

POLYMER NANOCOMPOSITES WITH AND WITHOUT CONVENTIONAL FLAME RETARDANTS: REACTION TO FIRE AND SYNERGY

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INTRODUCTION

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 [1]-[3]. Gilman and other groups subscribed this approach and developed hybrid polymeric materials including organomodified clays [4]-[7], nanoparticles of TiO₂ [8], nanoparticles of silica [9], layered double hydroxides (LDH) [10]-[11], carbon nanotubes (CNT) [12]-[13] or polyhedral silsesquioxanes (POSS) [14]-[16]. All those materials exhibit low flammability associated to other properties such as enhanced mechanical properties. Typically, peak of heat release rate (PkHRR) is decreased by 50 up to 70% in a cone calorimeter experiment. However, UL-94 rating and 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/m² [3] while UL-94 test fails (no rating) and LOI is only 23 vol.-% [17]. It is the main goal of this paper to investigate the combination of intumescent flame retardants (phosphate and phosphinate) with nanofillers (CNT, nanoparticles of zinc oxide and MMT) in different thermoplastics including polylactide (PLA) and thermoplastic polyurethane (TPU). The paper is organized in two main sections including the investigations of the flame retardancy of PLA and TPU nanocomposites and then their combination with conventional flame retardants (FR).

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/cm³) 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.

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). Nanoparticles of ZnO were supplied by Umicore under the brand name ZANO (spherical geometry and particle size of about 30 nm). Poly(vinylsilsesquioxane) (FQ-POSS) was supplied under the brand name Fire Quench by Hybrid Plastics.

Flame retardants (FR): Ammonium polyphosphate or APP (Exolit AP 422, soluble fraction in water < 1wt.-%) in powder was supplied by Clariant. Exolit OP1311 was supplied in powder by Clariant and is the combination of aluminum phosphinate salt with melamine polyphosphate. These two flame retardants were used as received.

Preparation of the nanocomposites.

PLA/clay: PLA was melt-mixed with the clay using a counter-rotating twin-screw extruder at different shear stress (25 and 50 rpm) and at 185°C. The clay loading (Cloisite 30B; C30B) was 4 wt.-% organoclay.

PLA/MWNT and TPU/MWNT; ZnO; POSS: PLA and TPU were mixed with MWNT (1 and 2 wt.-%) or ZnO (in TPU at 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.

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 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.

Fire testing.

LOI (Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics) was measured using a Fire Testing Technology instrument on sheets (100 X 10 X 3 mm³) 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 X 12.7 X 3.2 mm³) 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 mm x 100 mm x 3 mm in horizontal orientation. External heat flux of 35 kW/m² 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 kW/m², HRR is reproducible to within ±10%. The data reported in this paper are the average of three replicated experiments.

RESULTS

PLA 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 [18]. PLA has good mechanical properties, thermal plasticity and biocompatibility, and is readily fabricated, and is thus a promising polymer for various end-use applications including packaging (e.g. food films, candy wrappers, beverage cups, bread bags ...) [19], biomedical applications such as sutures, bone screws, and scaffolding for tissue engineering [20] or infrared mask cover of notebook personal computers [21]. Of particular interest is the developed nanocomposite technology consisting of a polymer and organically modified MMT because they often exhibit remarkably improved mechanical and various other properties as compared with those of virgin polymer. In PLA nanocomposites it was reported that this family of composite materials 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... [22].

PLA/clay nanocomposites were prepared by melt blending using a counter-rotating twin screw extruder at different shear stress (25 and 50 rpm). TEM pictures at low magnification (not shown) reveal that clay is evenly dispersed in PLA and at high magnification (Figure 1) they reveal a structure with tactoids of different size. At 50 rpm, few individual MMT platelets can be detected and numerous tactoids of 3-4 layers in size can be observed. On the contrary at 25 rpm, many individual MMT platelets are observed associated with few small tactoids of 2-3 layers in size.

