"Elaboration of poly(lactic acid)/halloysite nanocomposites by means of water assisted extrusion: structure, mechanical properties and fire performance"

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ABSTRACT

Poly(lactic acid) (PLA)/halloysite nanotube (HNT) nanocomposites were prepared using a water assisted extrusion process. Morphology, structure, thermomechanical properties and flame retardant properties of these nanocomposites were compared to those obtained in the case of nanocomposites obtained via the conventional extrusion process. Whatever the synthesis route used, mechanical tests indicate that HNTs have a reinforcing effect ascribed, at least partially, to the dispersion of the HNTs in the PLA matrix. Differential scanning calorimetry also shows that HNTs improve PLA crystallization and play the role of a nucleating agent. Moreover, cone calorimeter experiments show a drastic improvement in the reaction to fire of PLA when HNTs are added, especially at high filler content. This improvement arises from the fact that HNTs induce the formation of a protective inorganic layer at the surface of the sample. As the main results of this study, it has been shown that water assisted extrusion not only induced a better dispersion of the HNTs into the matrix but also that this process prevents polymer degradation during the extrusion. This unusual effect has been ascribed to a barrier effect of the water molecules that preferentially locate at the HNT–matrix interface. Even if not fully explained, it could be ascribed to a decrease in local shear levels (mechanochemical effect) and/or to a decrease in the catalytic effect of the HNT surface (chemical effect). Consequently this study reveals that water-assisted extrusion is a reliable route to prepare PLA/halloysite nanocompo...

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Elaboration of poly(lactic acid)/halloysite nanocomposites by means of water assisted extrusion: structure, mechanical properties and fire performance

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Poly(lactic acid) (PLA)/halloysite nanotube (HNT) nanocomposites were prepared using a water assisted extrusion process. Morphology, structure, thermomechanical properties and flame retardant properties of these nanocomposites were compared to those obtained in the case of nanocomposites obtained via the conventional extrusion process. Whatever the synthesis route used, mechanical tests indicate that HNTs have a reinforcing effect ascribed, at least partially, to the dispersion of the HNTs in the PLA matrix. Differential scanning calorimetry also shows that HNTs improve PLA crystallization and play the role of a nucleating agent. Moreover, cone calorimeter experiments show a drastic improvement in the reaction to fire of PLA when HNTs are added, especially at high filler content. This improvement arises from the fact that HNTs induce the formation of a protective inorganic layer at the surface of the sample. As the main results of this study, it has been shown that water assisted extrusion not only induced a better dispersion of the HNTs into the matrix but also that this process prevents polymer degradation during the extrusion. This unusual effect has been ascribed to a barrier effect of the water molecules that preferentially locate at the HNT–matrix interface. Even if not fully explained, it could be ascribed to a decrease in local shear levels (mechanochemical effect) and/or to a decrease in the catalytic effect of the HNT surface (chemical effect). Consequently this study reveals that water-assisted extrusion is a reliable route to prepare PLA/halloysite nanocomposites with enhanced properties.

Introduction

Poly(lactic acid) (PLA) is an aliphatic polyester obtained from renewable resources such as sweet corn and sugar beets. PLA exhibits many interesting physico-chemical properties, such as high strength, biocompatibility, thermoplastic grease and oil resistance, and an excellent aroma barrier.1–4 Consequently this polymer is foreseen to be a good candidate for the replacement of petroleum based polymer in some applications. However, this polymer suffers from a lack of good properties that could increase its number of applications. PLA in particular exhibits poor fire resistance properties and a lower elastic modulus than poly(ethylene terephthalate) (PET) or poly(styrene) (PS).3 One of the ways to address this lack of properties is the formation of nanocomposites. This technology, consisting of incorporating into the polymer matrix inorganic fillers having at least one nanometric size, has attracted increasing interest since the pioneering work carried out by Toyota’s research group, which has revealed that the incorporation of only a few percent of nanofiller can strongly improve the material’s properties.6–9 This strategy has been largely applied to the case of PLA in the past and there are currently a large number of studies devoted to the synthesis and characterization of PLA nanocomposites.

