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Effect of magnesium dihydroxide nanoparticles on thermal degradation and flame resistance of PMMA nanocomposites

Fouad Laoutid^{a*}, Rodolphe Sonnier^b, Damien Francois^a, Leila Bonnaud^a, Nicolas Cinausero^b, José-Marie Lopez Cuesta^b and Philippe Dubois^a

The influence of magnesium dihydroxide (MDH) nanoparticles on thermal degradation and fire behavior of poly(methyl methacrylate) (PMMA) has been investigated by thermogravimetric analysis (TGA), cone calorimeter, and pyrolysis-combustion flow calorimeter (PCFC) tests, respectively. MDH nanoparticles with either lamellar or fibrous shape have been synthesized via a sol-gel technique and characterized by transmission electron microscopy (TEM) and X-ray diffraction analysis. PMMA–MDH nanocomposites have been prepared by melt blending the recovered MDH nanoparticles within PMMA at different loadings (5, 10, and 20 wt% MDH). According to TGA results, the incorporation of lamellar or fibrous MDH nanoparticles into PMMA leads to a significant improvement in PMMA thermal stability, both under air and inert atmosphere. The results obtained by PCFC and cone calorimeter tests show an important decrease in the peak of heat release rate (pHRR) concomitant with charring during the combustion. Lamellar MDH nanoparticles were found to be more efficient than fibrous MDH nanoparticles.

Keywords: poly(methyl methacrylate); PMMA; nanocomposite; magnesium dihydroxide; nanoparticles; thermal degradation; fire retardancy; cone calorimeter

INTRODUCTION

It has been shown that the incorporation of nanoparticles, such as organo-modified clays, carbon nanotubes, and metallic oxides, at lower rate often leads to an enhancement of the polymer thermal stability and a significant decrease in the peak of heat release rate (pHRR) during cone calorimeter test.^[1] More precisely and as far as poly(methyl methacrylate) (PMMA) is concerned, the dispersion of nanoclay or nanometric metallic oxides such as titanium oxide (TiO₂), ferric oxide (Fe₂O₃), and alumina (Al₂O₃) into PMMA were found to reduce pHRR as recorded by cone calorimeter test, while a substantial increase in thermal stability was noticed.^[2] Some authors have suggested that the improvement in the thermal stability is likely due to some restriction in polymer chain mobility combined with a catalytic effect of the nanoparticle surface, at least in the case of TiO₂ nanoparticles.^[3] The use of magnesium dihydroxide (MDH) nanoparticles as flame retardant agents in ethylene-co-vinyl acetate copolymers (EVA) resulted in the increase in the limiting oxygen index (LOI) value of Mg(OH)₂/EVA (1:1) nanocomposite to 38.3% (with respect to 24% as recorded for the corresponding (micro)composites.^[4] Such an observation might be explained by the initial good dispersion of MDH nanoparticles throughout the matrix and the formation of a more compact char layer upon polymer combustion. The dispersion of MDH nanoparticles in EVA was found to be further improved with the use of a special compound powder of cross-linked rubber/nano-MDH prepared by co-spray drying of the fluid mixture of nano-MDH slurry and irradiated rubber latex.^[5] The ternary composition showed a better fire resistant behavior as evidenced by cone calorimeter test, where an increase in the time to ignition (TTI) and a decrease in the heat release rate (HRR) were observed in comparison with the basic nano-MDH nanocomposite. These few

selected examples clearly highlight the potential of nanoparticles such as MDH as fire retardant additive for polymers.

The aim of the present work is to further study the interest of nanometric MDH as flame retardant agents in PMMA. More specifically, this study focuses on the effect of the nanoparticle shape, either lamellar or fibrous nano-MDH, on both thermal stability and combustion behavior of PMMA nanocomposites as investigated by cone calorimeter test. The complementarity of cone calorimeter and pyrolysis-combustion flow calorimeter (PCFC) allows us to determine the mechanism of flame retardancy.