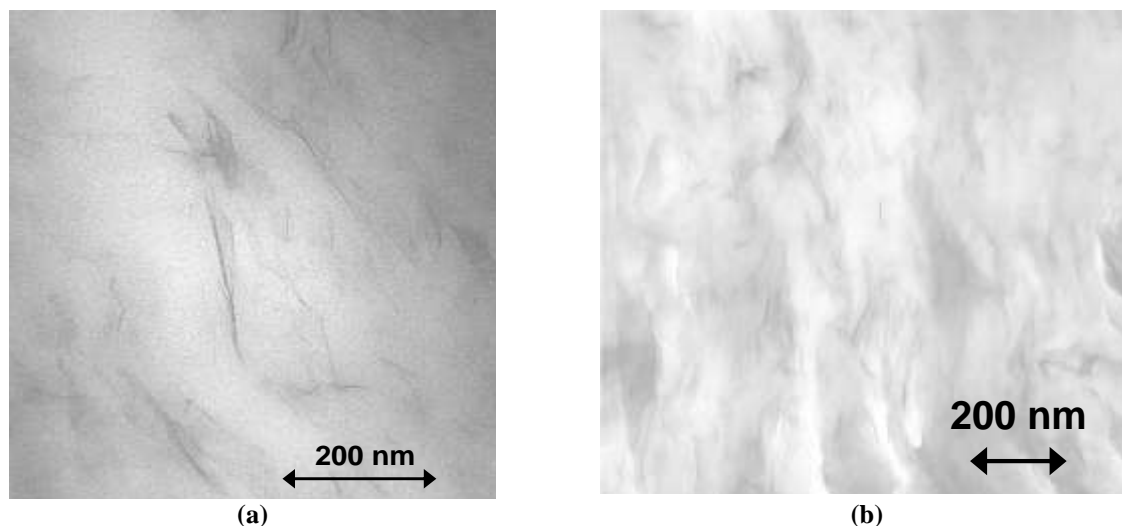


Figure 1. TEM images at high magnification PLA/ MMT nanocomposites at 4 wt.% C30B prepared with a counter-rotating twin screw extruder at 25 rpm (a) and at 50 rpm (b)

Adding a small amount of clay has been shown to reduce peak of HRR (PkHRR) for polymer nanocomposites however, to our knowledge, no published data are available for melt-processed PLA nanocomposites except our recent paper on knitted fabrics made in PLA/clay nanocomposite [23]. Figure 2 shows significant reduction in PkHRR in PLA (PLA prepared at 25 rpm) when dispersing at the nanoscale 4 wt.-% of MMT platelets. PkHRR is decreased by 40%. The suggested mechanism by which clay nanocomposites function involves the formation of a char and accumulation of minerals at the surface that serves as a potential barrier to both mass and energy transport [24]. Visually a smooth char layer is formed at the surface of the nanocomposite leaving a black char residue at the end of the experiment. In the case of pure PLA, vigorous bubbling is observed when the polymer is burning and there is no residue left at the end of the experiment.

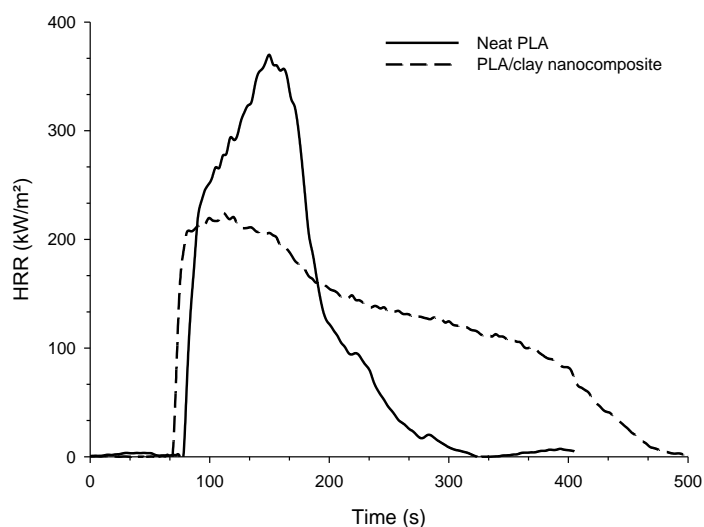


Figure 2. HRR as a function of time of pure PLA and PLA/clay nanocomposite (external heat flux= 35 kW/m²)

The incorporation of MWNT in PLA does not enhance the flame retardancy of PLA (no reduction in PkHRR and no enhancement of LOI; 21 vol.-% in the two cases). TEM images (Figure 3) 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 [25].

