

Plastic additives for fire safety with weight reduction, thermal stability in processing and waste management Morpholino-poly(piperazinyl-morpholinyl-triazins)*

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Research Article

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Abstract

This paper is not just about the benefits of the smart plastics, but also about the potential remedies of the environmental concerns of their use. It is also a discussion about a potential pathway to an efficient use of fossil (combustion) fuels and the reduction of the emissions caused due to their use, in general.

Morpholino-poly (piperazinyl-morpholinyl-triazin) imparts sustainable fire-safety and subdued incineration behaviour to plastics combined with weight reduction, and facilitates their melt processing. Additionally, it enables their ultimate environmentally friendly disposal as waste, after the ultimate use, coupled with simultaneous generation of usable energy. The knowledge & experience thus gained from energy extraction of waste plastics provide guidelines for future research to increase the efficiency of energy extraction and the reduction of emissions from combustion fuels in general. The technology is also intended to safeguard against open burning of plastics that leads to air-pollution flashover and forest fires.

The various aspects of the experimental data generated are presented and plausible mechanisms of the technology are discussed.

Introduction:

Plastics, the polymer composites, perhaps the smartest materials ever created in recent times, have enabled quantum leaps possible in our evolution & lifestyle (electric and electronics, health-care, food/feed-production-preservation-distribution, consumer-care, mobility and so on [1-4]. Thanks to their (mostly) bio-inertness and impermeability, plastics have particularly proven to be indispensable to prevent the incubation, growth and spread of infectious diseases & pandemics such as coronavirus [5-7].

However, there are many lingering issues with plastics to make them even more valuable & indispensable:

- a. More efficient and environmentally friendly fire safety while-in-use, particularly in electric and electronics, mobility, and building & construction (only to name a few). Fire retardancy of plastics should also be intended to safeguard against open burning of plastic waste that leads to air-pollution, flashover and forest fires [8-10].
- b. Visible and invisible degradation, of both polymer and the ingredients, in mostly inevitable melt-processing (thermoplastics) [11, 12].
- c. However, perhaps the most important of all, the environmentally friendly terminal disposal of and energy extraction from used plastics [13-22].
- d. Plastics fundamentally being solid fuels, the knowledge & experience thus gained from energy extraction and cold incineration of waste plastics should provide guidelines for the future research to

increase the efficiency of energy extraction and the reduction of emissions from combustion fuels in general. For, much of the energy generated from combustion fuels is lost/wasted in combustion gases & emissions.

To contribute towards the resolution of the said issues, MCA technologies GmbH in Switzerland has developed morpholino-poly(piperazinyl-morpholinyl-triazins, a multifunctional technology that on one hand provides safety in melt processing and imparts a sustainable fire-safety-in-use to plastics, combined with weight reduction, for the sake of energy saving in mobility. On the other hand, it enables their ultimate environmentally friendly disposal as waste, coupled with efficient generation of usable energy.

Materials Discussion:

Fire-Safety:

For the fire-safety while-in-use of plastics, morpholino-poly(piperazinyl-morpholinyl-triazin) (PPMT-HF, I), is of particular interest as an environmentally friendly universal fire retardant synergist that reduces the usage of the fire retardant additive. Moreover, it suppresses the formation of smoke & toxic gases in the event of fire [23], and enables “cold-incineration” of the waste plastics.

Depending upon the chemistry of the primary fire retardant of choice to be used in combination, such fire retardancy is provided either by char formation (the so-called intumescence) and/or by the formation of ceramic nitrides/oxynitrides at the fire point, preventing the proliferation of the fire. Formation of potentially hazardous gases is thereby either suppressed due to the exceptionally slow rate of burning at lower temperatures (cold-incineration), enabling systematically their capture as nitrides/oxynitrides and other derivatives of the fire retardants in use. This unique synergism particularly reduces the total requirement of the fire retardant addition for any specific purpose. Although less efficient, PPMT-HF itself acts as a fire retardant, due to the formation of some carbon nitride material [24].

The pictures of the residues at the points of fire ignition/extinction, in a typical fire test (Limiting Oxygen Index; LOI) [25], are shown in figures 2a-2d.

enough for many fire safety purposes of plastics. In addition, economy, processibility, recycling and environmentally friendly ultimate waste disposal make such plastics most sustainable of all other options.

The combinations of morpholino-poly(piperazinyl-morpholinyl-triazin), PPMT-HF, with the mixture of metal hydroxides and carbonates usually seem to be more efficient than with the corresponding individual components. Liberation of water from metal hydroxides during the combustion facilitates the capture of carbon monoxide, carbon dioxide and other acidic gases by metal hydroxides, thus reducing their emissions. On the other hand, self-immolation of PPMT-HF with triazine ring acting as a template for the formation of ceramic nitrides/oxynitride as fire barriers such as shown in Fig.3 [26]. It is obvious therefore, that none of these individual components would be as effective on their own.

The formation of a mushroomed, red colored fire residue with combination of poly(piperazinyl-morpholinyl-triazin), PPMT-HF, magnesium dihydroxide & kaolin (Fig 2c), never observed before, is perhaps due to the formation of some unique hybrids of nitrides/oxynitrides.

Ammonium polyphosphate (APP) as a fire retardant undergoes decomposition to phosphoric acid in the event of fire, causing charring of the polymer and fire retardancy at the fire point. However, in the presence of morpholino-poly(piperazinyl-morpholinyl-triazin), PPMT-HF, phosphoric acid thus liberated reacts partially with PPMT-HF to form ultimately phosphorus oxynitrides as additional fire barriers (Fig. 2d). The chemistry of the chain reactions perhaps occurring in situ during the fire process is depicted in Fig. 4.

“The cone calorimeter has become one of the most important and widely used instruments for the research and development of fire retarded polymeric materials” [27-29]. Thus, in our cone calorimetric study it is observed that in case of the polypropylene composites PP/10IS and PP/20IS containing 10% and 20% of the fire retardant: Ammonium Polyphosphate + PPMT- HF, the peak flux (kW/m^2) of heat release is considerably reduced, the rate of burning considerably prolonged (Fig 5a), and the smoke formation appreciably diminished (Fig 5b). Ammonium polyphosphate alone, unable to form nitrides, is less effective as a fire retardant, and also thermally less stable (Thermogravimetric Analysis TGA [34], Fig 7a)

The combinations of morpholino-poly(piperazinyl-morpholinyl-triazin), PPMT-HF, with phosphinates such as Aluminium diethyl phosphinate (the major component of Exolite 1230 [30-32], also seem to ultimately provide ceramic phosphorous oxynitride (fig. 4), IV and V) as fire barriers.

