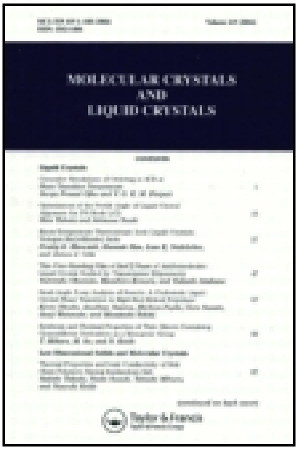

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Characterization and Reaction to Fire of Polymer Nanocomposites with and without Conventional Flame Retardants

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Characterization and Reaction to Fire of Polymer Nanocomposites with and without Conventional Flame Retardants

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In this work, the reaction to fire of polymer nanocomposites (thermoplastic polyurethane, polylactide and polyamide-6) containing different nanofillers (organoclay, polyhedral silsesquioxanes or POSS and carbon nanotube) is investigated. When high level of nanodispersion is achieved (shown by transmission electron microscopy (TEM)), they exhibit good flame retardancy in specific scenarii (high heat flux), but fail to flammability tests (LOI, UL-94). The mechanism of protection is the formation of mineral layer associated to char promotion but the protective coating is not efficient enough to provide the highest standard of protection. It is shown that this technology gives the best results combined with conventional flame retardants and leads to synergistic effects. The aspects of nanodispersion of the filler with the flame retardant are also fully commented in the paper using TEM and electron microprobe.

Keywords: carbon nanotube; electron microprobe; PA-6; PLA; POSS; reaction to fire; TEM; TPU

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INTRODUCTION

Polymeric materials are commonly used in everyday life increasing fire hazards and so flame retardants are very often incorporated into them to limit their flammability [1]. This approach is often preferred to provide low flammability to polymeric materials because it is an acceptable compromise between cost and properties. Nevertheless, the total loading lies usually between 15 and 25 wt.% to achieve acceptable performance. In some cases, it modifies the other properties of the polymers like the mechanical properties. Moreover the processing has to be done in an appropriate and limited window (temperature, shear etc.).

Of particular interest is the developed nanocomposite technology consisting of a polymer and nanoparticles because they often exhibit remarkably improved mechanical and various other properties as compared with those of virgin polymer at a loading as low as 3–5 wt.% [2]. The pioneering work of Gilman et al. has demonstrated that the presence of nanodispersed montmorillonite (MMT) clay in polymeric matrices produces a substantial improvement in fire performance [3–5]. Gilman and other groups subscribed this approach and developed hybrid polymeric materials including organomodified clays [6–9], nanoparticles of TiO_2 [10], nanoparticles of silica [11], layered double hydroxides (LDH) [12,13], carbon nanotubes (CNT) [14,15] or polyhedral silsesquioxanes (POSS) [16,17]. All those materials exhibit low flammability associated to other properties such as enhanced mechanical properties. Typically, peak of heat release rate (PHRR) is decreased by 50 up to 70% in a cone calorimeter experiment. However, UL-94 rating and limiting oxygen index (LOI) of polymer nanocomposites are poor. As an example, the peak of HRR of PA-6/clay nanocomposites is decreased by 63% compared to virgin PA-6 at $35\,kW/m^2$ [5] while UL-94 test fails (no rating) and LOI is only 23 vol.% [18].

The goal of this article is to investigate the use of nanoparticles (CNT, POSS and MMT) in different thermoplastics including polylactide (PLA), polyamide-6 (PA-6) and thermoplastic polyurethane (TPU) to achieve low flammability. The combination of them with conventional flame retardants (FR) (phosphate and phosphinate) is also evaluated to examine potential synergistic effects. The paper is organized in two main sections including the investigations of the flame retardancy of PLA, PA-6 and TPU nanocomposites, and then their combination with conventional FRs.

EXPERIMENTAL

Materials

Polymers: PLA (number average molar mass = 74500 g/mol, residual monomer content = 0.18%, D-isomer content = 4.3%, melt flow index

(190°C, 2.16 kg) = 6.61 g/10 min and density: 1.25 g/cm^3) was supplied by NatureWorks and dried overnight at 110°C before use. TPU is polyester polyurethane supplied by BASF (Elastollan C85A) as pellets and used as received. PA-6 was supplied by Rhodia (France) under the trade name Technyl S27 and was dried for 48 h at 80°C before use.