Up to now most of the synthesised nanocomposites are based on fillers, organically modified or not, that have a platelet like shape, such as layered silicates. The reported studies indicate that the incorporation of MMT into PLA can improve its properties, such as its mechanical or permeability properties. For example Sinha Ray et al. have shown that the flexural modulus of PLA can be increased from 17% to 27%, depending on the surfactant used, when 4 wt% organomodified Montmorillonite or mica is added.10 In the same way Chiu et al. showed that adding 7 wt% carbon nanotubes increases the elastic modulus by 20%.11 More generally, a review of the works dealing with the synthesis and characterization of polymer

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nanocomposites reveals that the degree of improvement in properties strongly depends on both the achieved dispersion state of the filler and, secondly, on the affinity between the polymer and the matrix. Particularly high dispersion and strong affinity between the filler and the matrix will lead to the greatest property enhancement. In addition to the improvement in mechanical properties previously discussed, the synthesis of nanocomposites can also drastically enhance the fire resistance properties. For this purpose fillers that act as flame retardants are currently used, as they may involve a significant improvement in the fire retardation properties.\textsuperscript{12-14} Regarding other kinds of fillers, recent studies have shown that filling PLA with clays or carbon nanotubes can also improve their fire resistance properties. For example Murariu \textit{et al.} report a decrease of 35% of the peak of Heat Release Rate (pHRR), accompanied by the formation of a char when 3 wt% of Cloisite30B is added to PLA\textsuperscript{15} and a decrease by 30% when 6 wt% of expandable graphite is added.\textsuperscript{16}

Recently, a “new type” of inorganic filler emerged and is increasingly studied: the halloysite nanotubes (HNTs). Halloysite is a naturally occurring aluminosilicate (Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}(OH\textsubscript{2}) \cdot 2H\textsubscript{2}O) with a predominantly hollow tubular structure mined from natural deposits in countries such as America, China, New Zealand, France and Belgium.\textsuperscript{17} Halloysite exhibits high elastic modulus\textsuperscript{18} and unique surface chemical property due to the multi-layer structure with only a few hydroxyl groups located on the surface of the nanotubes.\textsuperscript{19} As compared to other layered silicates, halloysite can thus be easily dispersed in a non-polar polymer matrix like polypropylene (PP) due to weak secondary interactions among the nanotubes.\textsuperscript{20} Moreover the high polarity of the polyamide (PA) matrix enables to obtain efficient dispersion of the nanotubes by formation of H-bonds between polymer and filler.

During the past years an increasing number of research groups have studied the elaboration and characterization of polymer nanocomposites based on HNTs.\textsuperscript{21-24} Most of the publications were devoted to the elaboration and study of mechanical properties of polymer/halloysite composites. Besides it was reported a significant improvement of tensile strength, tensile modulus and elongation at break at low HNTs content.\textsuperscript{19,21-26}

Recently, several studies have been focused on the elaboration and characterization of PLA based HNTs nanocomposites. All these works report that adding HNTs into PLA involves an enhancement of mechanical properties and thermal stability\textsuperscript{27-29} while thermal properties such as glass transition of crystallization kinetics remains mostly unaffected. For example, Wu \textit{et al.}\textsuperscript{30} reported an increase of about 20% of the tensile modulus when 7 wt% of HNTs is added. The reinforcing effect was correlated to the high aspect ratio, excellent dispersion and high intrinsic stiffness of the nanotubes. These works also indicate that a better dispersion degree and consequently a higher properties enhancement was achieved with the use of surface treated HNTs.\textsuperscript{30-32} Finally, regarding the effect of HNTs on the barrier properties, reported results indicate a slight enhancement of water barrier and gas properties.\textsuperscript{32,33}

In addition to the reinforcing effect, the incorporation of halloysite may also improve the fire retardation properties.\textsuperscript{34} For example Marney \textit{et al.} have shown, in the case of Polyamide 6, that halloysite nanotubes influence the fire resistance due to the fact that a thermal insulation barrier is developed at the surface of the composite during combustion. This barrier acted to retard burning (high decrease of heat release rate) without stopping it and more than doubled the total burning time (to be compared to the slow burning of a candle). The same behavior was observed by Lecouvet \textit{et al.} on PP/halloysite nanocomposites.\textsuperscript{35} In their study, authors show that the incorporation of HNTs into polypropylene (PP) can drastically enhance the fire resistance properties of PP, only if the HNTs are well dispersed. To achieve this goal they use the water assisted extrusion route, which allows access to a better dispersion of HNTs as compared to conventional routes.\textsuperscript{36} The synergistic effect of injecting water during the extrusion process on the dispersion degree of the filler has already been demonstrated, mainly in the case of nanocomposites based on polyamides.\textsuperscript{37-39}