Fig 6a shows the behaviour of morpholino-poly(piperazinyl-morpholinyl-triazin), PPMT-HF, alone and in combination with Exolite OP 1230 for the fire retardancy of polymethyl methacrylate, (PMMA). Polymethyl methacrylate (PMMA), also known as “PLEXIGLAS”, is a material used extensively for protective barriers to prevent the spread of corona virus. Being highly inflammable, use of non-fire

protected PPMA is a fire hazard. Moreover, the ultimate disposal of the contaminated PMMA could also be an issue to be considered.

Spectacular is not only the reduction of heat release in the event of fire but also the least smoke production with PPMT-HF (MCA-HF) alone. We believe this to be due to the capture of graphene, contained in the black smog produced in the burning of PMMA, by carbon nitride, formed simultaneously from PPMT-HF in the burning process [25]. Evidence of this assumption is provided by the TGA analysis of the corresponding samples (Fig 6b). Whereas PPMA and MCA PPM-HF on their own are completely consumed in TGA analysis, with 100 % weight loss and 0 % residue, the residues of the TGA analyses of the composites of PPMA containing PPMT-HF vary between 8-12 % . . Reduction of the smoke release also seems to be directly related to the content of PPMT-HF in the composite.

Thermal Stabilization & Processing/Recycling:

Most Surprisingly, it is found that morpholino-poly(piperaziny-morpholiny-triazin), PPMT-HF, additionally acts as a heat stabilizer of polymers, beyond anti-oxidants, to retard visible and invisible degradation during melt-processing and reprocessing (*recycling/upcycling*) of invariably high-loaded (and heat sensitive) phosphorous containing fire retardant composites.

Thus the thermal stabilization with PPMT-HF of polypropylene containing ammonium polyphosphate + PPMT-HF, in air atmosphere and under nitrogen atmosphere is shown in fig 8a respectively 8b. Particularly to be remarked is the difference between the air atmosphere and the nitrogen atmosphere. In air atmosphere, the TGA graphs of the composites fall apart, due to the thermal stabilization granted by PPMT-HF both to the polymer as well as to the fire retardant.

Under nitrogen, there is no oxidative thermal degradation of the polymer to be expected and hence the T_{onst} of the polypropylene itself is distinctly higher (422 °C vs 271 °C). However the composites PP/10IS and PP/20IS containing 10% and 20% of the fire retardant system show lower T_{onst} (413 °C & 399 °C) corresponding to the lower thermal stability of the fire retardant itself. The presence of PPMT-HF still seems to influence slightly both T_{onst} & T_{max} , over and above the already much higher thermal stability of all composites under nitrogen.

The improved thermal stabilization of one of the most difficult to process glass-filled PA 66 composite containing aluminium diethyl phosphinate (i.e. Exolite OP 1230, Clariant) as the primary fire retardant, and used extensively as an engineering polymer, is illustrated in Fig. 8.

The temperature difference in TGA analysis between the state-of-the-art combination of Exolite OP 1230 with melamine polyphosphate and now the most stable combination of Exolite OP 1230 with PPMT-HF is almost +82 °C. This distinct difference is particularly due to the inertness of PPMT-HF towards the polymer itself. Besides getting decomposed melamine, salts are known to cause degradation of polyamides in melt-processing [35], and induce corrosion of the processing equipment.

Effect of PPMT-HF on the thermal stability of PMMA composites is seen in Fig. 6b. (+25 °C).

PPMT-HF also reduces the rate of decomposition of thermal sensitive fillers such as calcium carbonate or kaolin (Fig 9) in polymers:

No matter in what polymer and in what combination we tested, we always found the thermal stabilizing effect.

Mechanism Of Thermal Stabilization

Stabilization is perhaps imparted due to heat energy absorption by the principle of boat-chair switching of the piperazine and morpholine moieties of the molecule in melt processing, with rigidity being provided by the flat heterocyclic rest, without over-stressing the covalent bondings within the basic structure. This “Flip-Flop” mechanism of thermal stability due to PPMT-HF as illustrated in Fig 10 is further supported by a similar boat-chair thermal switching-over behaviour of piperazinyl pyridines [36].

Energy Extraction & Terminal Waste Disposal [37-45]:

Plastics are fundamentally solid fuels, mostly derived from naturally occurring combustible materials such as fossil fuels or even the naturally growing or artificially grown renewable materials. Of all the alternatives available, the most logical procedure of their disposal-after-use should be by incineration in closed systems. In this process, it should be possible to generate useful energy as well. The complex separation of different types of plastic for reuse as low-quality secondary raw materials, which also need to be ultimately disposed of, would not necessarily be required. The environmental and health impacts of waste incinerators strongly depend on emission control technology, as well as incinerator design and operation, but above all, on the composition of the waste, that needs to be strictly regulated. Use of plastic additives and colorants that can generate toxic substances upon incineration must be restricted.

In many countries, open burning of plastic waste is of great environmental concern. It is important, therefore, that open waste burning of the plastics is made inherently difficult, if not impossible, since such

open burning causes direct release of toxic emissions in the atmosphere and danger of the spread of fires.

For a safe, environmentally friendly (generation of less pollutants, especially nitrogen oxides and other toxic volatile materials, prevention of open burning) and an efficient energy generation during incineration, the combustion process must be inherently controlled (i.e. rather than “Molotov cocktail” like explosive flammability, slow but steady heat-release), and needs to be conducted at lower temperatures (cold-incineration) to ensure efficient energy capture, and particularly to avoid energy losses in combustion gases.

Although the potential fire hazard of plastics is known almost ever since plastics exist, the focus has been on the fire safety for some specialty purposes of their use. The focus of the present investigation is on safe and sustainable disposal of the plastics including energy extraction, with the aid of suitable fire retardancy.

We, therefore, propose that certain minimum requirement of fire retardancy should be extended to all plastics to enable their safe-incineration accompanied by efficient energy extraction as waste after-use. Such fire resistance can also prevent their open burning, at any time.

The aspects of recycling and ultimate fate of plastics thus need to be borne in mind from the very beginning of their conception.

We are of the opinion that morpholino-poly(piperazinyl-morpholinyl-triazin) (PPMT-HF) could be a facilitator not only in recycling/upcycling due to its thermal stabilizing effect, but also for environmentally safer ultimate disposal and energy extraction from waste plastics.

As an example, Figures 11a-c show the cone calorimeter results (flux 50 kW/m²) of the polypropylene composites discussed above under “Fire Retardancy (LOI Fig. 2a- Fig. 2c) for the characteristics of their incineration behaviour, particularly for the disposal after-the-us.