Nanoparticles: MMT originated from Southern Clay Products, Inc (Gonzales, TX – USA). The starting material, sodium-MMT, was commercially modified using methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride (Cloisite 30B). CNT are multiwall carbon nanotube (MWNT) supplied by Nanocyl (Nanocyl-7000 at 90% purity). Poly(vinylsilsesquioxane) (FQ-POSS) was supplied by Hybrid Plastics (USA) under the brand name Fire Quench.

Flame retardants (FRs): Ammonium polyphosphate or APP (Exolit AP 422, soluble fraction in water < 1wt.%) in powder was supplied by Clariant. MP200 was supplied by Ciba and is a melamine polyphosphate. Exolit OP1230 and Exolit OP1311 were supplied in powder by Clariant and are aluminum phosphinate salt and the combination of aluminum phosphinate salt with melamine polyphosphate respectively. The FRs were used as received.

Preparation of the Nanocomposites

PA-6/MMT: PA-6 was melt-mixed with the clay using a Brabender mixer running in nitrogen flow at 50 rpm and at 250°C. The clay loading (Cloisite 30B) was 5 wt.% organoclay.

PLA/MWNT and TPU/MWNT; POSS: PLA and TPU were mixed with MWNT (1 and 2 wt.%) or POSS (in TPU at 10 wt.%) at 185°C (PLA) or 180°C (TPU) using a Brabender laboratory E350 mixer measuring head (roller blades, constant shear rate of 50 rpm) for 10 min in nitrogen flow to avoid oxidation (TPU) or hydrolysis (PLA).

Polymer/FR/Nanoparticles: Polymers (PLA and TPU) were melt-mixed with the nanoparticles and the FR using the same protocol as described above. The total loading varies from 10 wt.% up to 30 wt.%.

Transmission Electron Microscopy

All samples were ultra microtomed with a diamond knife on a Leica ultracut UCT microtome, at room temperature for PLA samples and at cryo temperature (−120°C) for TPU and PA-6 samples, to give sections with a nominal thickness of 70 nm. Sections were transferred to Cu grids of 400 meshes. Bright-field TEM images of nanocomposites were obtained at 300 kV under low dose conditions with a Philips CM30 electron microscope, using a Gatan CCD camera. Low magnification images were taken at 17 000x and high-magnification images were taken at 100 000x. The materials were sampled by taking several images of various magnifications over 2–3 sections per grid to ensure that analysis was based on a representative region of the sample.

Electron Probe Microanalysis

The sample was carbon coated with a Bal-Tec SCD005 sputter coater. The electron probe microanalyzer (EPMA) using wavelength dispersive X-ray spectrometers was used to perform element analysis. The microanalytical work was carried out on a Cameca SX-100 microprobe analyser at 10 kV 40 nA for back scattered electrons (BSE) images and at 10 kV 20 nA for silicon (Si), phosphorous (P) and aluminum (Al) X-ray profiles. For the profiles, a TAP crystal was used to detect the Si and Al K_α X-rays and a PET crystal to detect the P K_α X-ray.

Fire Testing

LOI (Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics) was measured using a Fire Testing Technology instrument on sheets ($100 \times 10 \times 3\,\mathrm{mm}^3$) according to the standard 'oxygen index' test (ISO4589). It measures the minimum concentration of oxygen in a nitrogen/oxygen mixture required to just support combustion of a test sample under specified test conditions in a vertical position (the top of the test sample is ignited with a burner).

UL-94 classification was obtained on sheets ($127 \times 12.7 \times 3.2\,\mathrm{mm}^3$) according to the conditions of the standard test (ASTM D 3801) i.e. in a vertical position (the bottom of the sample is ignited with a burner). This test provides only a qualitative classification of the samples (V0, V1 and V2 labeled samples).