Consequently, in this study, it is proposed to elaborate and to characterize PLA nanocomposites based on HNTs, using the water assisted extrusion process. Water assisted extrusion process has been used with the aim of improving the dispersion degree of the HNTs into the PLA matrix. For the sake of comparison, nanocomposites elaborated using a conventional extrusion process, \textit{i.e.} without water injection, were also studied. On the one hand particular attention has been paid to finely characterizing the morphology and the structure of the elaborated nanocomposites. On the other hand mechanical, rheological and fire resistance properties, as well as the thermal stability of PLA, were studied in order to give the structure property relationships of these materials. The influence of the HNT content has also been studied.

**Experimental**

**Materials & elaboration**

The PLA investigated in this work, containing 4.3 mol% \(\nu\)-isomer units (grade 4042D), was purchased from Natureworks (USA). Halloysite nanotubes were purchased from Sigma Aldrich (Germany) and used without any chemical modification. Typical specific surface area of this halloysite is 64 m\(^2\) g\(^{-1}\); cation exchange capacity 8 meq. g\(^{-1}\); pore volume 1.25 ml g\(^{-1}\); and specific gravity 2.53 g cm\(^{-3}\).

The PLA nanocomposites were synthesised by melt blending in a co-rotating twin-screw extruder Coperion Mega Compounder WP ZSK25 (\(L/D = 40\)). Water, when used, was pumped into the extruder in the high compression zone. The special design of the screw allows the pressure to increase up to 125 bars in this zone, which prevents water evaporation. The water is degassed in the transport zone and fully removed using a vacuum pump. The processing temperature, the throughput (TP), the screw speed (SP) and the water injection rate (W) were adapted to the particular experiment. A more detailed description of this process is available elsewhere.\textsuperscript{40-41} The synthesis conditions used in this study are listed in Table 1.
Nanocomposites filled with HNTs, with contents varying from 0% to 17 wt%, have been synthesised. Structural and morphological characterizations were performed on the as-extruded pellets. Mechanical and fire retardation property characterizations were carried out on compression molded samples from 0.5 mm thick and 3 mm sheets, respectively, molded at 190 °C under 90 bars. Prior to compression molding, the pellets were dried at 50 °C under vacuum for 12 h. For the sake of clarity, samples will be denoted PLA-HX-W, where X represents the weight percentage of halloysite content and W the fact that water was injected during the extrusion.

### Molecular weight determination

Average molecular weight ($M_w$) of both the pellets and extruded materials were measured by Size Exclusion Chromatography (SEC). A waters 2695 separation module equipped with a waters filter guard column and three PLgel 5 μm (100 A, 10^4 A and 10^5 A pore sizes) 300 × 7.5 mm^2 columns as well as a differential refractometer, were used for $M_w$ determination. Tetrahydrofuran (THF, Biosolve, stabilized with butylhydroxytoluene) was used as the mobile phase at a heating rate of 10 °C min^-1. SEC calibration was undertaken using polystyrene (PS) standards and using universal calibration standards. Data acquisitions were performed by Waters Millennium software. Prior to analysis, solutions were filtered through 0.45 μm filters (Millex FH – Millipore).

### Structural characterization

Wide-Angle X-ray Scattering (WAXS) analyses were carried out using Genix micro-source equipment (Xenocs, France) operating at 50 kV and 1 mA. The Cu Kα radiation used ($\lambda = 1.54$ Å) was selected with a curved mirror monochromator (Fox2D-121Inf, Xenocs). Analyses were carried out on the 0.5 mm thick solid molded samples in transmission mode. WAXS patterns were recorded on a 2D CCD VHR camera (Photonic science), the distance between sample and detector (D) being set at 7 cm for WAXS. The working distance was calibrated using silver behenate as standard. Standard corrections such as distortion, dark current subtraction and background correction were applied before analysis. The 2D WAXS patterns obtained were then azimuthally integrated using the fit2D software.