Whereas the polypropylene alone (Fig. 11a) shows a peak heat release of 880 kW/m² and a total burning time of < 500 seconds (Fig 11b), the fire retarded samples PP14 and PP8 show the peak heat release rates of < 125 kW/m² (Fig. 9a) and a burning time of over 1100 seconds (Fig 9b) . Of particular importance is also the less smoke production (Fig 11c), relevant for the emissions of toxic gases. Lower controlled incineration temperature ensures efficient energy extraction with less energy losses in combustion gases of P14 and PP8.

We have carried out similar studies with many other major polymers of commercial importance, with similar results.

Chemistry/Technology:

Composed of C, H, N & O elements and characteristically insoluble, like an organic pigment,

MCAT-HF does not bloom out or bleed during the service life of the polymers, a necessary requirement of all polymer additives. The unique multistep process of its production is summarized in figure

The technology is particularly characterized by the strategy that: a) no dendrimeric (only linear chain) polymers are formed [46], for the sake of ease of dispersibility in the substrates; b) for the ecology considerations, no solvent is used in any step of the synthesis; c) uniform sub-micron particles are formed in situ to facilitate their later on incorporation into the polymer metrics; and d) the end-product does not contain any residual halogen as the terminal end-group to meet the newer regulatory requirements.

Physics:

Particular characteristic of the technology employed is the fact that small sub-micron particles (< 1 μm) of regular diamond shape and size are directly formed in the synthesis, requiring no further engineering manipulations to make their ease of incorporation and fine homogeneous distribution in the polymers.

Conclusions

PPM Triazine technology on one hand imparts sustainable fire-safety-in-use coupled with weight reduction, and provides safety in melt processing to plastics, and on the other hand, it enables their ultimate environmentally friendly disposal after-the-use, coupled with efficient extraction of usable energy. The knowledge & experience thus gained from energy extraction of waste plastics could provide guidelines to increase the efficiency of energy extraction and reduction of emissions from combustion fuels in general. For example, it might perhaps be possible to impart fuel consumption efficacy of gasoline to the levels of diesel fuel for similar performance.

The technology is also intended to safeguard against open burning of plastic waste that causes pollution, and can lead to uncontrollable flashover and forest fires.

Even if not incinerated, use of hydrophilic and/or acid-sensitive fire retardants (such as phosphates, metal oxides and carbonates) could accelerate degradation of plastics in landfills, waterways and in the nature (accounting for almost 79% of the plastic waste) by environmental degradation.

The breakthrough of this concept, however, hangs substantially from relevant legislations, voluntary constrains and the demand of the public for such concepts. The recycling and waste disposal aspects of plastics thus need to be borne in mind from the very beginning of their conception.

Declarations

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Major materials:

PPM-HF = Morpholino-poly(piperazinyl-morpholinyl-triazin) (MCA Technologies) [45], APP = Ammonium polyphosphate (Clariant Exolite 202) MPP = Melamine pyrophosphate & Melamine polyphosphate (Budenheim, Budit 311 & 312); Exolite OP 1230 (Clariant, main component : Aluminium diethyl phosphinate) ; PA-66GF (Lanxess, Durethan AKV35CXH2.0Lanxess, Polyamide 66 glass-filled), MDH = Magnesium hydroxide , APYMAG 60S, Nabaltec); CC = Calcium Carbonate (Omyacarb 1T-AV, Omya), PP = Polypropylene (Moplen HP 500N, LyondelBasell); Kaolin (Chinafill, Quarzwerke Germany) .

Experimental conditions and test methods:

Procedure A : The materials were dry-blended in the required proportions and extruded using the twin screw co-rotating extruder Leistritz 18-40D as per the required experimental conditions described in [45]. The resulting granulates were pressed to samples of different sizes and subjected to various tests such as cone calorimetry [27-29], LOI [25], UL-94, TGA [34] & other tests as per the test standards, described in the text above.

Procedure B: Polymer pellets were mostly melt-mixed with the different additives in an internal mixer apparatus (HAAKE) at 190 °C and 80 rpm for 6 min. PA66 blends were, however, prepared using this machine at 280 °C and 60 rpm during 6 min. All blends were grinded and then hot pressed and molded using an Agila machine under 60 bars at 240 °C during 6 min for most blends and 80 bars at 190 °C during 8 min for PA blends, to obtain the specimens in the form of sheets. Samples of various sizes were obtained according to the cone calorimetry [27-29], LOI [25], UL-94, TGA [34] & other tests as per the standards described in the text above.

For comparison, the blank polymer samples were prepared using the same procedures.

Author:

Former global head of Pigment Technology Research at Clariant, the largest pigment producer worldwide, with over 50 years of work experience, and over 75 Patents. Dr. Kaul has invented, from conception to commercialisation, many new chemical moieties, given lectures at many scientific and technical conferences world- wide, educated doctoral and post-doctoral students at five different universities in GB, USA, Canada & France, made numerous research publications and is author of chapters in many handbooks.