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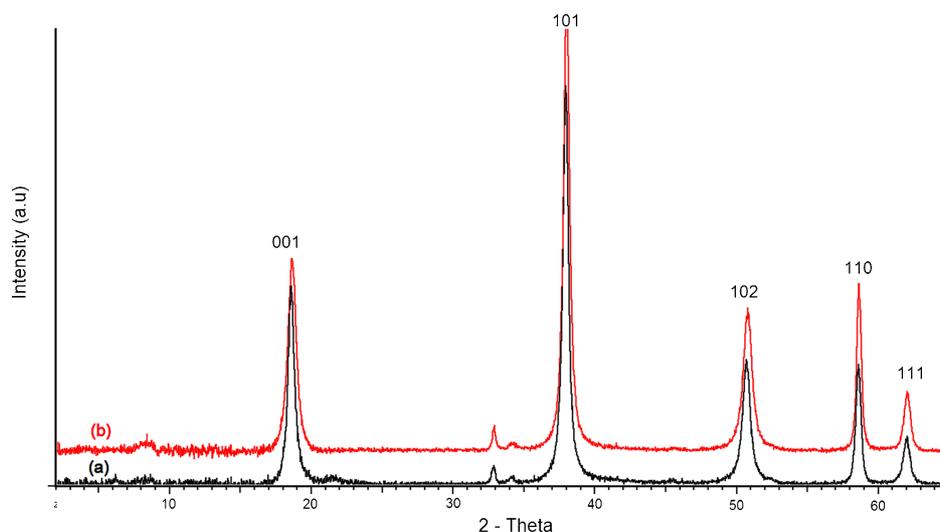


Figure 1. XRD patterns of Lamellar (a) and fibrous (b) MDH nanoparticles. This figure is available in color online at wileyonlinelibrary.com/journal/pat

EXPERIMENTAL

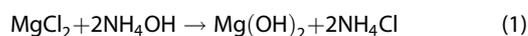
Materials

PMMA (Altuglas V825 T) was supplied by Arkema, France. Polyvinylpyrrolidone (PVP, average molecular weight 58×10^3 g/mol) was supplied by Acros, Belgium. Potassium oleate salt was furnished by Aldrich (Belgium) and magnesium chloride hexahydrate flakes ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was purchased from Chem-lab, Belgium.

The $\text{Mg}(\text{OH})_2$ nanoparticles were prepared by following the surfactant-mediated solution method.^[4] At 20°C , 100 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 5 g potassium oleate salt, and 1.25 g PVP were dissolved in 150 ml of distilled water. Then, 486 ml of an alkaline solution (NaOH or NH_4OH , 2 mol/L) was slowly added by using a peristaltic pump (3 ml/min) under vigorous stirring and the formed suspension was aged for 1 hr. The powder collected was washed with distilled water six times and finally dried at 100°C for 4 hr. The X-ray analysis of the collected powders (Fig. 1) shows the presence of MDH characteristic peaks.^[6]

Depending on the chemical composition of the alkaline solution, two precipitation reactions can occur and lead to the formation of different shapes of MDH nanoparticle (Fig. 2). When NH_4OH was used, lamellar MDH nanoparticles were obtained,

while the use of NaOH favors the formation of fibrous MDH nanoparticles, according to the following reactions.



TGA curves of both lamellar and fibrous MDH nanoparticles, under nitrogen ($20^\circ\text{C}/\text{min}$), are reported in Fig. 3. In the temperature range of $300\text{--}400^\circ\text{C}$, it undergoes a thermal decomposition of residual oleic acid and an endothermic decomposition with water release.

Structural characterisation

TEM micrographs analyses were performed with a philips CM100 apparatus using an acceleration voltage of 100 kV. X-ray diffraction analysis (XRD) data were collected using a BRUKER D8 diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The scattering angle (2θ) domain studied ranged from 2° to 63° , with a rotation step scanning of $0.01^\circ 2\theta$ and a step time of 0.007 s.

Processing

Blending of MDH nanoparticles within molten PMMA was carried out in a Brabender internal mixer at 225°C (10 min mixing at 50 rpm). For the cone calorimeter test, plates ($100 \times 100 \times 4 \text{ mm}^3$)

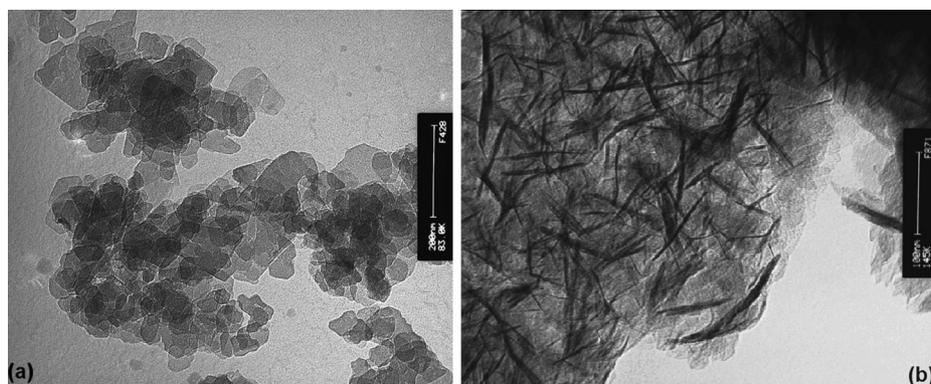


Figure 2. TEM images of lamellar MDH (a) and fibrous (b) MDH nanoparticles.

