loadings (external heat flux = 50 kW/m²). PA: polyamide.

Table 2. Cone calorimeter data of pure PA, PA-H4-W nanocomposite and PA plates coated with PA-H films of 200 μm containing different amounts of clay. Tests were conducted at an external heat flux of 50 kW/m².

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
<th>pHRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Residue (w%) (±0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>47 ± 4</td>
<td>724 ± 29</td>
<td>83 ± 5</td>
<td>0.0</td>
</tr>
<tr>
<td>PA-H4-W</td>
<td>48 ± 4</td>
<td>568 ± 21</td>
<td>72 ± 2</td>
<td>3.7</td>
</tr>
<tr>
<td>PA/(PA-H16 200 μm)</td>
<td>42 ± 3</td>
<td>529 ± 14</td>
<td>75 ± 2</td>
<td>0.6</td>
</tr>
<tr>
<td>PA/(PA-H30 200 μm)</td>
<td>58 ± 2</td>
<td>520 ± 16</td>
<td>74 ± 3</td>
<td>1.1</td>
</tr>
</tbody>
</table>

pHRR: peak of HRR; THR: total heat released; HRR: heat release rate; PA: polyamide.

TTI – time to ignition was determined as the time at which the HRR first increased to 25 kW/m².

Figure 4 wherein the curve of the conventional PA-H4-W nanocomposite is included for comparison.18 The most important flammability parameters (TTI, pHRR, THR and final residue) are gathered in Table 2. When the polymer matrix is covered with a thin film of PA-H16, the pHRR is already reduced by 27%. However, there is no further decrease in pHRR with increasing filler fraction up to 30 wt.%. Interestingly, pHRR values of surface-coated samples are slightly lower than that of PA-H4-W nanocomposite, although the total amount of clay is only of 1 and 1.9 wt.% for PA/(PA-H16) and PA/(PA-H30), respectively. A change in the shape of HRR curves is detected for the hybrid systems, especially for the nanocomposite film with 30 wt.% HNTs. After a fast increase in HRR following ignition, the slope of the curve of PA/(PA-H30) decreases before reaching its peak value.

Based on visual observations during cone experiments, the combustion process of the surface-coated specimens is a bit slowed down thanks to the rapid formation of an
inorganic-rich layer at the surface of the burning material. Optical photographs of the cone calorimeter residues are shown in Figure 5. While an ‘island-like’ morphology is observed during burning of PA-H4-W nanocomposite (Figure 5(a)) with poor insulating properties, a thin continuous layer appears at the surface of hybrid samples in the early stages of combustion. This latter results from the degradation of the nanocomposite film throughout the pre-ignition period leaving the clay particles behind. The protective layer mainly consists of a net-like structure of HNTs with a small amount of thermally stable organic components (i.e. carbonaceous residue). Surprisingly, the final residues of the hybrid samples differ a lot in appearance depending on the clay fraction in the PA film. At intermediate loading (16 wt.% HNTs, Figure 5(b)), the protective coating exhibits poor mechanical resistance under the internal pressure exerted by the degradation products. Several large cracks are observed during cone experiments leading to a discontinuous layer covering only partially the underlying material.

In contrast, the protective shield formed at the sample surface of PA/(PA-H30 200 μm) (Figure 5(c)) displays higher physical strength thanks to the mechanical reinforcement
brought by the higher amount of aluminosilicate nanotubes, and hence can impede the formation of cracks caused by vigorous bubbling of low viscous PA. However, the inorganic-rich char skin is very thin, highly flexible and becomes progressively inflated by the volatile species (Figure 5(d)). Therefore, it behaves as a temporary reservoir of flammable gases causing side shrinkage and the formation of preferential pathways at the extremities of the sample holder for the out-diffusion of fuel to the flame zone.

The TTI of virgin PA does not seem to be significantly affected by the presence of PA-H16 nanocomposite film at the surface of the polymer substrate, as previously reported for classical PA-H nanocomposites. However, ignition is slightly slowed down for PA/(PA-H30 200 µm) because of the accumulation of the combustible degradation products below the bell-shaped thin layer.

In terms of the THR, there is no relevant difference between hybrid samples, classical nanocomposite and reference matrix. The slight decrease in THR for filled PA systems may be attributed to a dilution effect of the inorganic minerals, indicating that the physical barrier reduces only the fire intensity without decreasing the total amount of combustible material. This is confirmed by the mass of the final residues, which is very close to the initial halloysite content in the composite systems.

Based on these preliminary results, the next step of this work is to evaluate the influence of nanocomposite film thickness on the formation and mechanical properties of the protective layer, for a given halloysite concentration of 30 wt.%.