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Figures

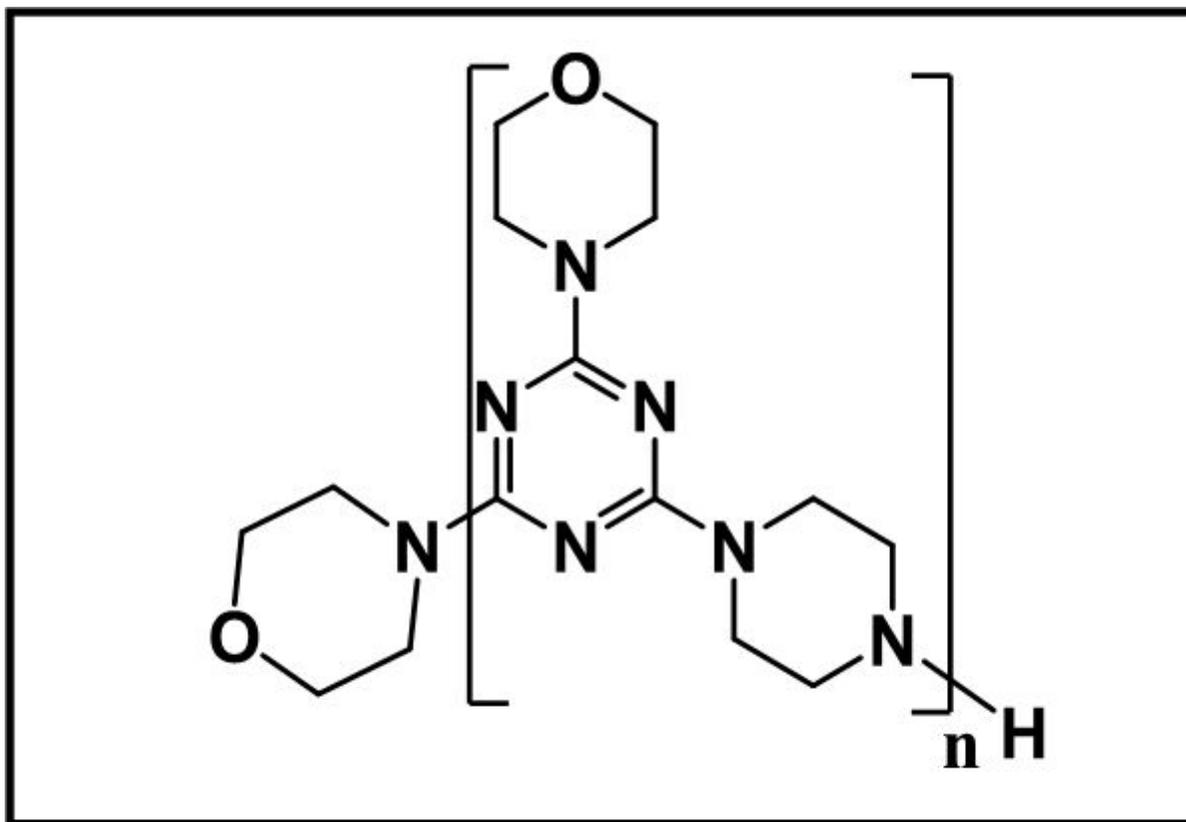


Figure 1

Morpholino-poly(piperazinyl-morpholinyl-triazin, (PPMT-HF, I)



Figure 2

2a-1d: Residues of fire retardancy tests (Limiting Oxygen Index; LOI) of various polypropylene composites: Fig.2a: polypropylene (LOI, 17.2); Fig.2b (PP14): polypropylene+ calcium carbonate + PPMT-HF (LOI 21.8); Fig. 2c (PP8)) polypropylene +calcium carbonate + kaolin + MDH + PPMT- HF (LOI, 29.7); Fig. 2d(PP20IS); polypropylen+ Ammonium Polyphosphate + PPM- HF (LOI, 30)

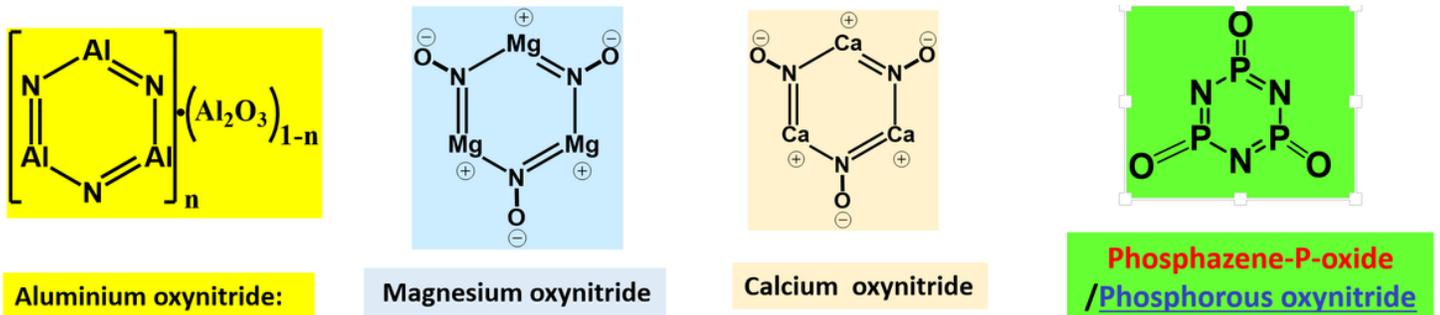


Figure 3

Possible structures of organo-inorganic fire barriers formed in situ with PPMT-HF