### Morphology characterization

Samples morphologies and dispersion degree of the HNTs into the PLA matrix were characterized at different scale levels by means of Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

OM micrographs were obtained by means of a binocular optical microscope Olympus AX41 equipped with a numerical camera Olympus DP12. The examined area of the produced composites was prepared from a ±0.5 mm thin film cut from the elaborated pellets using a razor blade. Micrographs of the samples were taken with a magnitude of 10 to provide an actual visual representation of the samples. Degree of clay dispersion and exfoliation were examined by means of SEM and TEM. SEM analyses were carried out on cryofractured samples using a LEO 982 (Zeiss) SEM operating at 1 kV. The TEM micrographs were recorded using a CM30 (Phillips) transmission electron microscope operating at 300 kV. The analyzed samples were thin films, having thickness of approximately 70 nm, micromotned from bulk samples at room temperature using a Leica Reichert FCS microtome and collected on a 300 μm^2 mesh copper grid.

### Thermal properties

Thermal properties were determined by means of Differential Scanning Calorimetry (DSC) on a Pyris Diamond apparatus from Perkin Elmer. The 10 mg samples, placed into aluminium pans, were scanned at a heating rate of 10 °C min^-1 under nitrogen gas flow. The temperature and heat flow scales were calibrated using a high purity indium sample according to standard procedures. The crystalline weight fraction was computed from the enthalpy of the melting exotherm using the specific enthalpy of fusion of the perfect crystal, $\Delta H_m = 94$ J g^-1 [ref. 42] for PLA.

The thermal stability of the materials was studied by Thermo Gravimetric Analysis (TGA). The analyses were performed using a TGA/SDTA 851e (Mettler-Toledo, Switzerland). Samples of about 13 mg were heated from room temperature to 600 °C at a constant heating rate of 10 °C min^-1 under a nitrogen atmosphere with a flow rate of 100 ml min^-1. TGA results are presented as temperatures at 10% weight loss (T10). This temperature is usually considered as the onset of the degradation.

### Mechanical behavior

Uniaxial tensile tests were carried out using an Instron machine Model 4466. The dumbbell specimens of 22 mm and 5 mm in gauge length and width were cut out from the 0.2 mm thick sheets and strained at a constant crosshead speed of 50 mm min^-1, i.e. an initial strain rate $\dot{\varepsilon} = 3 \times 10^{-2}$ s^-1. Five specimens were tested for each blend and experimental condition. The yield stress, $\sigma_y$, is defined at the stress overshoot prior to necking at room temperature (RT). The strain at break, $\varepsilon_{break}$, is defined as the ratio of the sample length at break to the initial gauge length of the sample.
Fire properties

The cone calorimeter tests were carried out using a FTC (Fire Testing Technology) Mass Loss Calorimeter following the procedure defined in ASTM E 906. The equipment is similar to the one used in oxygen consumption cone calorimetry. The only difference is the use of a thermopile at the top of the chimney to measure the heat release rate (HRR) instead of employing the oxygen consumption principle. The specimens (100 x 100 x 3 mm$^3$) were irradiated in a horizontal position by an external flux of 50 kW m$^{-2}$ and the flame ignition was initiated using a spark igniter. The flammability parameters considered in this study are: heat release rate (HRR), peak of heat release rate (PHRR), total heat release (THR), residue and the time to ignition (TTI). The cone data reported in this paper are based on the average of three replicated experiments and are reproducible with variation less than 10%.

Results

Molecular weight determination

The thermo-mechanical properties of PLA are highly sensitive to its molecular weight. Thus the influence of both the processing conditions used and the HNT content on the molecular weight were studied. Fig. 1 depicts the evolution of the weight average molecular weight ($M_w$) as a function of the clay content for samples elaborated with and without water injection during the extrusion.

Regarding unfilled materials, it appears that extruded samples exhibit a lower $M_w$ as compared to the PLA pellets ($M_w \approx 205$ kg mol$^{-1}$). This decrease of $M_w$ is explained by thermal and/or mechanical degradation of PLA that induces chain scissions during the extrusion process. Worth noting is that this degradation is more pronounced in the case of water assisted extrusion, indicating a negative effect of adding water in the case of unfilled PLA. This stronger decrease of $M_w$ probably arises from hydrolysis of the PLA chains by the water molecules.