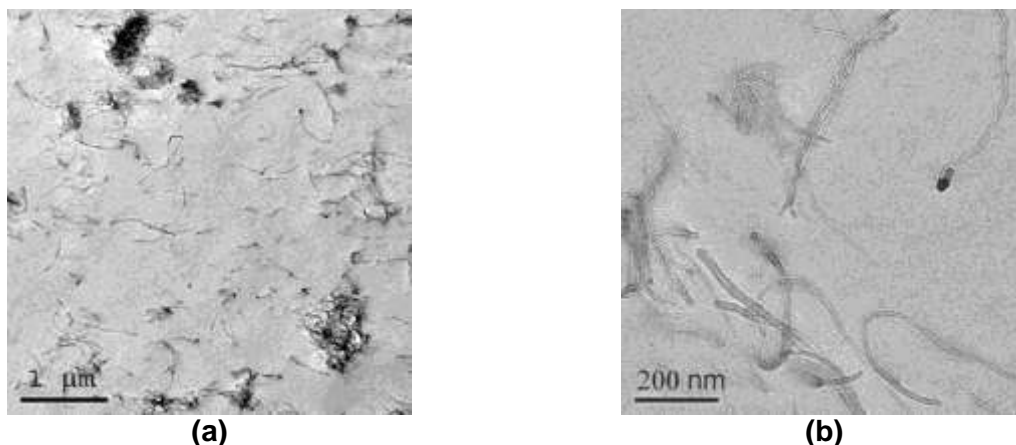


Figure 3. TEM images at high magnification PLA/ MWNT nanocomposites at low magnification (a) and at high magnification (b)

TPU nanocomposites.

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 G. Beyer [26] showing the substantial effect of organoclay on the PkHRR.

In a previous work [15], we showed that TPU/POSS composite used as coating on woven PET fabrics permitted 50% reduction in PkHRR. 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 PkHRR (Figure 4-a) 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 (Figure 4-b) suggesting that in this particular case the nanodispersion is not crucial to get high reduction in PkHRR.

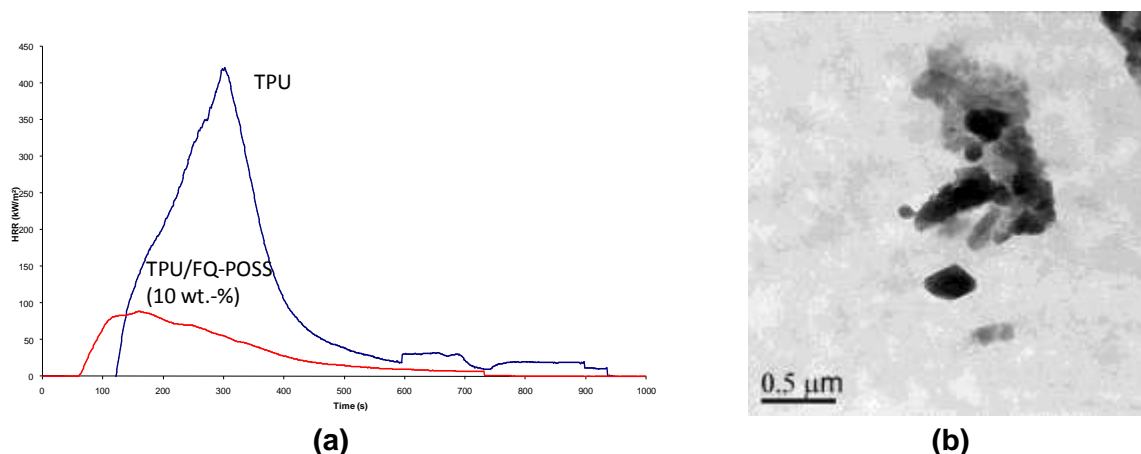


Figure 4. HRR as a function of time of pure TPU and TPU/FQ-POSS composite (external heat flux= 35 kW/m²) (a) and TEM image of TPU/FQ-POSS composite (b)

TEM image reveals that MWNTs are evenly dispersed in TPU (Figure 5-b) and that many single MWNTs can be observed in the polymeric matrix. Cone calorimetry confirms it in an indirect way since PkHRR of TPU/MWNT is decreased by 50% compared to the virgin TPU (Figure 5-a). LOI and UL-94 are not enhanced with the incorporation MWNT.