Mechanism of phosphorous-nitrogen synergism for fire retardancy with PPMT-HF

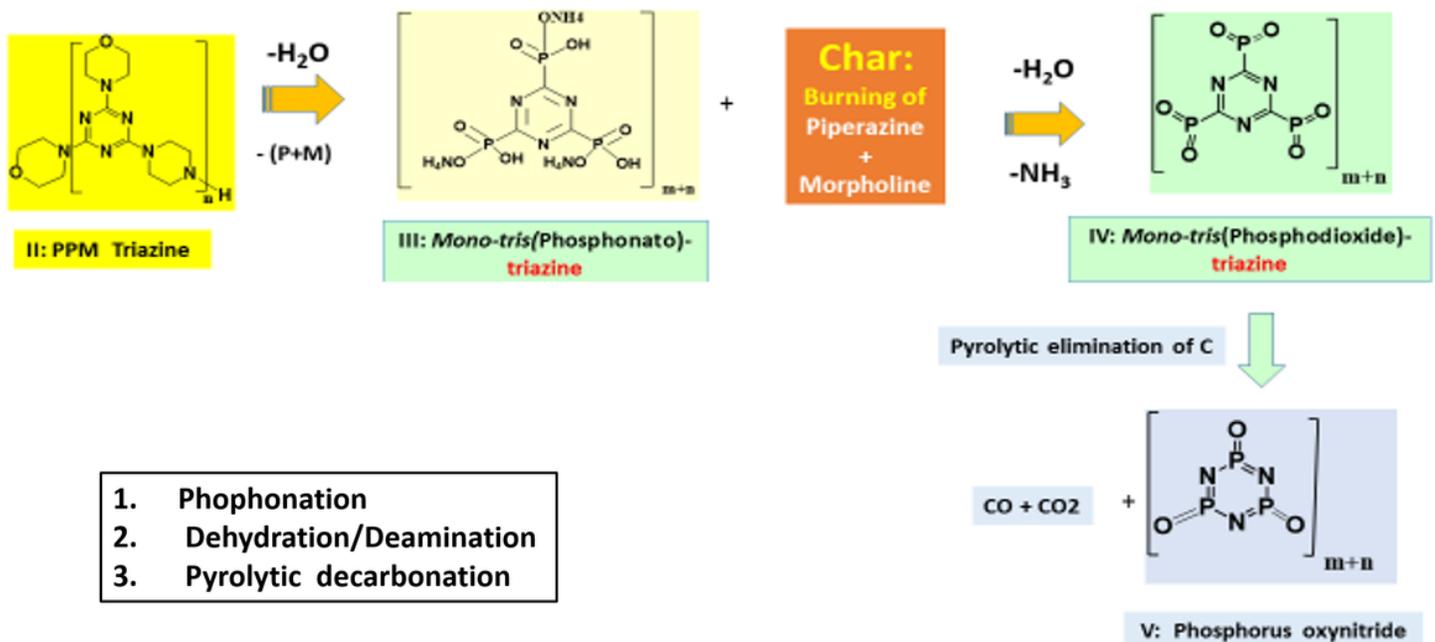


Figure 4

Chemistry of the fire retardancy with phosphorus-triazin systems

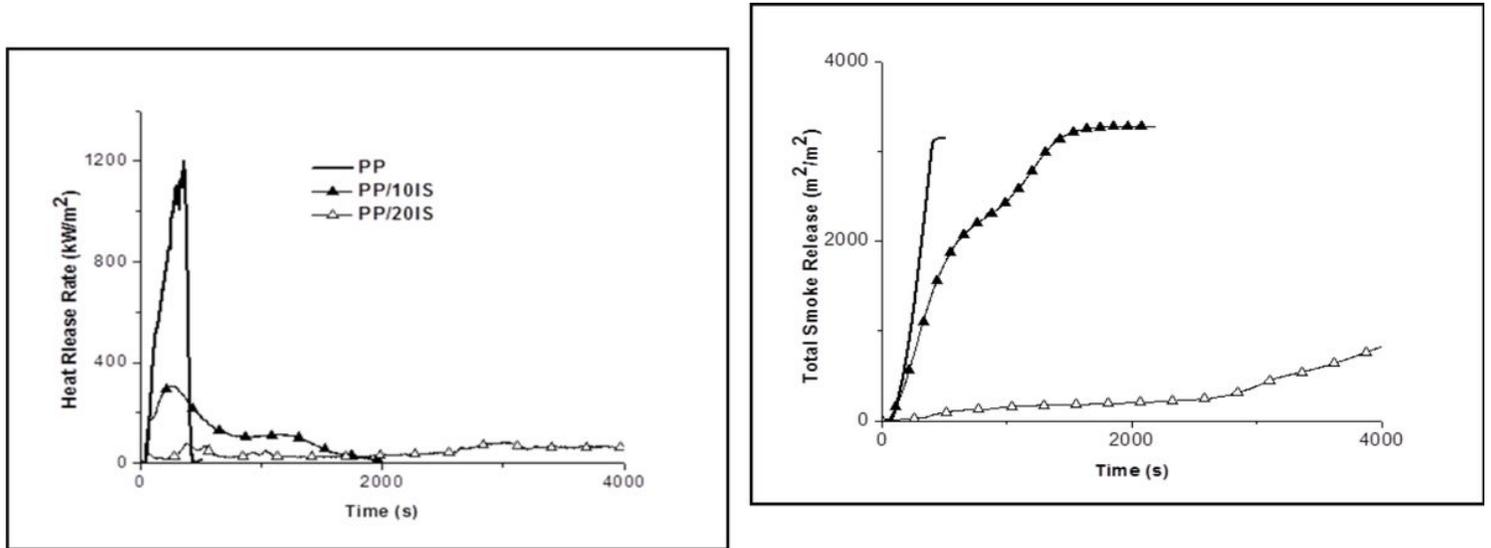


Figure 5

5a, b: Cone calorimetry (50 kW /m2) of polypropylene ((PP) without and with fire retardant system (IS (Ammonium Polyphosphate + PPM Triazine HF)

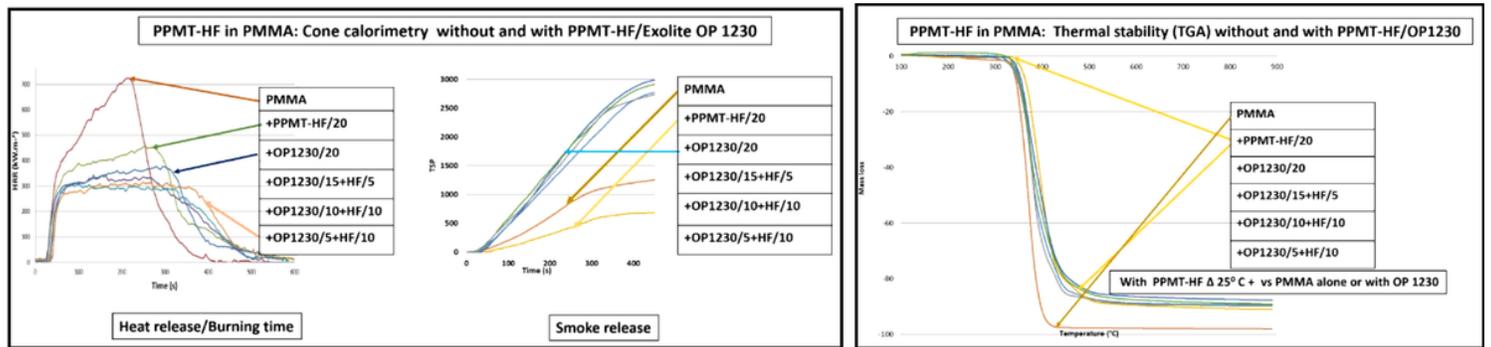


Fig.6a: Cone calorimetry (50 kW /m2) of PMMA composites

Fig. 6b: TGA of PMMA

Figure 6

Fig.6a: Cone calorimetry (50 kW /m2) of PMMA composites Fig. 6b: TGA of PMMA composites