**Effect of film thickness.** Figures 6(a) and (b) shows, respectively, the HRR and mass loss curves of PA, PA-H16-W nanocomposite and three PA plates coated with PA-H30 nanocomposite films of different thicknesses. The respective cone data are listed in Table 3. The TTI of hybrid systems increases by approximately 10 s compared to both the unfilled material and the highly loaded nanocomposite. However, this parameter remains unchanged with increasing film thickness from 200 to 500 µm.

As previously mentioned, the presence of the nanocomposite films at the surface of the PA substrate reduces the pHRR. Moreover, the use of a thicker film further enhances the flame retardancy of the hybrid structures through an additional decrease in pHRR combined with a shift of the mass loss towards longer burning times. For example, the pHRR drops from 520 to 402 kW/m² and the combustion time is delayed by about 70 s with increasing film thickness from 200 to 350 µm. Nevertheless, the superposition of both HRR and mass

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI (s)</th>
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<tr>
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<td>48 ± 3</td>
<td>348 ± 8</td>
<td>60 ± 1</td>
<td>14.2</td>
</tr>
<tr>
<td>PA/(PA-H30 200 µm)</td>
<td>58 ± 2</td>
<td>520 ± 16</td>
<td>74 ± 3</td>
<td>1.1</td>
</tr>
<tr>
<td>PA/(PA-H30 350 µm)</td>
<td>60 ± 3</td>
<td>402 ± 12</td>
<td>66 ± 4</td>
<td>2.3</td>
</tr>
<tr>
<td>PA/(PA-H30 500 µm)</td>
<td>57 ± 2</td>
<td>362 ± 20</td>
<td>63 ± 4</td>
<td>3.5</td>
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</tbody>
</table>

pHRR: peak of HRR; THR: total heat released; HRR: heat release rate; PA: polyamide.

TTI – time to ignition was determined as the time at which the HRR first increased to 25 kW/m².
loss curves for PA plates coated with nanocomposite films of 350 and 500 μm points out the existence of a critical thickness above which there is no additional improvement in the fire resistance of the polymeric material.

An influence of film thickness on the shape of HRR curves is also noted. Indeed, the tendency of HRR profiles to follow a two-step increase is more obvious at 350 and 500 μm. The first increase corresponds to the rapid build-up of a ceramic char-inorganic layer once

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**Figure 6.** (a) Heat release rate and (b) mass loss as a function of time for neat PA, PA-H16-W nanocomposite and PA plates coated with PA-H30 films of various thicknesses (external heat flux = 50 kW/m²). PA: polyamide.
the specimen is ignited. Figure 7(a) shows an optical photograph of PA/(PA-H30 350 μm) just after ignition. The black layer observed at the sample surface confirms that charring occurs and leads to the formation of a coherent inorganic-rich carbonaceous residue, which inflates under the intensive bubbling of evolved degradation products. Once formed, the protective layer reduces heat and mass transfer between the flame and the substrate. Both the thermal degradation of the polymer and the emission of volatile products are slowed down (Figure 6(b)), and heat is released over a much longer period (Figure 6(a)). However, its efficiency is not enough to inhibit the combustion process due to some side shrinkage (Figure 7(b)) increasing the exposure of the organic material to the external environment. Therefore, the small shoulder in the HRR curve is instantly followed by a second increase up to the maximum value (pHRR, Figure 6(a)).

The higher fire retardant performance of thicker nanocomposite films is ascribed to the larger amount of HNTs available for the formation of a continuous network protective layer with superior mechanical strength. Rigid nanofillers reduce the flexibility of the thin char skin, keeping it at least partially from moving out of the sample holder when subjected to fuel pressure. This tougher layer retards the combustion process without stopping it. The entire polymer does eventually burn and the residual mass of hybrid samples corresponds to the initial inorganic content.