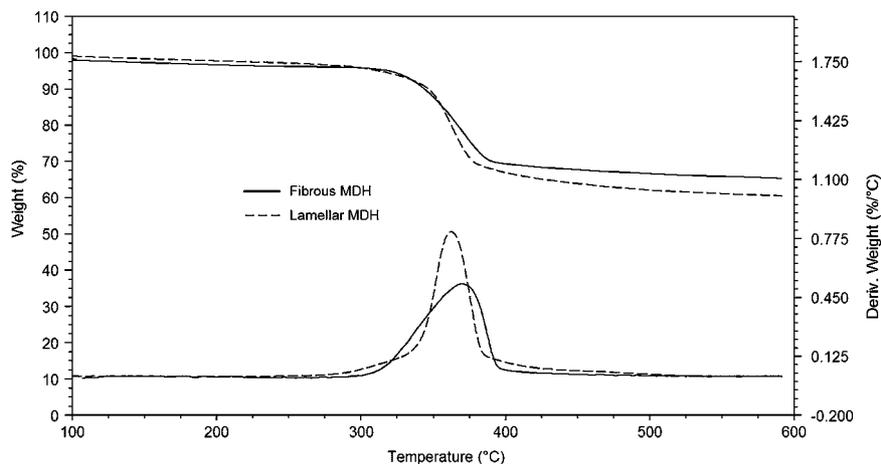


Figure 3. TG curves of lamellar and fibrous MDH nanoparticles under nitrogen (20°C/min).

were then compression molded at 250°C using an Agila PE20 hydraulic press. More precisely, the material was first pressed at low pressure for 200 sec (three degassing cycles), followed by a high-pressure cycle at 150 bars for 180 sec. The samples were then cooled down under pressure (80 bars).

Thermal analysis and fire testing

Thermogravimetric analysis (TGA) was used to study the oxidative and non-oxidative thermal decomposition of the PMMA and PMMA nanocomposites under a flow of 69 ml/min of helium for non-oxidative thermal degradation and 60 ml/min of air for oxidative thermal degradation. In the case of nanocomposites, approximately 10 mg of the sample was submitted to a temperature ramp from 25 to 700°C at a heating rate of 10°C/min whereas TGA analyses were performed under nitrogen on 5 mg of dried MDH nanoparticles (12 h at 80°C) by an isotherm at 100°C for 20 min followed by a 20°C/min ramp to 700°C. All the TGA experiments were performed using a TGA 2950 device from TA Instruments. The fire behavior was tested by cone calorimeter (fire testing technology) according to the ISO 5660 standard. A 100 × 100 × 4 mm³ sheet was exposed to a radiant cone (35 kW/m²). Results were obtained from the average values of three separated samples for each formulation. PCFC from fire testing technology (FTT) was performed on samples as small as 1–3 mg. The heating ramp was fixed at 1°C/sec up to 750°C under nitrogen. Gases released during the pyrolysis were evacuated into an oven at 900°C under nitrogen/oxygen 80/20 atmosphere, which allows a complete combustion of the gases. More details are given in Reference [7].

RESULTS AND DISCUSSION

Thermal and thermo-oxidative degradation

The effect of the incorporation of MDH nanoparticles on the thermal stability of PMMA has been studied by TGA under air and helium. Figures 4 and 5 show the thermogravimetric (TG) curves of unfilled PMMA and PMMA nanocomposites containing 5, 10, and 20 wt% of lamellar or fibrous MDH nanoparticles. From these curves, it appears that MDH nanoparticles, regardless of their morphology, significantly increase PMMA thermal stability, in both oxidant and inert atmospheres unlike ZnO nanoparticles,

which improved the thermal resistance of PMMA only in air.^[8] TG curves of all formulations are shifted to higher temperatures in comparison to pristine PMMA. Moreover, at relatively low content of MDH nanoparticles (5 wt%), the thermal stability of PMMA/fibrous MDH nanocomposite under air ($T_{-20\text{wt}\%} = 338^\circ\text{C}$ and $T_{-60\text{wt}\%} = 365^\circ\text{C}$) reaches the thermal stability level of pristine PMMA under inert atmosphere ($T_{-20\text{wt}\%} = 339^\circ\text{C}$ and $T_{-60\text{wt}\%} = 366^\circ\text{C}$). Remarkably enough, with lamellar MDH, TG curve is shifted to higher temperatures and the corresponding