Regarding the HNT filled materials, it appears on the one hand that in the case of conventional extrusion, $M_w$ steadily decreases with increasing HNT content. This result, ascribed to an increase of thermomechanical degradation in the presence of filler has previously been reported and ascribed to the catalytic effect of the clay$^{45,46}$ and also probably arises from a local overheating, induced by shear concentrations. On the other hand, in the case of water assisted extrusion, it appears, surprisingly, that (i) $M_w$ is not affected by the presence of the HNTs and (ii) $M_w$ for the filled materials is higher than that of the unfilled sample. This result is unusual as much as PLA is known to suffer from hydrolytic degradation$^{47}$ and also due to the fact that, as observed in the case of conventional extrusion, the presence of HNTs also promotes polymer degradation. This point will be discussed later in the manuscript.

Morphological & structural characterizations

A key parameter that governs the thermo-mechanical properties of polymer nanocomposites is the dispersion state of the filler. In order to assess the presence of agglomerates, the nanocomposites were first observed by means of Optical Microscopy (OM). Characteristic pictures of the morphology are reported in Fig. 2.

Regarding the nanocomposites having a HNT content of 4 wt%, no aggregates were detected, whether water was injected or not during the extrusion (pictures not shown here). This may suggest that a good dispersion state is achieved in both cases. For higher HNT contents, OM micrographs indicate that some aggregates are still present in the material. Worth noticing is that the number of visible aggregates having micronic sizes is lower in the case of the nanocomposites extruded with water. To support this point, the morphology of the nanocomposites was observed by SEM.

SEM micrographs depicted in Fig. 3 show the morphology of PLA nanocomposites at low (4 wt%) and intermediate (8 wt%) HNT loadings. A homogeneous distribution of the clay is achieved for PLA-H4 systems, whatever the processing route (Fig. 3a and b). Most of the tubes (i.e. white spots) are well individualized into the organic matrix without any significant trace of aggregation. At 8 wt% HNTs, a heterogeneous structure is present.

![Fig. 1](image1.png) Molecular weight as a function of both filler content for PLA nanocomposites extruded with and without water injection.

![Fig. 2](image2.png) Optical micrographs of (a) PLA-H8, (b) PLA-H17, (c) PLA-H8-W and (d) PLA-H17-W.
observed in nanocomposites elaborated by classical extrusion due to the presence of more aggregates (Fig. 3c). Interestingly, the use of water during melt compounding improves the nanoscale dispersion of halloysite, as revealed by the higher density of single nanotubes in PLA-H8-W nanocomposite (Fig. 3d) as compared to the reference system (Fig. 3c).

Finally to get a local representation of the nanocomposites morphologies, TEM analyses were carried out with the aim of finely characterizing the dispersion degree of the HNTs as a function of both the clay content and the process used. Micrographs representative of the microstructure of the nanocomposites having clay contents of 8 and 17 wt% synthesised with and without water injection are reported in Fig. 4.

TEM analyses confirm the previous SEM and OM results. To summarize, while at 4 wt% of clay the HNTs are fully exfoliated, some aggregates are still present at higher clay content. Moreover, the beneficial effect of injecting water during the extrusion is clearly highlighted as the exfoliation degree at clay contents above 4 wt% is somewhat higher for the water-assisted extruded nanocomposites.

Finally, structural characterization was performed by means of WAXS. Integrated intensity profiles computed from the 2D WAXS patterns are reported in Fig. 5.

Regarding the filler, HNT exhibits two main diffraction peaks at $2\theta = 12.5^\circ$ and $2\theta = 20.5^\circ$, assigned to the diffraction of $d_{101}$ planes. Unfilled materials exhibit both a broad diffusion scattering and no diffraction peaks, indicating the amorphous character of the neat materials. For the nanocomposites a broad diffusion scattering characteristic of an amorphous material is also observed, whatever the clay content and the process used. Indeed the two peaks at $2\theta = 12.5^\circ$ and $2\theta = 20.5^\circ$, visible on the intensity profiles, are attributed to the diffraction from HNTs and are not related to any crystalline phase of PLA. In summary all the materials in this study are amorphous.