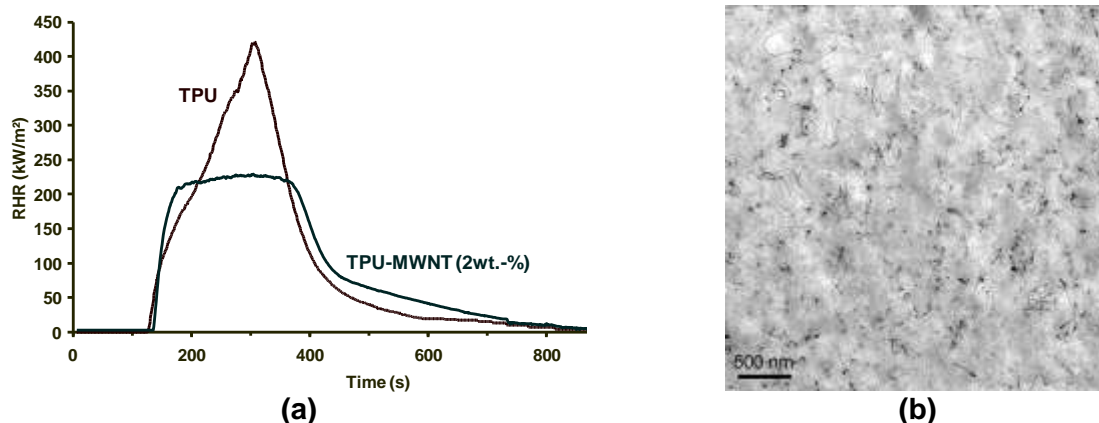


Figure 5. HRR as a function of time of pure TPU and TPU/MWNT nanocomposite (external heat flux= 35 kW/m²) (a) and TEM image of TPU/MWNT nanocomposite (b)

ZnO particles have been applied for varistors and other functional devices, and also can be used as reinforcement phase, wear resistant phase and anti-sliding phase in composites in consequence of their high elastic modulus and strength [27]. No study reports the application of ZnO nanoparticles in polymer to enhance flame retardancy but a recent work pointed out substantial enhancement of thermal stability in polyacrylate coating [27]. The incorporation of 2 wt.-% of ZnO nanoparticles in TPU does not provide any reduction of PkHRR (Figure 6-a) probably because of the relatively poor dispersion of the nanoparticles in the polymeric matrix (Figure 6-b). It is noteworthy that an intumescent behavior of TPU/ZnO composite is observed during the cone experiment (Figure 7). This intumescent coating does not provide any protection and is very crumbly. Nevertheless further development should be done to get this intumescent effect beneficial.

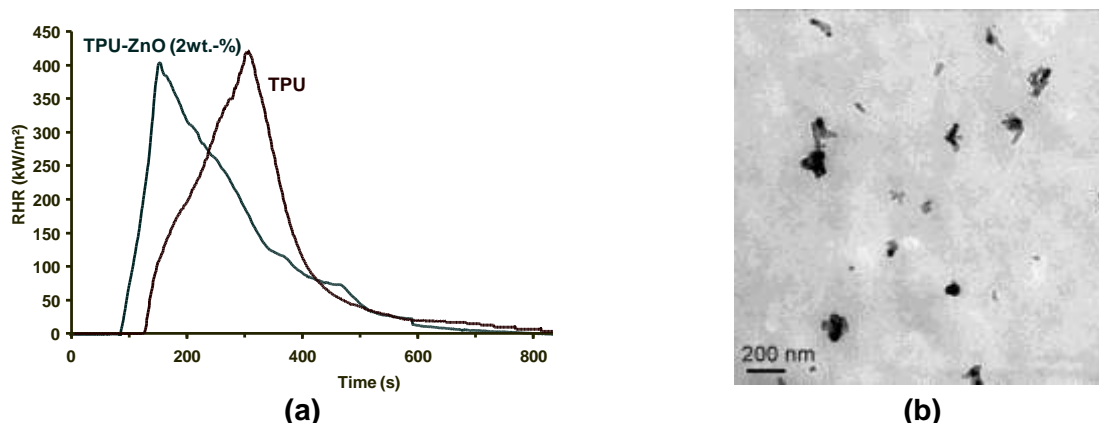


Figure 6. HRR as a function of time of pure TPU and TPU/ZnO composite (external heat flux= 35 kW/m²) (a) and TEM image of TPU/ZnO composite (b)