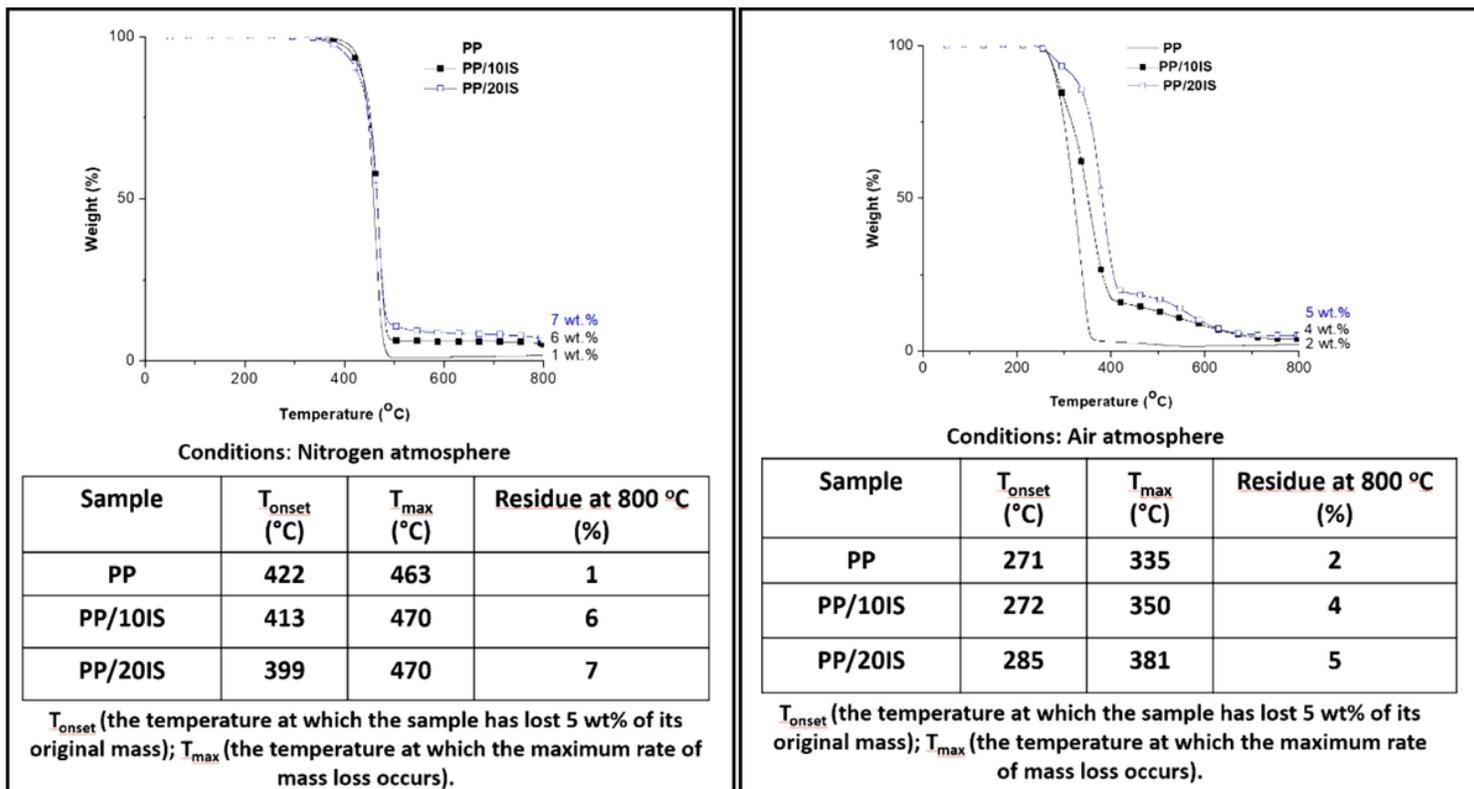


Figure 7

Fig.7a, b: TGA graphs of polypropylene ((PP) without and with fire retardant system (IS): (Ammonium Polyphosphate + PPM Triazine HF); fig 7a: air atmosphere; Fig 7b: nitrogen atmosphere

Composition	TGA °C**	LOI	UL 94
GF PA 66 (LANXESS)	N.C.	24.3	N.C.
+ 20% OP1230 (Clariant)	331	48	V-1
+ 12% OP 1230 + 8% PPMT-HF	373	37.3	V-1
+ 12% OP 1230 + 8% MPP (Budenheim)	291	28.3	V-0
+12% OP 1230 + 4% PPMT HF+ 4% MPP	316	30.7	V-0

(** Onset of weight loss)

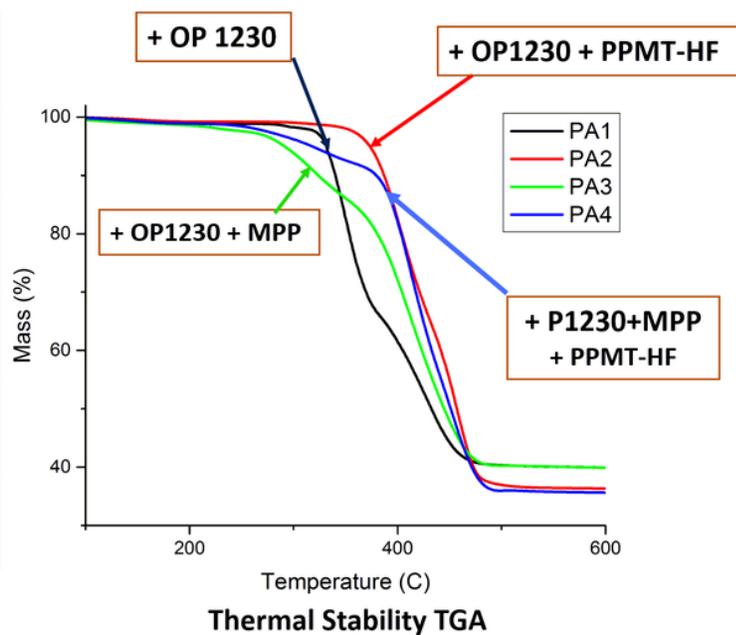


Figure 8

Thermal stability (TGA graphs [30]) and fire retardancy of glass filled* PA66 *(Durethan AKV35CXH2.0, containing 35 wt. % glass fibers, LANXESS) with various fire retardant systems