**Rheological properties**

The storage modulus ($G''$) and complex viscosity ($\eta^*$) of neat PLA and its nanocomposites prepared with or without water
injection are logarithmically plotted as a function of angular frequency in Fig. 6a and b, respectively. At the measuring temperature of 180 °C and in the frequency range $10^{-2}$–$10^{2}$ rad s$^{-1}$, the pure polymer exhibits a Newtonian behaviour characterized by a slope of 2 for $G'$ (i.e. $G' \propto \omega^2$) and a plateau for $\eta^*$ in the low frequency region. On the contrary, no terminal regime is observed for the nanocomposites at low frequencies, even at the lowest filler concentration (4 wt% HNTs). $G'$ increases with increasing clay fraction and a plateau is observed starting from 17 wt% HNTs. This latter indicates a transition from a liquid-like to a solid-like behaviour resulting from the formation of a percolated network structure, wherein interactions between well-dispersed nanotubes start to dominate the relaxation process. Moreover, it is well-known that the viscoelastic properties of composites at high frequencies are directly related to the polymer terminal relaxation and hence to the molecular weight of macromolecules.

Compared to neat PLA, nanocomposites show lower moduli and viscosities at high frequencies associated with shorter relaxation times of polymer chains, especially for the highly loaded conventional formulations synthesised without water. This observation is in good agreement with results obtained from SEC measurements, confirming that the hydrolysis of PLA can be effectively prevented only when combining water injection and HNTs.

### Thermomechanical properties

Thermal properties of the nanocomposites have been analyzed by means of DSC. Thermograms recorded upon the 2nd heating for PLA and its nanocomposites extruded with and without water are reported in Fig. 7.

Upon heating, a cold crystallization occurs in the 110 °C–130 °C temperature range, followed by a double melting peak around 155 °C. This double melting peak has already been reported in the case of PLA and is ascribed to a phase transformation phenomenon. Indeed, below 120 °C it is the defective $\alpha'$ crystalline form that is induced and at around 150 °C this phase melts and transforms into the $\alpha$ stable crystalline form. Calculations of the initial crystallinity show that all the samples were initially amorphous, confirming the WAXS results.

Nucleating effect of the filler was assessed by the study of isothermal crystallization kinetics. Fig. 8 reports the crystallinity evolutions as a function of time for PLA-H0-W and PLA-H17-W samples isothermally crystallized at $T = 110$ °C.

It appears that nanocomposites exhibit faster crystallization kinetics than the unfilled samples. Indeed while the half crystallization time $t_{1/2}$ is reached after 60 min and 30 min for PLA-H17-W and PLA-H17, respectively, half of the crystallization is not attained after 120 min for the PLA-H0-W sample. This demonstrates the nucleating effect of the HNTs on the PLA crystallization. Furthermore the faster crystallization kinetics of the PLA-H17 sample as compared to that of the PLA-H17-W sample can be ascribed to the lower molecular weight of the sample extruded without water injection.

Particular interest has also been paid to follow the evolution of the glass transition temperature ($T_g$). The values of $T_g$ for the different materials, calculated from the DSC thermograms, are reported in Fig. 9.
...while PLA-H17-W nanocomposites.

In other words it seems that the values of weight. Consequently it is assumed that the evolutions of the behavior was observed for the evolution of the molecular injection. It is worth noting that the same kind of increasing HNT content for the materials fabricated without water injection. This can be explained by the fact that there are few interactions between the HNT surface. Indeed DSC results previously discussed suggest a slight increase of mechanical properties is observed may arise from the non-organomodification of the HNT surface. Indeed DSC results previously discussed suggest few interactions between the filler and the matrix.

Moreover, it appears that this rigidity increase is relatively low as compared to the morphology of the nanocomposites that are nearly exfoliated. The main explanation for this result is that HNTs, due to their particular cylindrical structure, have a fairly low weight-specific area ratio as compared to platelet like fillers such as Cloisite or Montmorillonite (MMT). Indeed while the specific area of MMT is about 600–700 m² g⁻¹, the specific area of HNTs is around 60 m² g⁻¹, i.e. about 10 times lower. Taking into account the fact that this specific area is a key parameter that will govern the gain, in terms of mechanical properties, the moderate enhancement of mechanical properties observed in this study has to be relativized. As an example, in the case of exfoliated nanocomposites, a HNT content of 10 wt% is equivalent to 1 wt% MMT in terms of specific area.