FTT (Fire Testing Technology) Mass Loss Calorimeter was used to carry out measurements on samples following the procedure defined in ASTM E 906. The equipment is identical to that used in oxygen consumption cone calorimetry (ASTM E-1354-90), except that a thermopile in the chimney is used to obtain heat release rate (HRR) rather than employing the oxygen consumption principle. Our procedure involved exposing specimens measuring $100\,\mathrm{mm} \times 100\,\mathrm{mm} \times 3\,\mathrm{mm}$ in horizontal orientation. External heat flux of $35\,\mathrm{kW/m}^2$ was used for running the experiments. This flux corresponds to common heat flux in mild fire scenario. The mass loss calorimeter was used to determine heat release rate (HRR). When measured at $35\,\mathrm{kW/m}^2$, HRR is reproducible to within $\pm 10\%$. The data reported in this article are the average of three replicated experiments.

RESULTS AND DISCUSSION

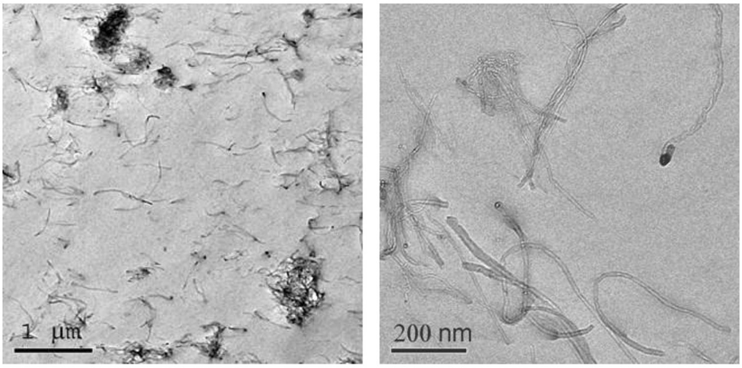
Polymer Nanocomposites

Aliphatic polyesters, and particularly PLA, currently deserve a particular attention in the area of environmentally degradable polymer materials. They are well suited for the preparation of disposable devices because of their biodegradability [19–22]. In PLA nanocomposites it was reported that this family of composites exhibits improved properties including a high storage modulus both in the solid and melt states, an increased flexural properties, a decrease in gas permeability, increased heat distortion temperature, an increase in the rate of biodegradability of pure PLA, etc . . . [23].

Kashiwagi et al. reported the first study on the flammability of polymer carbon nanotube nanocomposites [24]. They showed significant flame retardant effectiveness of polypropylene (PP)/multi-walled carbon nanotubes (MWNT) (1 and 2% by mass) nanocomposites. Concurrently, Beyer demonstrated a small improvement in flammability properties of ethylene-vinyl acetate (EVA)/MWNT (2.5 and 5% by mass) nanocomposites [25]. Based on those results, we have incorporated MWNT in PLA. Unfortunately, we have not observed any enhancement of the flame retardancy of PLA (no reduction in PHRR and no enhancement of LOI; 21 vol.% in the two cases). TEM images (Fig. 1) reveal that MWNTs aggregate and only few single MWNTs can be observed. It might explain the poor FR properties of the composites because we have shown that the highest nanodispersion of MWNTs is needed to get the best performance [26].

TPU is well known for its high performance (excellent abrasion resistance, high tensile, compressive and tear strength, good flexibility over a wide range of temperatures, good hydrolytic stability, selection of a wide range of hardness) but it exhibits as many thermoplastics poor flame retardancy. Few papers report flame retardancy of TPU nanocomposites except a recent paper of Beyer [27] showing the substantial effect of organoclay on the PHRR.

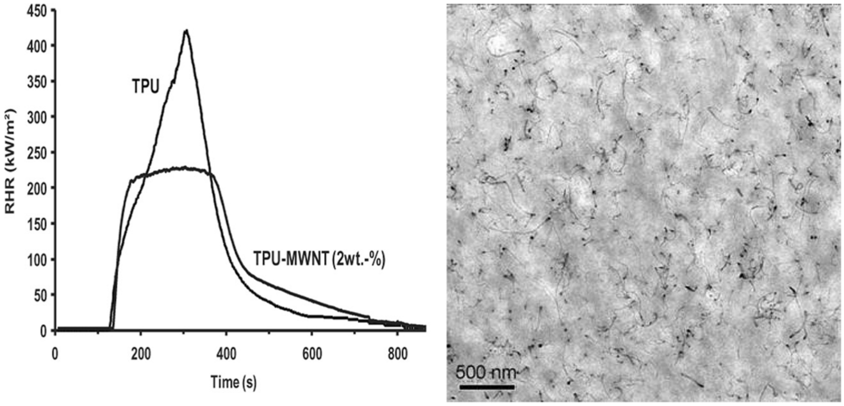
The incorporation of MWNT in TPU permits to decrease the PHRR by 50% compared to the virgin TPU (Fig. 2a) but LOI and UL-94 are not enhanced with the incorporation MWNT. TEM image reveals that MWNTs are evenly dispersed in TPU (Fig. 2b) and that many single MWNTs can be distinguished in the polymeric matrix. In this particular case, the good dispersion of MWNT in TPU might explain the good flame retardancy properties. The mode of action of CNT as flame retardant was investigated by Kashiwagi et al. [14,15,28]. They found that the shape of carbon particles appear to be important for