Moreover, it seems that there is an optimum thickness (≈ 350 μm) of the PA-H30 nanocomposite films regarding the extent to which the flammability behaviour of the hybrid structures can be improved. In order to explain this observation, the nanocomposite film can be regarded as the superimposition of a large number of extremely thin and independent layers characterized by the same dispersion state of the aluminosilicate nanotubes. Upon exposure to the cone heater, the temperature of the top layer first increases up to its onset decomposition temperature, releasing flammable products in the gas phase and leaving the clay nanotubes behind. This is immediately followed by the thermo-oxidative degradation...
and/or pyrolysis of the second layer with the progressive accumulation of nanofillers on the molten polymer surface. Next, the third one starts to decompose and so on. In this sequential degradation process, each layer gradually contributes to the build-up of an inorganic-rich layer until the entire surface of the burning material is covered. Based on this simplified physical mechanism, it is reasonable to expect that, for a certain HNTs content in the polymer film, there is a critical thickness required for the formation of a continuous protective barrier with optimal mechanical properties to avoid cracking or any other disturbance caused by bubbling; the higher the clay fraction in the nanocomposite film, the lower the required thickness (for constant dispersion state). At still higher thickness, hybrid samples behave more and more like conventional nanocomposites, where HNTs from the bottom part of the film do not contribute during the pre-ignition period to the formation of the insulating layer. Once formed, the inorganic-rich char skin inflates under the fuel pressure, while nanoparticles in excess are transported to the external surface by vigorous bubbling of evolved degradation products and are pushed away from the bursting area. Their local accumulation does not allow an effective reinforcement of the barrier properties, with no further decrease in flame intensity.

The comparison between the classical nanocomposite approach and this innovative concept of hybrid materials shows additional interesting effects. The HRR curve of the PA-H16-W nanocomposite (Figure 6(a)) has a maximum value close to those reported for PA plates coated with thick PA-H30 films (Table 3), but the total combustion time is severely shortened (300 s instead of 400 s for PA/(PA-H30 350 μm)). It must be emphasized that 16 wt.% HNTs are required to obtain such level of fire performance in a ‘bulk’ nanocomposite, whereas only 3.1% total mass fraction of halloysite is used in the polymer coated with a nanocomposite film of 350 μm. This observation again supports the suggestion that hierarchically designed materials are more effective than conventional ‘bulk’ nanocomposites to flame retard polymeric materials while reducing the global filler loading, that is, the cost of the final product.

The above-proposed mechanism for the build-up of a clay-rich surface layer can easily explain the differences in terms of fire behaviour observed between the two configurations. A simplified schematic illustration of the combustion process is illustrated in Figures 8(a) and (b) for a classical nanocomposite and a hybrid material, respectively. Based on the assumption that the total nanofiller concentration is the same in both systems, the mechanisms that play a role in the physical barrier formation are a little different.

During combustion of polymer–clay nanocomposites, an inorganic barrier is gradually formed at the sample surface by a combination of ablative reassembling and migration of the nanoparticles (Figure 8(a)). However, alongside the positive role played by rising bubbles as carriers for nanoclay migration, their bursting at the surface of low viscous polymer melt propels the accumulated nanofillers outward from the bursting area resulting in the formation of island-like floccules with uncovered region. The size of the protective floccules increases progressively as the degradation front moves forward into the material. Therefore, a non-negligible amount of polymer must be sacrificed to enable the build-up of a uniform protective layer shielding the entire surface of the residual material.

In contrast, the highly loaded nanocomposite film coated on the surface of a bulk polymer starts to decompose upon heating and is rapidly transformed into a continuous thin layer made of a net-like structure of aluminosilicate nanotubes with a small amount of carbonaceous char (Figure 8(b)). As a consequence, a physical barrier is provided in a shortened time reducing the amount of sacrificial resin. Although the negative effect of bubbling reported
for conventional nanocomposites does not affect the development of the clay-reinforced char skin, it inflates the insulating layer during burning through the storage of volatile products at the sample surface. As a consequence, the protective coating adopts progressively a bell-like shape and creates preferential pathways at the extremities of the sample holder for the release of flammable gases. An optimized thickness of the highly loaded nanocomposite film can mitigate such adverse effect. In order to upgrade the fire performance of these hierarchical materials, it could also be appropriate to tailor the physical properties (e.g. melt viscosity) of the polymer substrate as well as the mechanical resistance of the clay-containing shield. This will be the aim of the following section.

**Influence of melt viscosity.** In the field of fire retardant polymer nanocomposites, melt viscosity of the resin has been found to be a key parameter controlling the bubbling intensity during the combustion process, and hence the formation of a continuous insulating layer.\(^{21}\) Vigorous bubbling can be suppressed by increasing melt viscosity at high temperatures using higher molecular mass polymer and/or nanoparticles with large aspect ratio via the formation of a percolated network structure in the material.\(^{8,27}\) As an example, Kashiwagi et al. have shown that the bursting of gas bubbles at the sample surface of polypropylene can be prevented by adding only 1 wt.% well-dispersed CNTs through the formation of a net-like protective layer covering the entire surface without any cracks.\(^7\)

In this work, 2 wt.% CNTs have been incorporated in the PA substrate. HRR and mass loss curves of the PA-C2 nanocomposite uncoated and coated with a film of PA-H30 350 \(\mu\)m are presented in Figures 9(a) and (b), respectively. Table 4 summarizes the flammability parameters monitored during cone calorimeter measurements.