Figure 7. Residue of TPU/ZnO composite after a cone calorimeter experiment. Note it exhibits an intumescent behavior.

Polymer nanocomposites with conventional flame retardant.

OP1311 is a flame retardant designed for polyamides and polyesters. As far as we know, no work reports its use in PLA. LOI of the formulations PLA/OP1311 jumps from 21 vol.-% to 30 vol.-% at only 15 wt.-% OP1311 and reaches 38 vol.-% at 20 wt.-% (Figure 8). Note that LOI is not enhanced at higher loading (LOI decreases at 25 wt.-% loading compared to that at 20 wt.-%; 35 vol.-% vs. 38 vol.-%). This effect is not very clear to us and work is in progress to elucidate the mechanism of action. From visual observations, we suspect that the intumescent behavior of the formulation should provide a part of the protection. In addition to this, all formulations exhibit V-2 at 3.2 mm at UL-94 test from 10 wt.-% loading.

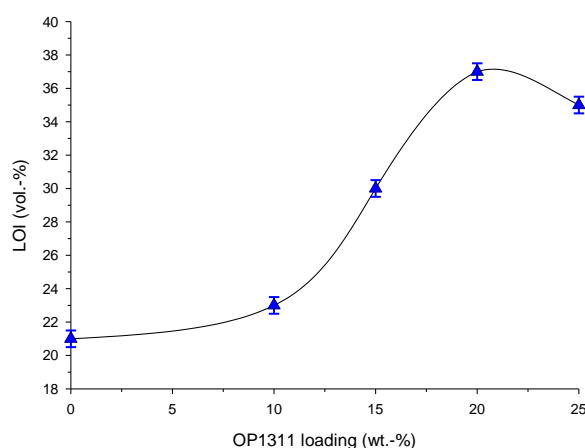


Figure 8. LOI of PLA/OP1311 as a function of OP1311 loading.

In previous works [28]-[29], we showed the benefit of using MMT as synergist in intumescent formulation. So, C30B was evaluated in PLA/OP1311 formulations as well as MWNT because we have noticed that this latter permitted an “anti-dripping” effect. Total loading is kept at 10 wt.-% and OP1311 is substituted by MWNT or C30B measuring LOI and UL-94 (3.2 mm) (Figure 9). The higher synergistic effect (in terms of LOI) is observed substituting 1wt.-% OP1311 by C30B or MWNT (LOI jumps from 23 vol.-% to 27 vol.-%). Unfortunately, all formulations remains V-2 rated but it is noteworthy that quantitatively speaking, dripping seems to be reduced. V-0 rating (3.2 mm) is only achieved at 25 wt.-% loading substituting 1 wt.-% OP1311 by C30B or MWNT in the formulations PLA/OP1311-Nanoparticles.

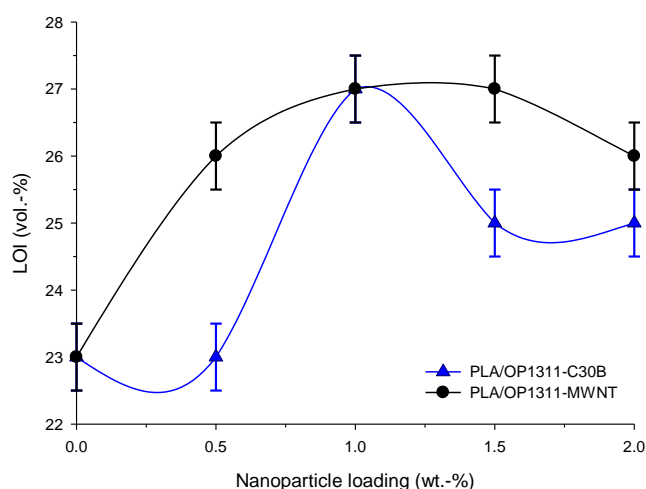


Figure 9. LOI of PLA/OP1311-Nanoparticles (C30B or MWNT) as a function of nanoparticles loading keeping constant the total loading at 10 wt.-%.