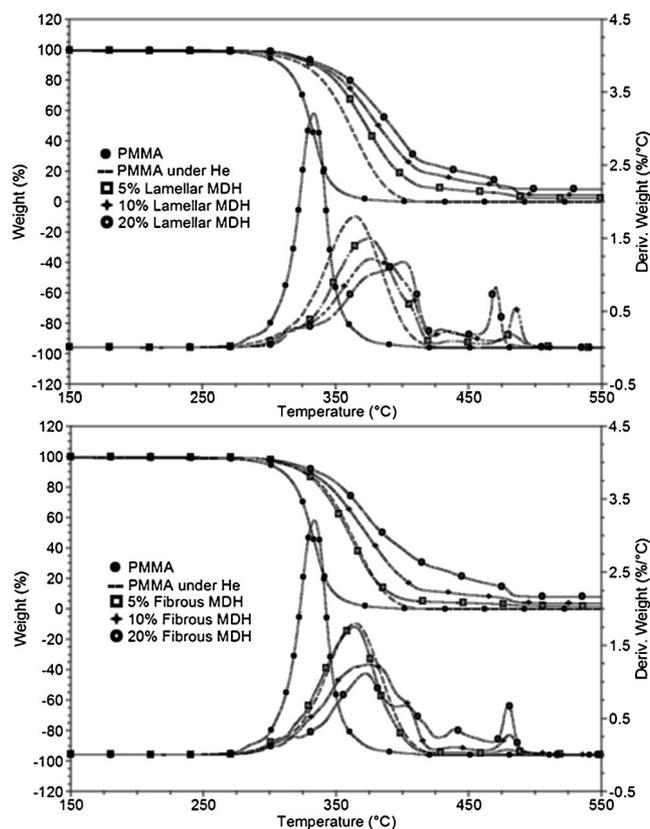


Figure 4. TG curves of PMMA containing MDH nanoparticles under air (for sake of comparison, a curve of unfilled PMMA as recorded under helium is also included).

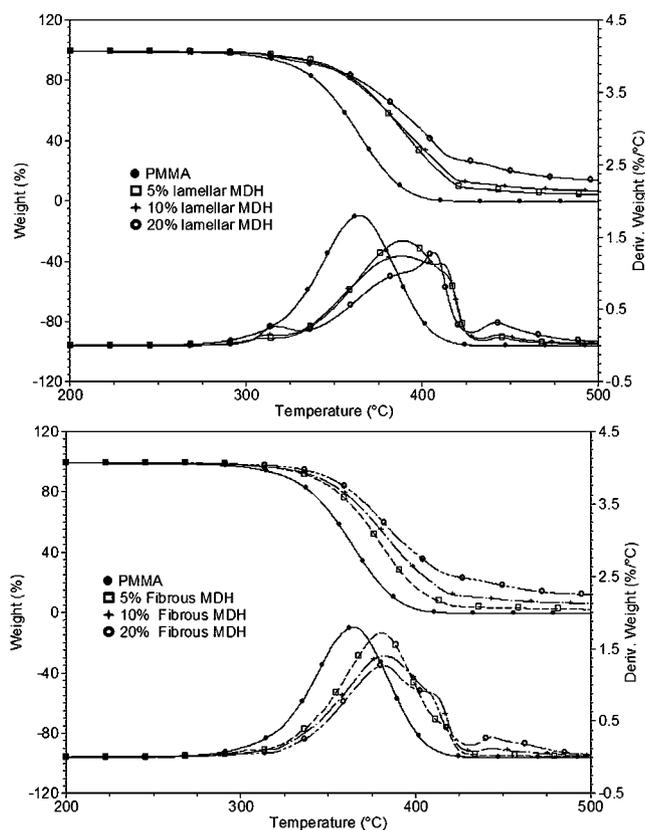


Figure 5. TG curves of PMMA containing (lamellar and fibrous) MDH nanoparticles under helium.

nanocomposite becomes more thermally resistant ($T_{-20\text{ wt}\%} = 350^\circ\text{C}$ and $T_{-60\text{ wt}\%} = 380^\circ\text{C}$) (Table 1).