(a) (b)

FIGURE 1 TEM images at high magnification PLA/MWNT nanocomposites at low magnification (a) and at high magnification (b).

effectively reducing the flammability (comparison carbon black vs. MWNT) and that the flame retardant performance is achieved through the formation of a relatively uniform network-structured floccule layer covering the entire sample surface without any cracks or gaps. It is then formed a network layer acting as a heat shield to slow the thermal degradation of the polymer.

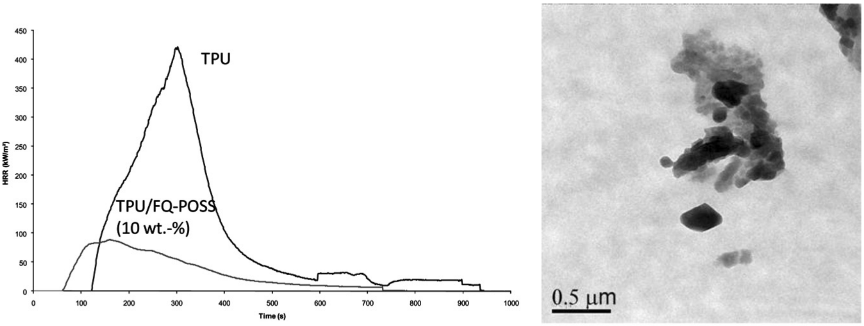


(a) (b)

FIGURE 2 HRR as a function of time of pure TPU and TPU/MWNT nanocomposite (external heat flux $= 35\,\mathrm{kW/m^2}$) (a) and TEM image of TPU/MWNT nanocomposite (b).

In a previous work [17], we have shown that TPU/POSS composite used as coating on woven PET fabrics permitted 50% reduction in PHRR. The suggested mechanism is char formation at the surface of the material which can act as an insulative barrier. Here the incorporation of 10 wt.% FQ-POSS in TPU permits to decrease by 80% the PHRR (Fig. 3a) without any significant enhancement of LOI (22 vs. 23 vol.%) and UL-94 (V-2 at 3.2 mm in the two cases). It is noteworthy that the dispersion of FQ-POSS is at the microscale and not at the nanoscale (Fig. 3b) suggesting that in this particular case the nanodispersion is not crucial to get high reduction in PHRR. Further investigations are in progress in our laboratory to explain this. The suggested mechanism is char formation at the surface of the material which can act as an insulative barrier [29]. The organic groups on POSS cages undergo homolytic Si–C bond cleavage at ~300–350°C in air. This process is immediately followed by fusion of POSS-cages to form a thermally insulating and oxidatively stable silicon-oxycarbide "blackglass" surface char ("Si–O–C ceramified char") [30].

In PA-6 nanocomposites it was reported that this family of composite exhibits improved properties including a high storage modulus both in the solid and melt states, an increased flexural properties, a decrease in gas permeability, increased heat distortion temperature [2]. Adding small amount of organoclay in PA-6 permits also significant reductions in PHRR. PHRR is decreased by 50% for PA-6/clay nanocomposite compared to virgin PA-6 (Fig. 4a). At low magnification, TEM images reveal that MMT is very well dispersed