TPU is a char former polymer and we have developed intumescent polyolefin-based formulations using TPU and polyamide-6 (PA-6) as carbonization agent combined with APP as acid source [30]-[33]. TPU/APP was an effective intumescent formulation in polypropylene [32]-[33] 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 (Figure 10-a). 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 (Figure 10-b).



Figure 10. Residues of TPU/APP (a) and TPU/APP-MWNT nanocomposite (b) after a cone calorimeter experiment (external heat flux = 35 kW/m²).

The development of an intumescent coating (TPU/APP and TPU/APP-MWNT) permits to decrease by 75% PkHRR of TPU (Figure 11-a). Note that the substitution of APP by MWNT is not beneficial in terms of PkHRR but from 200s HRR of TPU/APP-MWNT is close to zero compared to that of TPU/APP lying at 60 kW/m² leading to a reduced a lower total heat released (29 MJ/m² vs. 36 MJ/m²). It can be assigned to the higher quality of the char developed from the formulation TPU/APP-MWNT (Figure 10). 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 (Figure 11-b ; 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.

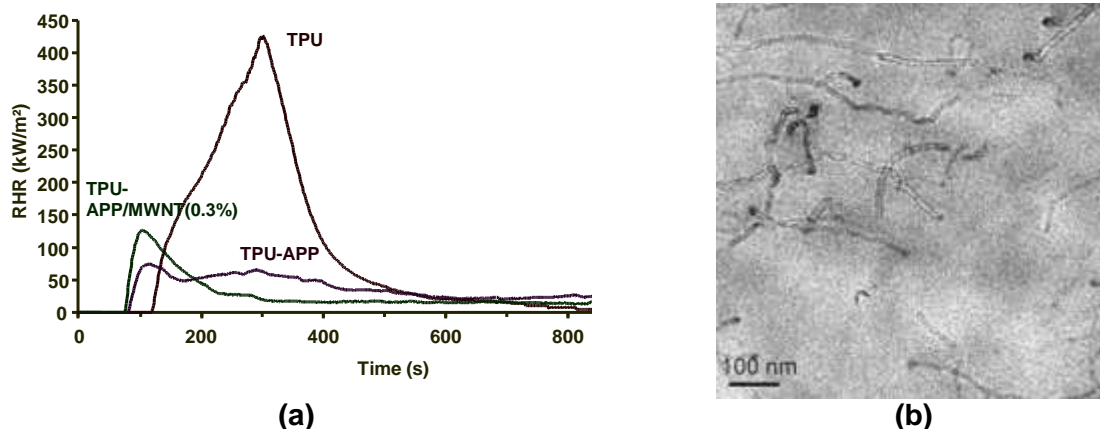


Figure 11. HRR as a function of time of pure TPU and TPU/APP-MWNT (external heat flux= 35 kW/m²) (a) and TEM image of TPU/APP-MWNT nanocomposite (b)

TPU/ZnO exhibits an intumescent behavior but associated with poor FR performance (see previous section). The idea is then to substitute partially APP by ZnO (from 1 to 5 wt.-%) in TPU/APP. PkHRR, LOI and UL-94 of TPU/APP (80 kW/m², 30 vol.-% and V-2 rating at 3.2 mm) are not improved by the substitution of APP by ZnO. The interesting feature is that the combination of APP/ZnO in TPU permits the good dispersion of small agglomerates of ZnO in TPU (Figure 12-a). Figure 12-b shows that those agglomerates are constituted by elementary particles of nanoparticles of ZnO. APP would play the role of 'compatibilizer' of ZnO in TPU. Further works are in progress to verify this.