The temperature range over which the nanocomposite decomposes shifts progressively to higher temperature when MDH nanoparticles loading rate is increased. At medium MDH content (10 wt%), $T_{-20\text{ wt}\%}$ under air increases from 320°C for pristine PMMA to 354°C for PMMA/lamellar MDH nanocomposite and 345°C for PMMA/fibrous MDH nanocomposite. $T_{-60\text{ wt}\%}$ follows the same evolution and is much higher when MDH nanoparticles are used ($T_{-60\text{ wt}\%} = 334^\circ\text{C}$ for PMMA, $T_{-60\text{ wt}\%} = 390^\circ\text{C}$ for PMMA/lamellar MDH and $T_{-60\text{ wt}\%} = 380^\circ\text{C}$ for PMMA/fibrous MDH nanocomposite). The enhancement level

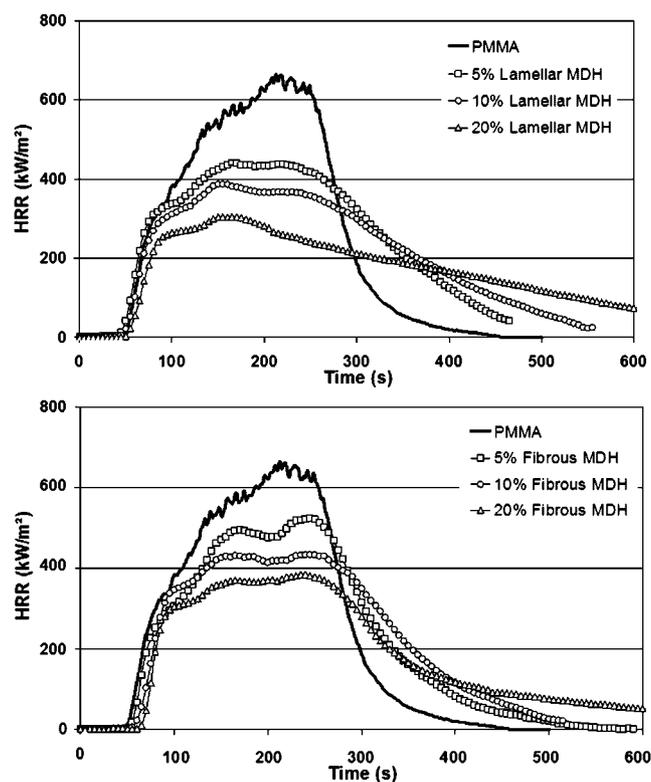


Figure 6. Evolution of the heat release rate (HRR) during cone calorimeter test (35 Kw/m^2) for PMMA and PMMA compositions containing lamellar or fibrous MDH nanoparticles.

is much more important when lamellar MDH is concerned. Furthermore, MDH nanoparticles modify the thermal degradation pathway both under oxidant and inert atmospheres of PMMA and lead to the apparition of a new decomposition step above 400°C , corresponding to the degradation of the char formed during the thermal decomposition of PMMA nanocomposites and likely catalyzed by the surface of dispersed MDH nanoparticles. Then, MDH nanoparticles lead to a significant improvement of PMMA thermal stability. Some mechanisms could be proposed to explain these results: MDH nanoparticles could act as a protective barrier that limits heat transfer into the material, volatilization of the combustible degradation products,

Table 1. Temperature values corresponding to 20% weight loss ($T_{-20\text{ wt}\%}$) and 60% weight loss ($T_{-60\text{ wt}\%}$) under air and under He of PMMA/MDH nanocomposites

	Under air		Under He	
	$T_{-20\text{ wt}\%}$ ($^\circ\text{C}$)	$T_{-60\text{ wt}\%}$ ($^\circ\text{C}$)	$T_{-20\text{ wt}\%}$ ($^\circ\text{C}$)	$T_{-60\text{ wt}\%}$ ($^\circ\text{C}$)
PMMA	320	334	339	366
5 wt% lamellar MDH	350	380	362	394
10 wt% lamellar MDH	354	390	351	396
20 wt% lamellar MDH	360	400	364	406
5 wt% fibrous MDH	338	365	353	383
10 wt% fibrous MDH	345	380	358	390
20 wt% fibrous MDH	355	399	362	400

Table 2. Time to ignition, peak of heat release rate, and reduced total heat evolved values for PMMA and PMMA compositions containing lamellar or fibrous MDH nanoparticles

	Time to ignition (sec)	pHRR (kW/m ²)	RTHE (kJ/g)
PMMA	47 ± 1	639 ± 7	23
5% lamellar MDH	44 ± 2	446.5 ± 12 (-30%)	23.5
10% lamellar MDH	45 ± 2	388 ± 12 (-39%)	23.7
20% lamellar MDH	50 ± 6	305 ± 15 (-52%)	23
5% fibrous MDH	47 ± 3	515 ± 9 (-19%)	23.5
10% fibrous MDH	55 ± 6	437 ± 16 (-31%)	23.7
20% fibrous MDH	59 ± 3	385 ± 12 (-39%)	24

and diffusion of oxygen into the material. They could also promote char formation through a catalytic effect. In the next section, we will discuss about these different explanations. But we have already pointed out that the amount of water released during the thermal decomposition of MDH nanoparticles is so low that the associated endothermic effect has no significant action on the thermal behavior recorded by TGA. Indeed, MDH powders lose 31% of their weight between 300 and 400 °C in TGA (Fig. 3), resulting in a loss of up to 6 wt% H₂O during the thermal decomposition of PMMA/20 wt% MDH composition.