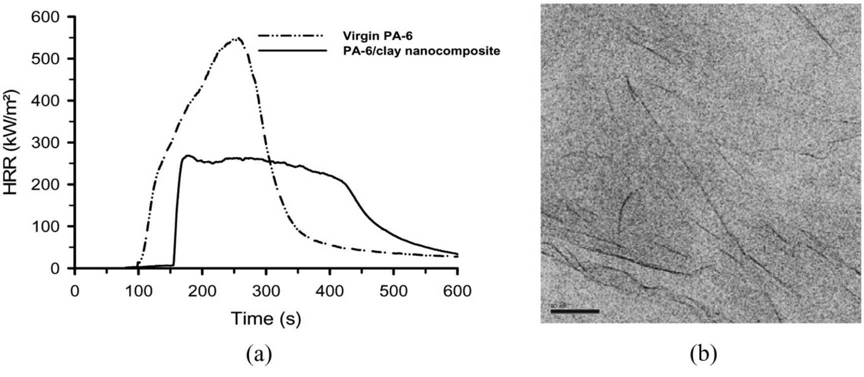


(a) (b)

FIGURE 3 HRR as a function of time of pure TPU and TPU/FQ-POSS composite (external heat flux = 35 kW/m^2) (a) and TEM image of TPU/FQ-POSS composite (b).

without formation of aggregates (not shown) and that at high magnification numerous MMT individual layers are observed suggesting an exfoliated morphology (Fig. 4b). The suggested mechanism by which clay nanocomposites function involves the formation of a char that serves as a potential barrier to both mass and heat transport [6]. A ceramic-like layer is formed at the surface of the material in which the efficiency is dependent on the homogeneity of the forming layer [31]. It was also suggested in addition to this mechanism that the clay acts as a char promoter slowing down the degradation and providing a transient protective barrier to the nanocomposite in combination with the alumino-silica barrier which arises from the clay [32].

As a conclusion of this section, we have seen that polymer (nano)-composite exhibits similar mechanism of flame retardancy. The key point is the formation of a protective charred layer lowering the heat release rate and hindering the combustion of the polymer. In one of our recent papers [33], we have drawn some conclusions about the ability of polymer nanocomposite to be considered as flame retarded polymer. When the dispersion of the filler is at the nanoscale, the resulting nanocomposite has a relatively limited contribution to fire associated with enhanced dripping behavior but it is not self extinguishing and it does not reduce the flammability of the materials (LOI, UL 94). Three parameters are then crucial: (i) the nanodispersion state, (ii) the quality and the rate of formation of the protective barrier, and (iii) the viscosity of the melt.



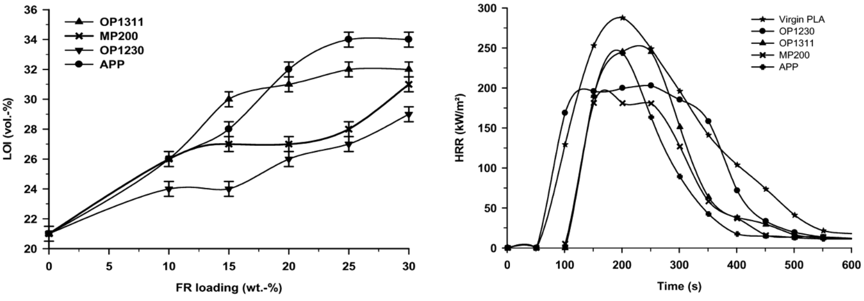
(a) (b)

FIGURE 4 HRR as a function of time of virgin PA-6 and PA-6/clay nanocomposite (external heat flux = $35\,\mathrm{kW/m^2}$) (a) and TEM image of PA-6/clay nanocomposite at high magnification (b).

Polymer Nanocomposites with Conventional Flame Retardant

As shown in the previous section, polymer nanocomposites exhibit low flammability while evaluated by cone calorimetry (sample in horizontal position) but fail to other tests, in particular those with samples in vertical position (e.g. LOI, UL-94). The purpose of this section is to investigate the combination of nanofillers with conventional FR (i) to pass conventional tests and (ii) to create potential synergistic effects.