Results show that the ignition time of the conventional PA-C2 nanocomposite increases a little and the pHRR is significantly reduced by about 55% in comparison with the unfilled matrix. The longer TTI of the PA-C2 nanocomposite is believed to result from two
phenomena working against each other. On one hand, the presence of CNTs may change the heat absorption characteristics of the polymer matrix. Incident radiation emitted by the cone heater may be absorbed and/or scattered by CNTs located near the sample surface increasing the decomposition rate of the top layer, which translates into shorter TTI. On the other hand, the thermal conductivity of the PA plate is expected to increase with increasing CNTs loading. Heat is mainly transferred by conduction from the external surface to the

Figure 9. (a) Heat release rate and (b) mass loss as a function of time for neat PA, PA-C2 nanocomposite and different surface-laminated samples with a nanocomposite film of 350 μm (external heat flux = 50 kW/m²). PA: polyamide.
interior of the sample delaying the ignition of the material. It has been found that the thermal conductivity of PP/multi-walled CNTs nanocomposites becomes the dominant factor governing the ignition process at filler concentrations above 1 wt.%.

Therefore, a mass fraction of 2% CNTs in the PA matrix is expected to slow down the ignition of the volatile products.

During cone experiments, a protective layer is formed on the surface of PA-C2, slowing the escape of volatile products, with consequent reduced mass loss rate (Figure 9(b)). However, several cracks appear in the shield at relatively early time (Figure 10(a)) and

### Table 4. Cone calorimeter data of neat PA, PA-C2 nanocomposite and different PA-based plates covered with a nanocomposite film of 350 µm. Tests were conducted at an external heat flux of 50 kW/m².

<table>
<thead>
<tr>
<th>Samples</th>
<th>TTI a (s)</th>
<th>pHRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Residue (w%) (± 0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>47 ± 4</td>
<td>724 ± 29</td>
<td>83 ± 5</td>
<td>0</td>
</tr>
<tr>
<td>PA/(PA-H30 350 µm)</td>
<td>60 ± 2</td>
<td>402 ± 12</td>
<td>66 ± 4</td>
<td>2.3</td>
</tr>
<tr>
<td>PA-C2</td>
<td>60 ± 2</td>
<td>325 ± 20</td>
<td>83 ± 2</td>
<td>3</td>
</tr>
<tr>
<td>PA-C2/(PA-H30 350 µm)</td>
<td>99 ± 7</td>
<td>233 ± 12</td>
<td>82 ± 3</td>
<td>4.8</td>
</tr>
<tr>
<td>PA-C2/(PA-H30-C2 350 µm)</td>
<td>109 ± 7</td>
<td>229 ± 14</td>
<td>72 ± 4</td>
<td>8.5</td>
</tr>
</tbody>
</table>

pHRR: peak of HRR; THR: total heat released; HRR: heat release rate; PA: polyamide.

aTTI – time to ignition was determined as the time at which the HRR first increased to 25 kW/m².

Figure 10. Optical photographs taken after ignition, during combustion and at the end of cone calorimeter tests for PA-C2 nanocomposite and PA-C2 plates covered with two different nanocomposite films of 350 µm (external heat flux = 50 kW/m²).

PA: polyamide.
become progressively deeper and wider. These cracks offer pathways to combustible gases, and bubbling is observed in the unprotected regions of the burning material. As a result, the protective layer gradually loses its continuous structure with only few island-like particles remaining at the end of the test (Figure 10(a)). This behaviour can be ascribed to the partial aggregation of CNTs in the initial morphology of the PA-C2 nanocomposite (Figure 3(b)). Aggregates cannot contribute to the formation of a continuous net-like structure, and areas with low density of individualized nanotubes provide sites for crack initiation. This result is in good agreement with the work of Kashiwagi et al., which has shown that the initial degree of dispersion of the nanofiller controls the physical process in the condensed phase.33

Interestingly, the coating of PA-C2 with a film of PA-H30 350 µm causes a further decrease in the flame intensity by 13%, that is, a total reduction in pHRR of 68%, with the same amount of heat released over a longer period of time (Figure 9 and Table 4). Moreover, ignition is substantially postponed (99 s instead of 47 s for virgin PA), probably thanks to the combined advantages of the higher thermal conductivity of the PA substrate brought by CNTs and the temporary fuel reservoir formed at the external surface by the inorganic-rich skin. Cone results can be interpreted based on visual observations of the specimen throughout the test. As shown in Figure 10(b), the clay-containing layer resulting from the nanocomposite film degradation still blows, but in this case without moving out of the sample holder. As mentioned above, the presence of CNTs in the PA plate mitigates the bubbling process, and hence, reduces the internal pressure exerted on the protective shield. The final residue confirms the absence of side shrinkage in PA-C2/(PA-H30) as compared to the reference matrix coated with the same nanocomposite film (Figure 7(c)). This is reflected in the plateau observed on the HRR curve (Figure 9(a)) after the initial increase ascribed to the build-up of the homogeneous protective layer.