Fire reaction

The effect of the incorporation of lamellar or fibrous MDH nanoparticles on fire properties of PMMA has been investigated by cone calorimeter test (irradiance of 35 Kw/m²). The results are presented in Fig. 6, TTI and pHRR are summarized in Table 2. In comparison with pristine PMMA, an overall decrease in pHRR values for all the compositions is observed and depends strongly on the shape and the filler content. The pHRR value is reduced by about 52% in the presence of 20 wt% lamellar MDH whereas it decreases by only 39 wt% when the same quantity of fibrous MDH is used. The pHRR reduction is more significant when lamellar MDH nanoparticles are used. With both types of MDH nanoparticles, the combustion of PMMA nanocomposites leads to the formation of a char layer (Fig. 7). Moreover, the MDH nanoparticles leads to a sharp decrease in the rate of mass loss

and an improvement in the thermal stability of the formed char residue, especially when lamellar MDH nanoparticles are used (Fig. 8).

The effect of MDH nanoparticles on the TTI is very limited and seems to increase when fibrous MDH nanoparticles are used. This can be attributed to a higher thermal conductivity with fibrous nanoparticles yielding faster energy dissipation through the materials and possibly ascribed to percolation effects.

Discussion

In this section, we try to determine more precisely the mode of action of MDH nanoparticles on fire behavior.

The reduced total heat evolved (RTHE; total heat evolved/mass loss) does not change for all the formulations (around 24 kJ/g; Table 2) showing that the combustion energy of the released gases does not change and it could be assumed that the MDH nanoparticles have no effect on the gas phase but only in the condensed phase. Moreover, this observation confirms that the water released is negligible, while it does not affect the RTHE.

To investigate the role of MDH nanoparticles on the combustion of PMMA, we have performed PCFC tests. Due to the very small size of the tested sample, the HRR measured by

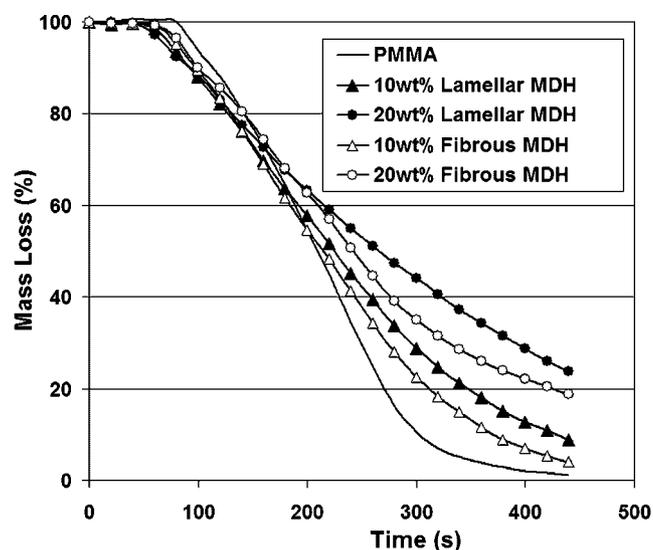


Figure 8. Mass loss versus time for PMMA and PMMA with 10 and 20 wt% of fibrous or lamellar MDH nanoparticles.

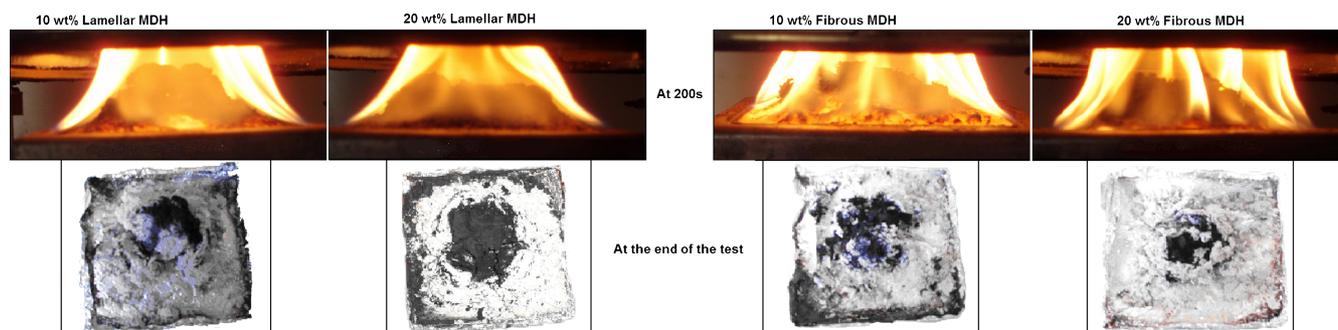


Figure 7. pictures of the intumescent char formed during cone calorimeter test at 200 sec and at the end of the test. This figure is available in color online at wileyonlinelibrary.com/journal/pat