OP series (see experimental) are FRs designed for polyamides and polyesters. As far as we know, no work reports their use in PLA. They will be compared to 'classical' FRs such as APP and MP200 in the following. LOI of the flame retarded PLA increases as a function of FR loading and jumps from 21 vol.% to 28 vol.% (PLA/OP1230) until 34 vol.% (PLA/APP) (Fig. 5a). In addition to this, all formulations exhibit V-2 rating (3.2 mm) at the UL-94 test from 10 wt.% loading but it requires 20 wt.% of MP200 and 25 wt.% of OP1311 to achieve V-0 rating (3.2 mm). PHRR is only decreased by 33% for MP200 while for the other FRs the reduction is poor (Fig. 5b). The ignition time is only improved using MP200 and APP (100s vs. 50s). Those results show that the FR performance remains relatively poor in PLA. Visually it is observed that PLA and FR PLA drip easily permitting to reach high LOI but only UL-94 V-2 rating. The poor reduction of PHRR can be assigned to the low viscosity of the FR PLA upon heating. The charred material formed by reaction between the additives and the polymer is not



(a) (b)

FIGURE 5 LOI as a function of FR amount in PLA (a) and HRR as a function of time of flame retarded PLA at 30 wt.% FR loading (external heat flux = 35 kW/m^2) (b).

viscous enough to be expanded by the fuel consisting of the degradation gases and then to make a protective coating.

In previous works [34], we showed the benefit of using MMT as synergist in intumescent (intumescence means the formation of an expanded and foamed char layer) formulations at very low loading (1 wt.%). So, MMT was evaluated in PLA/OP1311 formulations as well as MWNT because we have noticed that this latter permitted an "anti-dripping" effect in PLA. Total loading is kept at 10 wt.% and OP1311 is substituted by 1 wt.% MWNT or MMT measuring LOI and UL-94 (3.2 mm). No significant synergistic effect (in terms of LOI) is observed substituting 1 wt.% OP1311 by MMT or MWNT. All formulations remains V-2 rated but it is noteworthy that quantitatively speaking, dripping seems to be reduced.

TPU is a char former polymer and we have developed intumescent polyolefin-based formulations using TPU and PA-6 as carbonization agent combined with APP as acid source [35–38]. TPU/APP is an effective intumescent formulation in polypropylene [37,38] and for PU coating [39] and so, TPU/APP should exhibit an intumescent behavior as well. The incorporation of 30 wt.% APP in TPU provides the development of an intumescent coating when undergoing a heat flux (Fig. 6a). This intumescent char exhibits small holes at the surface but the substitution of 0.3 wt.% of APP by MWNT makes it more cohesive without holes (Fig. 6b). Measurement of the char strength (not shown) using a rheometer (see the detailed method in [40]) also indicates that TPU/APP-MWNT exhibits significant higher values than for TPU/APP.

The development of an intumescent coating (TPU/APP and TPU/APP-MWNT) permits to decrease by 75% PHRR of TPU (Fig. 7a). Note that the substitution of APP by MWNT is not beneficial in terms of PHRR but from 200 s HRR of TPU/APP-MWNT is close to zero compared to that of TPU/APP lying at 60 kW/m^2 leading to a lower total heat released (29 MJ/m^2 *vs*. 36 MJ/m^2). It can be assigned to the higher quality of the char developed from the formulation TPU/APP-MWNT (Fig. 6). Nevertheless, LOI of TPU/APP (30 vol.%) is not improved by the substitution of APP by MWNT but it permits to get V-0 rating at 3.2 mm (TPU/APP exhibits V-2 rating without MWNT). Finally, it is noteworthy that MWNTs are very well dispersed and well separated in single tubes in TPU/APP (Fig. 7b; low magnification TEM image (not shown) shows that MWNTs are evenly dispersed without agglomerate). It might explain the formation of a more cohesive char. Investigations of the potential interactions between APP and MWNT are in progress in our laboratory.