**Thermal stability**

Thermal stability of neat PLA and its nanocomposites was investigated by TGA analysis. Fig. 10 presents TGA curves of the different samples under nitrogen at a heating rate of 10 °C min⁻¹ and the inset table summarizes the respective onset decomposition temperatures (T10). The thermal degradation of PLA is widely documented in the literature and takes place primarily through intramolecular trans-esterification with the formation of the monomer unit (i.e. lactide), but also cyclic oligomers, acetaldehyde, ketene, carbon dioxide and carbon monoxide. As it can be seen from Fig. 10, the thermal stability of PLA decreases monotonically with increasing clay content regardless of the synthesis conditions used. As an example, T10 drops from 343 °C for neat PLA to 328 °C and 327 °C when...
8 wt% HNTs are added, without or with water injection, respectively. This observation may be ascribed to a catalytic action of halloysite on the pyrolysis of PLA due to the presence of Brønsted acid sites (i.e. Si–OH and Al–OH) on the external surface of the clay. Such catalytic effect of clay nanoparticles has already been discussed in the literature for the thermal degradation of PLA and polypropylene.

Fire resistance performance

The small-scale mass loss calorimeter was used to evaluate the role of halloysite on the flammability of PLA. HRR curves for reference and nanocomposites are shown in Fig. 11. The time to ignition (TTI), peak of heat release rate (pHRR), time to pHRR, total heat released (THR) and mass fraction of the residue are gathered in Table 3. The TTI does not seem to be affected by the presence of the aluminosilicate nanotubes, while the pHRR decreases continuously with increasing clay fraction. Moreover, a further reduction in the pHRR is achieved by using water-assisted extrusion. As an example, the incorporation of 17 wt% HNTs in PLA reduces the pHRR by about 29% and 43%, respectively, for samples prepared without and with water injection. This result is consistent with the structural investigation which highlights a beneficial effect of water on the clay dispersion (it was previously shown that high nanodispersion improves the fire resistance performance of the material). The slight reduction of THR for nanocomposites may be ascribed to a dilution effect of the clay, since the relative decrease in THR and the mass of the cone calorimeter residues correspond approximately to the initial inorganic content in the PLA matrix.

The mode of action of HNTs as flame retardant additives has already been detailed in a previous work as a combination of physical processes taking place in the condensed phase and including barrier, heat sink and fuel dilution effects. First, the presence of HNTs in the organic matrix enables the formation of an inorganic-rich layer at the sample surface during combustion through a combination of ablative reassembling of the nanotubes. This latter shields the underlying material from the external environment and limits the mass transport between condensed and gas phases. Second, the endothermic decomposition of halloysite absorbs a part of the external heat, keeping the surrounding material cooler, but also dilutes the fuel concentration through the release of water vapour. However, the cooling and dilution effects of HNTs are believed to contribute to a lesser extent to the flame retardancy of polymeric materials, due to the far lower global energy required by their endothermic transitions compared to conventional metal hydroxides.

Fig. 12 presents the residue aspect of PLA-H-W nanocomposites after the cone calorimeter test. At low and intermediate clay concentrations (Fig. 12a), an inhomogeneous layer is formed at the surface of the condensed phase during burning. This latter, characterized by a combination of grey island-like floccules surrounded by uncovered areas, results from the bursting of gas bubbles at the sample surface, propelling the accumulated nanotubes outward from the bursting zone. The size of the protective floccules increases progressively with increasing clay fraction, leading to the formation of a uniform inorganic layer covering the entire sample surface at 17 wt% HNTs (Fig. 12b). The structural integrity of the protective layer is well preserved during combustion, with only a few cracks observed under the pressure exerted by volatile decomposition products. Therefore, the high effectiveness of the inorganic layer may be ascribed to its good barrier properties, slowing down the escape of flammable volatiles and hence reducing the flame intensity (i.e. pHRR).