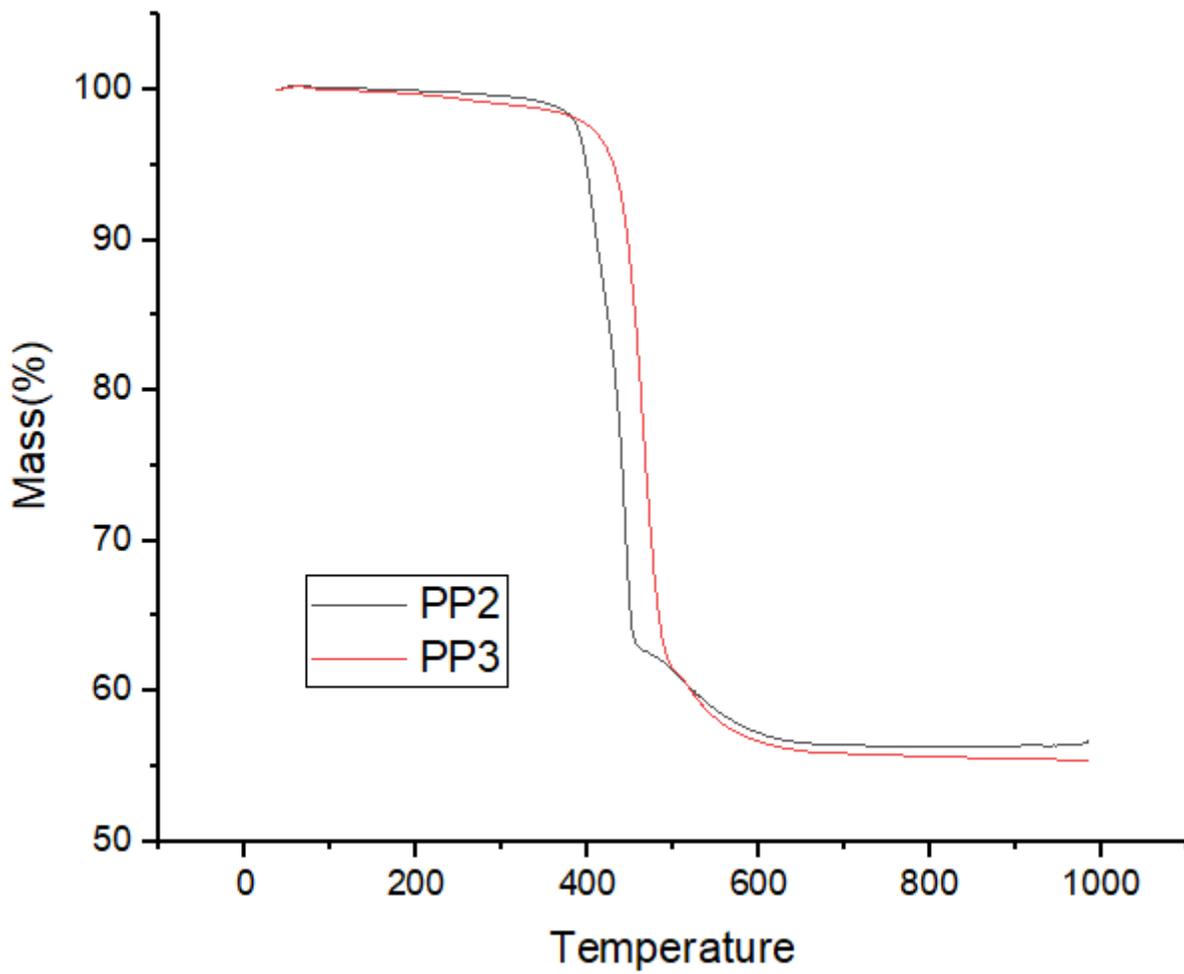


Figure 9

TGA Graph of Kaolin (66.7 %) filled polypropylene, without (PP2) and with (1.67%) MCA PPMT-HF (PP3): Difference, onset of weight loss $\Delta t +25$ OC.

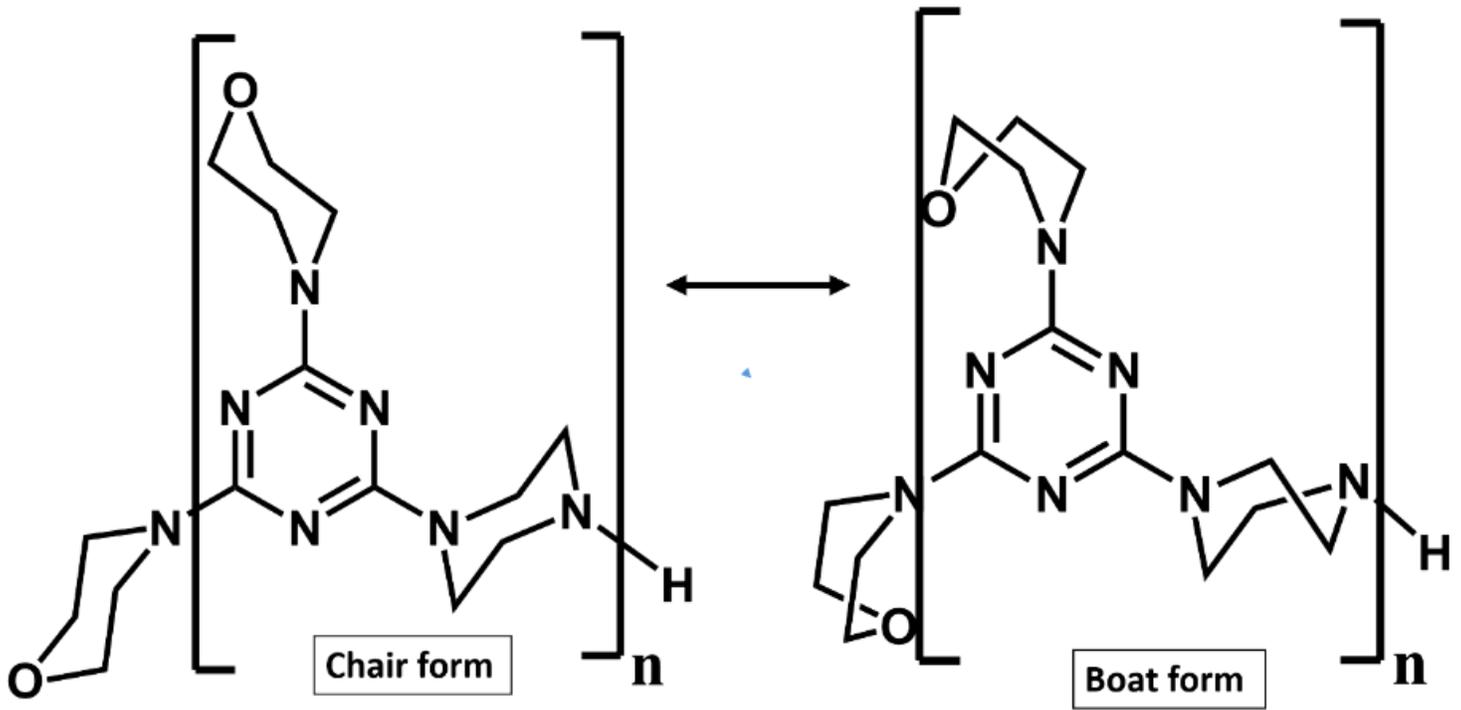


Figure 10

MCA® PPM Triazine HF, stereochemistry “Flip-Flop” switchover r responsible for thermal stabilization in melt processing