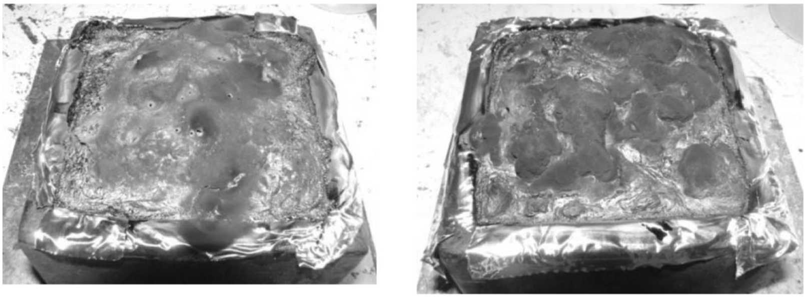
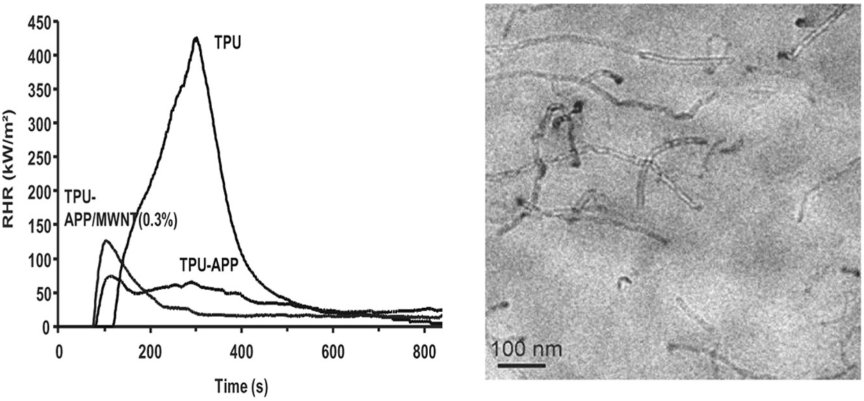

(a) (b)

FIGURE 6 Residues of TPU/APP (a) and TPU/APP-MWNT nanocomposite (b) after a mass calorimetry experiment (external heat flux $= 35\,\text{kW/m}^2$).

The incorporation of OP1311 (23 wt.% loading) in PA-6 permits to achieve V-0 rating (3.2 mm) and to reach a LOI of 29 vol.%. The substitution of OP1311 by MMT shows a slight synergistic effect; LOI jumps from 29 vol.% to 32 vol.% at 2 wt.% MMT substitution and then decreases gently to 30 vol.% at 10 wt.% MMT substitution (Fig. 8a). It is also shown on Figure 8-a, the comparison of LOI of PA-6/OP1311 and PA-6/OP1311-MMT at constant OP1311 loading (total loading remains constant equaling 23 wt.% for PA-6/OP1311-MMT and OP1311 loading decreases for PA-6/OP1311).



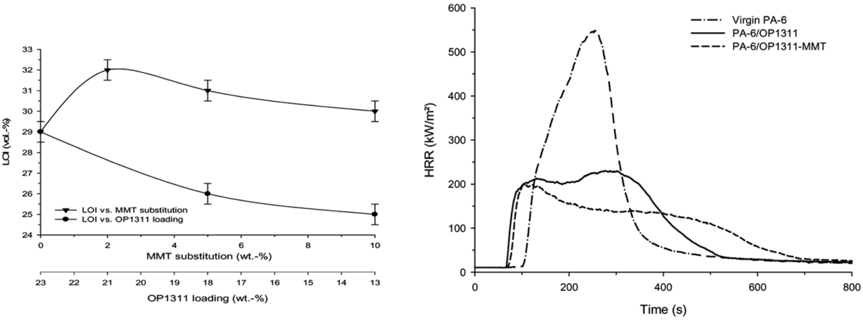
(a) (b)

FIGURE 7 HRR as a function of time of pure TPU and TPU/APP-MWNT (external heat flux $= 35\,\text{kW/m}^2$) (a) and TEM image of TPU/APP-MWNT nanocomposite (b).

In those cases, V-0 rating is achieve for all PA-6/OP1311-MMT formulations while PA-6/OP1311 containing 18 wt.% OP1311 exhibits V-1 rating and at lower loading (13 wt.%), the formulation is not rated.

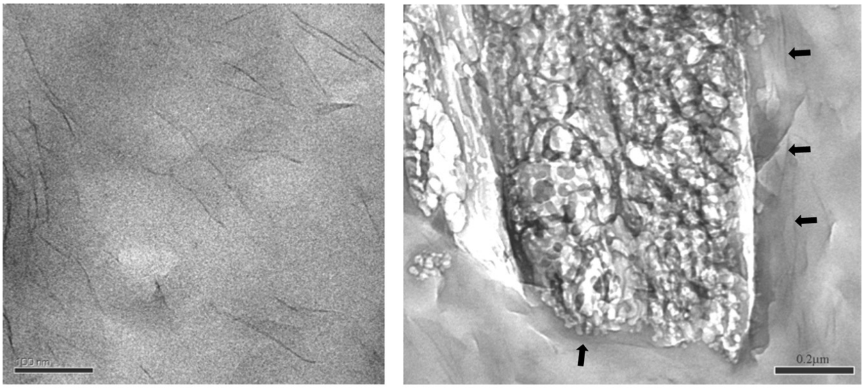
Mass loss calorimetry confirms the good FR performance of OP1311 in PA-6 (Fig. 8b). PHRR of PA-6/OP1311 and PA-6/OP1311-MMT is decreased by 60% but the time to ignition is not improved. The advantage of MMT does not appear in terms of reduction of PHRR but it permits to strongly reduce the second peak of HRR (at t ~ 300s). The first HRR peak can be assigned to the development of a protective charred layer reducing the escaping 'fuel' and the second peak to the formation of cracks in this charred layer limiting its efficiency. On the contrary, the presence of MMT in the protective layer increases its efficiency and as a consequence, HRR values are reduced and spread out over time.