Discussion

It was shown that using the water assisted extrusion process has a positive effect on the dispersion of the HNTs into the PLA matrix, resulting in improved performance materials. This is particularly highlighted by considering that the fire resistance...
performance of the materials is clearly better for the nanocomposites synthesised with water as compared to the ones fabricated via the conventional route. Another unexpected effect of using the water assisted extrusion process pointed out in this study is that it prevents thermomechanical degradation of PLA. A similar effect was observed in the case of a copolyetheramide copolymer.\textsuperscript{69}

More precisely, the thermodegradation effect encountered in the presence of HNTs in the case of conventional extrusion doesn’t occur if water is added. Otherwise when no HNTs are added the presence of water involves a degradation of the PLA chains. Thus it seems that even if water involves an “expected” degradation of PLA when extruded alone, this negative effect is inhibited by the presence of HNTs. To explain this point, it can be assumed that water molecules preferentially locate at the interface between the polymer and the HNTs. This preferential location arises from the high hydrophobicity of the surface of the HNTs, due to permanent negative charges, which exerts an attractive effect on the water molecules. This leads to the formation of hydrogen bonds.\textsuperscript{60}

The first implication of this is that water molecules are trapped on the HNT surface. This preferential location of water molecules can even lead to the creation of a kind of phase separation between, on the one hand, HNT surrounded by water and, on the other hand, neat PLA, hence avoiding molecular contact between water and PLA.

As a consequence, a first possible explanation of the observed “stabilization” phenomenon is of mechanochemical origin. It can be assumed that this “water-rich” second phase, including the HNTs, exerts a lubricant effect. This implies a decrease of the local shear stress concentration around the nanotubes, which prevents mechano-cisions of PLA chains. Such a lubrication phenomenon was already observed in the case of block copolymers leading to less degradation.\textsuperscript{66}

A second possible explanation is of chemical origin. As demonstrated by de Jong et al.,\textsuperscript{40} the hydrolysis of PLA is strongly dependent on the pH of the medium, with a minimum degradation rate at pH around 4.5 (ref. 60). While at more acidic pH the PLA degrades by acid-catalyzed ester hydrolysis, meaning polymer chain random scission, at pH values above 4.5 it degrades by cyclization at polymer end groups (“back-biting”), with elimination of the lactide cyclic dimer leading to a kind of depolymerization (unzipping). The first random mechanism leads to a fast decrease in molecular mass, with the production of acid end-groups by hydrolysis, while the second one does not. Hence, it can be suggested that the presence of HNTs somewhat stabilizes the pH on the “back-biting” side and limits the random chain scission of PLA by ester hydrolysis. Finally another possible consequence of the presence of water molecules is that, by forming H-bonds with the HNT surface, water molecules transform the Lewis acid sites present onto the surface into Brønsted ones, the catalytic effect of the latter on PLA hydrolysis being lower than the former ones.

**Conclusions**

The present study focused on the characterization of PLA/HNTs nanocomposites synthesised by means of water-assisted extrusion. Morphology characterization revealed that the injection of water during the extrusion has a beneficial effect on the dispersion degree of the clays, even for HNT contents as high as 17 wt% where a nearly fully exfoliated morphology is observed. Besides, even if untreated HNTs were used, degrees of dispersion comparable to the ones observed in the case of surface treated HNTs are reached. This shows that water assisted extrusion eliminates the need for organomodification of clays.

Moreover, it was shown that even if HNTs are well dispersed into the PLA matrix, only a moderate increase in mechanical properties was observed. This was ascribed to the lower specific area of HNTs as compared to more conventional fillers having a platelet shape. However, fire resistance performance of PLA was significantly improved with the addition of HNTs and is explained by the formation of an inorganic layer at the surface of the sample. Finally, a key point of this study is that the
injection of water during the extrusion of nanocomposites allows us to keep the molecular weight of PLA constant with addition of HNTs, while a significant decrease in this parameter is observed in the case of conventional extrusion. Besides, it seems that the injection of water inhibits the thermal degradation process of the macromolecular chains. This positive effect of injecting water was discussed and ascribed to a preferential location of the water molecules at the surface of the HNTs, leading to a kind of phase separation.

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Notes and references