PCFC test might be very different from cone calorimeter test, in particular when physical protection effects such as barrier insulation or intumescent layer formation occur during the cone calorimeter test. On the contrary, as far as PMMA–MDH nanoparticles are concerned, the variation in the pHRR obtained during PCFC tests is very similar to the one obtained with cone calorimeter (Fig. 9), and an excellent correlation between both pHRR measured is obtained (Fig. 10). Regarding these results, we can assume that the main effect of MDH nanoparticles could be attributed to a chemical and catalytic action of the surface of the nanoparticles leading to the formation of char during the polymer combustion. Furthermore, the incorporation of MDH nanoparticles, especially of lamellar shape, leads to an important decrease in the polymer flammability as attested by the heat release capacity (HRC) values (Table 3).

Moreover, a second heat release is observed above 450°C during the heating ramp for PMMA nanocomposites in PCFC and corresponds to the thermal decomposition of the formed char residue. This peak is much larger, especially when 20 wt% of fibrous MDH nanoparticles are used since this composition leads to the formation of an important amount of thermally unstable char residue, as previously observed by TGA analysis (Figs. 4 and 5) and cone calorimeter test (Fig. 7).

The thermal stability of the char, formed during the thermal degradation and the polymer combustion, is the key parameter that seems to be responsible for the fire behavior of PMMA/MDH nanocomposites. The chemical action of the surface of MDH nanofillers promotes the charring of PMMA that decreases the amount of the released combustible volatile products. The char formed acts as barrier against mass transport, oxygen diffusion,