TEM images show that MMT platelets are evenly and individually dispersed in PA-6/OP1311 suggesting an exfoliated structure (Fig. 9a). Nevertheless a part of them is located around the flame retardant forming a 'MMT shell-like' (Fig. 9b). To confirm this latter result, concentration profile in P, Al and Si has been recorded using electron microprobe along a line passing through both OP1311 particle and the polymer (Fig. 10a). Si is not present in the composition of OP1311 (but it is in MMT) and so, it is used as indicator of the localization of MMT platelets. Figure 10b shows as expected from TEM analysis that Si concentration jumps at the interface



(a) (b)

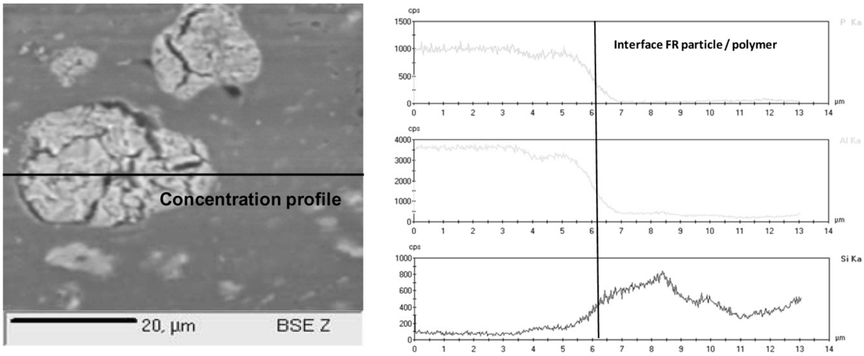
FIGURE 8 LOI as a function of MMT substitution in PA-6/OP1311 and as a function of OP1311 loading (a), and HRR as a function of time of PA-6/OP1311 with and without MMT (substitution of OP1311 by 2 wt.% MMT) at 23 wt.% total loading (external heat flux = 35 kW/m^2) (b).



(a) (b)

FIGURE 9 TEM images at high magnification showing the dispersion of MMT platelets in PA-6/OP1311 (a) and TEM image at low magnification showing a ‘particle’ of OP1311 surrounding by MMT platelets (some of them are shown by arrows) (b).

FR particle/polymer while the P and Al concentrations fall down. It demonstrates therefore that a part of MMT platelets are agglomerated around the flame retardant. This effect on the flame retardant behavior is investigating in our laboratory and will be published in a separate paper.



(a) (b)

FIGURE 10 Electron microprobe image in back scattered electrons (BSE) showing particles of OP1311 (a) and concentration profile in P, Al and Si recorded along the line (b).

CONCLUSION AND OUTLOOK

In this work, we have investigated the reaction to fire of polymer nanocomposites containing different nanofillers (i.e. organoclay, POSS and CNT). When high level of nanodispersion is achieved, they exhibit good flame retardancy in specific scenarii (high heat flux), but fail to flammability test (LOI, UL-94). The mechanism of protection is the formation of mineral layer associated to char promotion but the protective coating is not efficient enough to provide the highest standard of protection. This technology gives the best results combined with conventional flame retardants and leads to synergistic effects.

Nanofillers in flame retarded materials might offer an exceptional way for making fire safe polymers meeting the requirement of the legislation. Physical and chemical mechanisms of action should be still investigated because they are not fully understood and also, the role of the FRs on the dispersion of the nanofiller and this resulting influence on the reaction to fire of the material should be completely examined.

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