A last formulation has been developed by combining CNTs and HNTs in the nanocomposite film coated on the PA-C2 substrate. The idea is to reduce the flexibility of the thin protective layer, that is, increase the melt viscosity of the nanocomposite film, through the formation of a solid-like interconnected network structure composed of both nanofillers. As shown in Figures 9(a) and (b), cone calorimeter results are practically identical between the two PA-C2 samples with and without CNTs in the coating covering their surface. Nevertheless, visual observations of the combustion experiments indicate that the presence of CNTs in the nanocomposite film significantly affects the structural and mechanical properties of the protective layer during the test. Figure 10(c) shows that a continuous and flat layer is formed on the surface of PA-C2/(PA-H30-C2) during heating and prior to ignition. CNTs with high aspect ratio are expected to form a jammed network in the char layer, increasing its mechanical strength and thus preventing its swelling observed for PA-C2/(PA-H30) (Figure 10(b)). However, the shield loses rapidly its barrier properties with the creation and propagation of cracks under the stress due to external environment and internal pressure of degradation gases. The residue at the end of the test is very brittle and looks like a carbonaceous-silicate material (Figure 10(c)) with a slightly higher amount of char than that formed during burning of PA-C2/(PA-H30) (Table 4).

As a conclusion of this section, a suitable amount of CNTs (<2 wt.%) has to be incorporated in the nanocomposite film in order to enhance the fire performance of coated PA plates through the mechanical reinforcement of the inorganic-rich layer in a way that cracking is prevented. In other words, a balance is required between, on one hand, rigidity to avoid shrinkage and, on the other hand, flexibility to allow the shield to better accommodate the stress and hinder crack formation.
Conclusion

PA samples have been coated with highly loaded halloysite-based nanocomposite films and their fire behaviour under forced flaming conditions has been compared to that of homogeneous ‘bulk’ nanocomposites. Four major conclusions emerge from this research.

First, the fire retardancy of PA-H nanocomposites can be substantially improved through the elaboration of hierarchically designed materials where well-dispersed nanoparticles involved in the physical barrier formation are initially located at the exposed surface of the specimen. Above a certain level of clay content in the nanocomposite film, this configuration enables the rapid build-up of a uniform inorganic-rich layer covering the entire surface of the burning material. Once formed, the protective coating limits heat and mass transfer between the flame zone and the substrate, which translates into reduced flame intensity with the same amount of heat released over a much longer period of time.

Second, there is an optimum thickness for the highly loaded PA-H nanocomposite films (350 μm) regarding the extent to which the fire resistance of the polymeric material can be improved. In other words, a critical amount of aluminosilicate nanotubes is required to create a coherent carbonaceous-silicate layer preventing crack formation and also limiting any other disturbance caused by vigorous bubbling of low viscous polymer melt (e.g. swelling of the char skin under the internal pressure of flammable gases). Above this critical thickness, there is no further contribution of additional HNTs to the barrier properties of the insulating layer.

Third, the addition of a small amount of CNTs in the PA substrate can mitigate the bubbling process by increasing the melt viscosity of the condensed phase. As a consequence, the escape of volatile species is slowed down and the protective layer, subjected to lower internal pressure, is prevented from moving out of the sample holder.

Finally, CNTs may also be used as nanoreinforcement to reduce the flexibility of the thin protective skin through the formation of a solid-like interconnected network structure. However, results indicate that a suitable amount of nanofiller has to be found in order to improve the mechanical strength of the shield while preserving enough flexibility to accommodate the stress (i.e. fuel pressure) and hinder crack formation.

This work clearly demonstrates that hybrid structures are more effective than conventional nanocomposites to flame retard polymeric materials while dramatically reducing the total nanofiller content and hence, the production cost. Moreover, there is every reason to believe that this methodology can be extended to other types of nanoparticles and polymer resins, in particular to char-forming polymers for the sacrificial nanocomposite film.

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