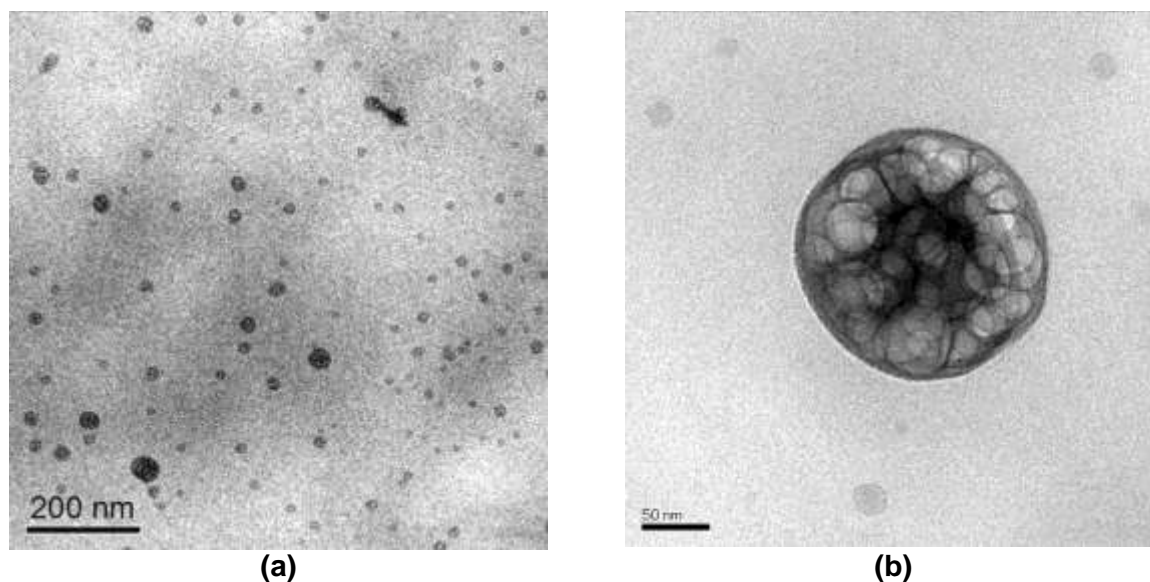


Figure 12. TEM image of TPU/APP-ZnO nanocomposite containing 25 wt.-% APP and 5 wt.-% ZnO at low magnification (a) and high magnification (b).

GENERAL DISCUSSION AND CONCLUSIONS

In this paper, we have shown that polymer nanocomposites exhibit low flammability while evaluated by mass loss calorimetry (sample in horizontal position) but fail to other tests, in particular those with samples in vertical position (e.g. LOI, UL-94). It is no longer true for TPU/ZnO but it is easily explained because of the poor dispersion of the nanoparticles. The case of TPU/FQ-POSS is very specific because FQ-POSS is an oligomer which cannot be dispersed like an organomodified nanoparticles. It acts as nanofiller in terms of FR performance but like a conventional flame retardant in terms of dispersion. In a critical paper on the flammability of layered silicate polymer nanocomposites, Scharrel et al [34] showed no relevant flame behavior enhancement at LOI and UL-94 except for the dripping which becomes limited. They proposed a mechanism of protection similar as that described above but they suggested the interesting feature that the influence of the barrier vanished for small external heat flux (like in the case of LOI and UL-94). They also noticed that the fire behavior observed for nanocomposites was different in terms of slower burning velocity and hindered dripping. They postulated that viscosity became the governing parameter. In addition to this, we should notice that in a typical cone calorimetry evaluation, nanocomposites tend to burn slowly and nearly completely. In terms of total heat evolved, no relevant difference between nanocomposites and reference materials is generally detected proving that the charred layer slows down escaping flammable molecules and spreads out the time of combustion.

Synergistic effects are observed when incorporating nanofillers in intumescent formulations. According to our previous papers [35]-[36], we may assume that the presence of nanofiller modifies the chemical (reactivity of the nanofiller versus the ingredients of the intumescent system) and physical (expansion, char strength and thermophysical properties) behavior of the intumescent char when undergoing flame or heat flux leading to enhanced performance. Nanofillers in intumescent materials 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 in particular, the potential role of 'compatibilizer' of the conventional flame retardant which can improve the dispersion of the nanofiller (e.g. TPU/APP-ZnO).

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