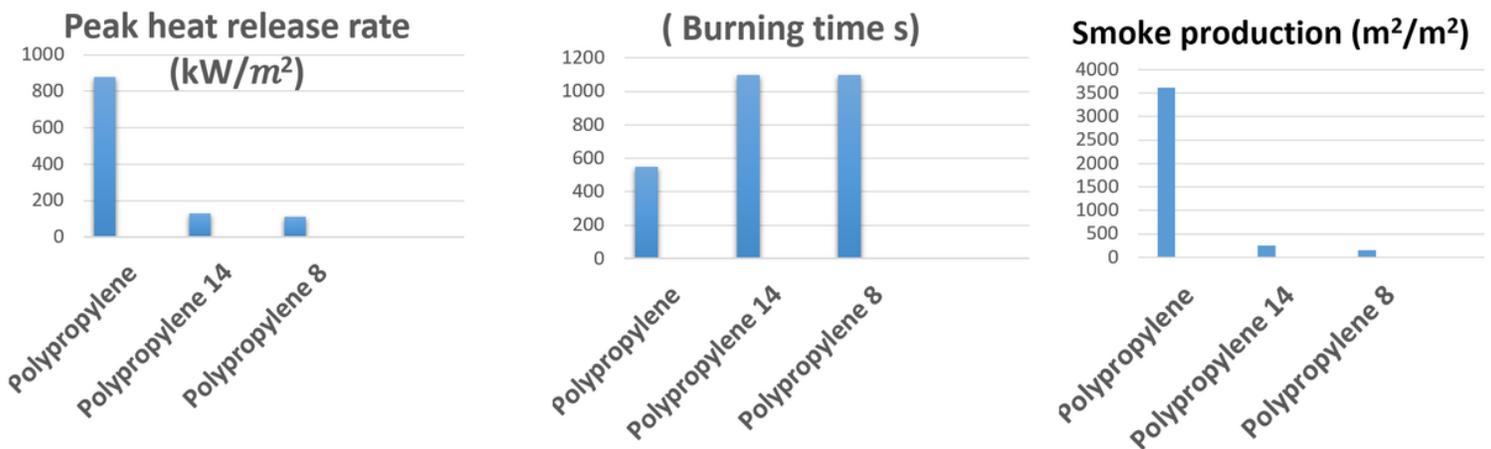
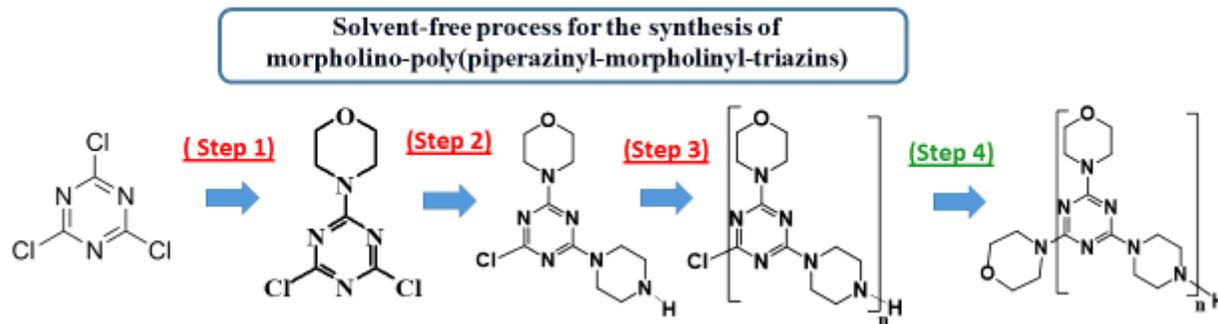


Figure 11

11a-c. MCA PPM Triazine Technology for safe plastic waste incineration and efficient energy extraction (example polypropylene)-Cone calorimetry at 50 kW/m². (samples 14 & 8 with inorganic fillers and PPMT-HF)



1. Step 1 : Condensation of cyanuric chloride with morpholine to 4-morpholino 2,6-dichloro-triazin (formation of dendrimer structures excluded)
2. Step 2 : Reaction with piperazin to form morpholino-piperazino-chlorotriazin
3. Step 3 : Suspension polymerization to chloro-poly(piperazinyl-morpholinyl-triazins) (hexagonal, sub-micro-particles)
4. Step 4: Reaction with morpholine to morpholino-poly(piperazinyl-morpholinyl-triazins)

The technology is particularly characterized by the fact that, for the sake of reducing carbon footprint of the synthesis, no organic solvent is used in any step; (USP 8,202,924, EP 213054!)

Figure 12

Chemistry and technology of morpholino-poly(piperazinyl-morpholinyl-triazin) (PPMT-HF)

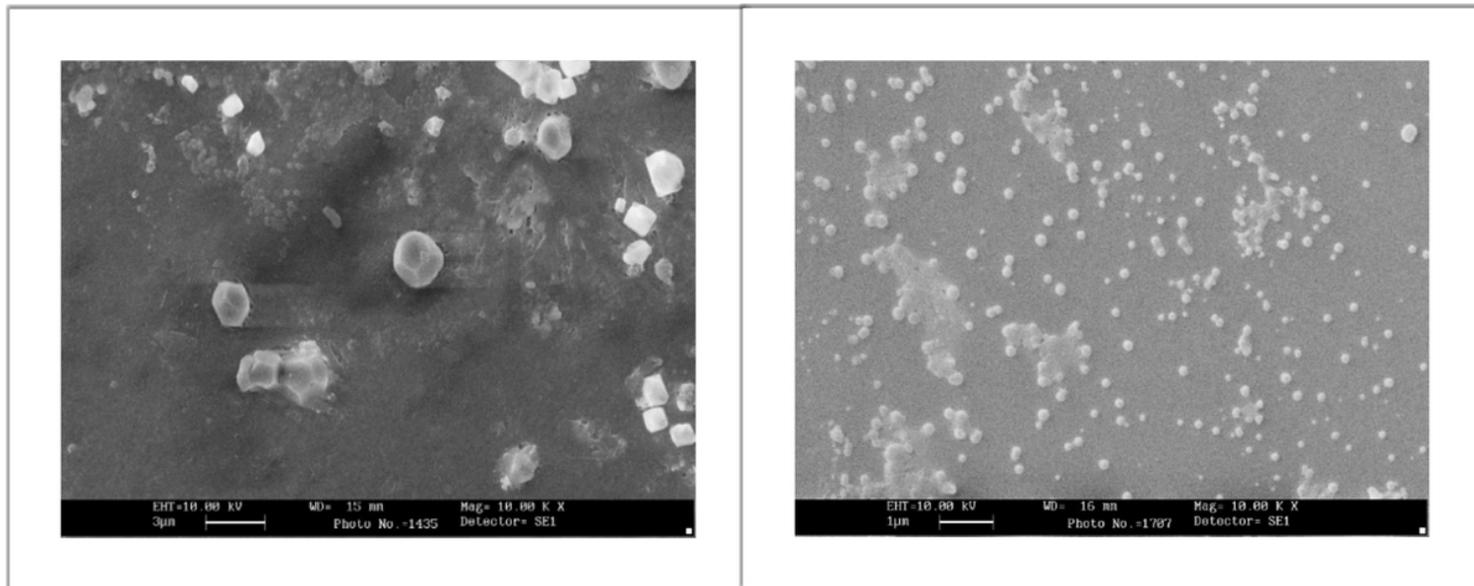


Figure 13

SEM picture of PPMT-HF: sub-micron, diamond shaped individual particles