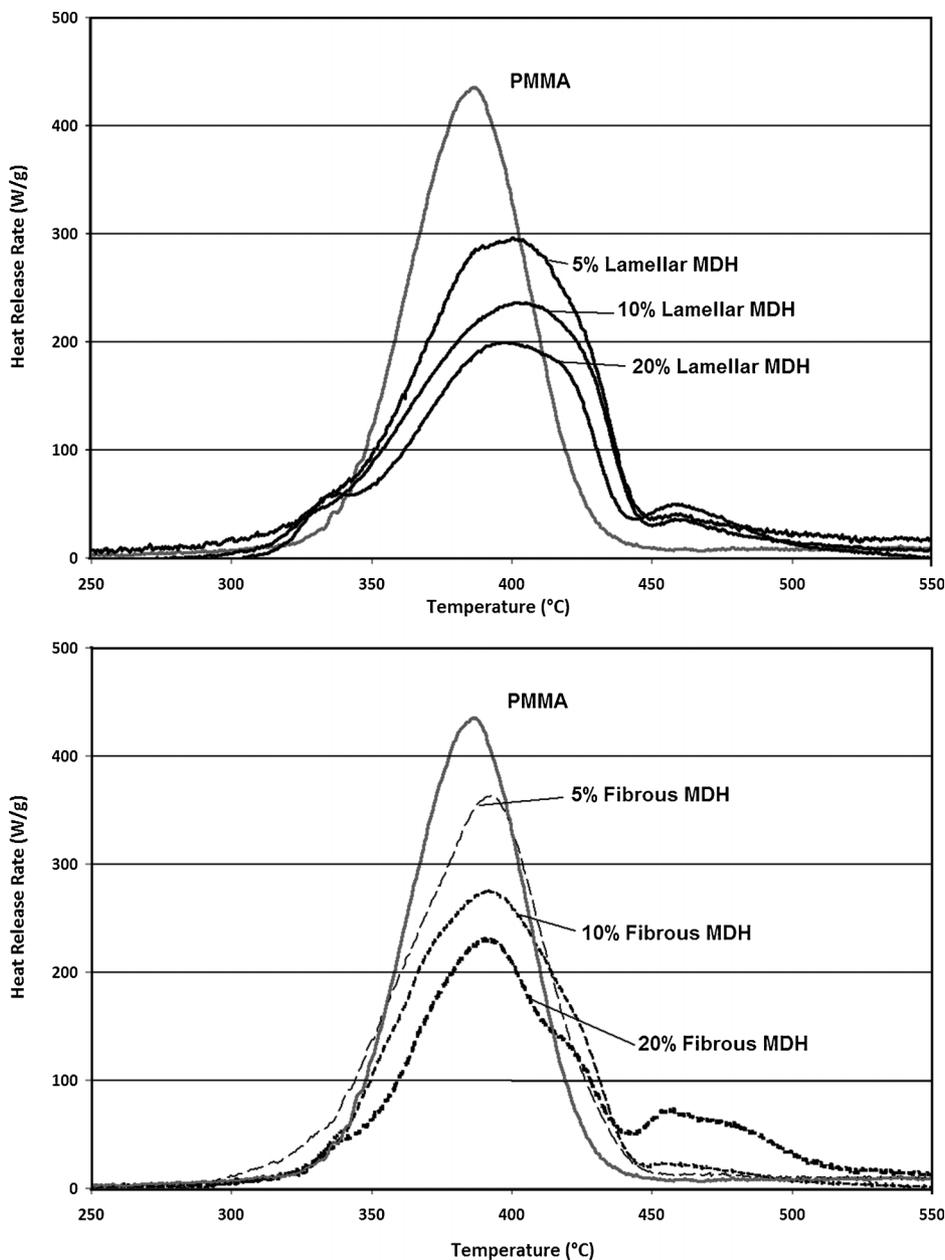


Figure 9. Heat release rate versus temperature for all formulations (PCFC tests).

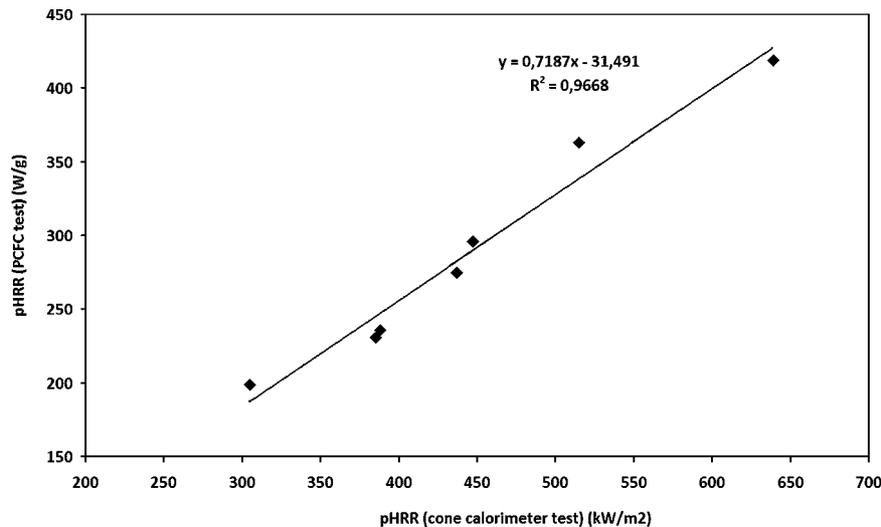


Figure 10. pHRR obtained by pyrolysis-combustion flow calorimeter test versus pHRR obtained by cone calorimeter test for PMMA/MDH nanoparticles.

Table 3. Peak of Heat release rate and Heat release capacity (HRC) obtained by pyrolysis-combustion flow calorimeter analysis

	pHRR (W/g)	HR Capacity (J/g K)
PMMA	419	413
5% lamellar MDH	287	285
10% lamellar MDH	220	232
20% lamellar MDH	204	201
5% fibrous MDH	358	353
10% fibrous MDH	277	273
20% fibrous MDH	224	223

and can also insulate the underlying polymer from heat. The char formed is more thermally stable when lamellar MDH nanoparticles are used. Lamellar shape appears more designed to ensure a better insulation and a more compact residue.

CONCLUSION

Lamellar and fibrous MDH nanoparticles have been readily synthesized via a sol-gel technique and PMMA/MDH nanocomposites were prepared by melt blending with different loadings (5, 10, and 20 wt% MDH). The incorporation of either lamellar or fibrous MDH nanoparticles into PMMA leads to a significant improvement in the thermal stability under air or inert atmosphere. In cone calorimeter test, a significant decrease in pHRR is observed, whatever the type of MDH nanoparticles. However, pHRR reduction proved more important when lamellar

MDH nanoparticles were used. The combination of cone calorimeter test and PCFC test allows to determine the main effect of MDH on fire behavior, i.e. chemical effect (char promotion) triggered by MDH nanoparticle surface. To summarize, MDH nanoparticles and, more specifically, lamellar MDH nanoparticles display remarkable effect on both thermal stability and fire resistant behavior of PMMA, more likely paving way for new flame retardant additives for PMMA and related acrylic-based composite materials.

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