

Central Lancashire Online Knowledge (CLoK)

Title	Fire retardant action of mineral fillers
Type	Article
URL	https://clock.uclan.ac.uk/2963/
DOI	##doi##
Date	2011
Citation	Hull, T Richard orcid iconORCID: 0000-0002-7970-4208, Witkowski, Artur orcid iconORCID: 0000-0002-0005-7520 and Hollingbery, Luke (2011) Fire retardant action of mineral fillers. Polymer degradation and Stability, 96 (8). pp. 1462-1469. ISSN 0141-3910
Creators	Hull, T Richard, Witkowski, Artur and Hollingbery, Luke

It is advisable to refer to the publisher's version if you intend to cite from the work. ##doi##

For information about Research at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLoK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the <http://clock.uclan.ac.uk/policies/>

Accepted Manuscript

Title: Fire retardant action of mineral fillers

Authors: T. Richard Hull, Artur Witkowski, Luke Hollingbery

PII: S0141-3910(11)00180-7

DOI: [10.1016/j.polymdegradstab.2011.05.006](https://doi.org/10.1016/j.polymdegradstab.2011.05.006)

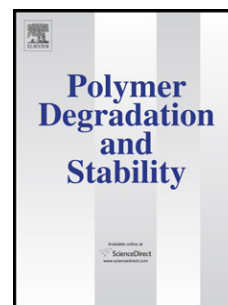
Reference: PDST 6370

To appear in: *Polymer Degradation and Stability*

Received Date: 9 February 2011

Revised Date: 22 April 2011

Accepted Date: 11 May 2011



Please cite this article as: Hull R, Witkowski A, Hollingbery L. Fire retardant action of mineral fillers, *Polymer Degradation and Stability* (2011), doi: 10.1016/j.polymdegradstab.2011.05.006

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

PDST-D-11-00115R1 Ready

Fire retardant action of mineral fillers

T Richard Hull*, Artur Witkowski, Luke Hollingbery

Centre for Fire and Hazards Science, University of Central Lancashire (UCLan), Preston PR1 2HE, UK

Abstract

Endothermically decomposing mineral fillers, such as aluminium or magnesium hydroxide, magnesium carbonate, or mixed magnesium/calcium carbonates and hydroxides, such as naturally occurring mixtures of huntite and hydromagnesite are in heavy demand as sustainable, environmentally benign fire retardants. They are more difficult to deploy than the halogenated flame retardants they are replacing, as their modes of action are more complex, and are not equally effective in different polymers. In addition to their presence (at levels up to 70%), reducing the flammable content of the material, they have three quantifiable fire retardant effects: heat absorption through endothermic decomposition; increased heat capacity of the polymer residue; increased heat capacity of the gas phase through the presence of water or carbon dioxide. These three contributions have been quantified for eight of the most common fire retardant mineral fillers, and the effects on standard fire tests such as the LOI, UL 94 and cone calorimeter discussed. By quantifying these estimable contributions, more subtle effects, which they might otherwise mask, may be identified.

Keywords

Aluminium hydroxide, ATH, fire, flame, retardant, filler, cone calorimeter, oxygen index, UL 94

* trhull@uclan.ac.uk

Introduction

Fire Retardants and Flammability

The widespread use of synthetic polymers has increased the flammability of our home, work and travelling environments. This has led to correspondingly wider use of different types of fire retardants, to limit this flammability. In 2008, the worldwide consumption of fire retardants was estimated at \$4.1bn, set to rise by 7% to \$6.1bn in 2014¹. Early fire retardants were halogen-based. Known as flame retardants, they operated in the gas phase, replacing the high energy free radicals responsible for flame propagation with more stable species, such as Cl· and Br·, thus quenching the flame. As additives, these flame retardants were easy to use, halogenated molecules were selected for compatibility with the host polymer and with its decomposition range. The flame retardant would be chosen to match the thermal stability of the polymer, in order of increasing thermal stability from aliphatic bromine, aromatic bromine, aliphatic chlorine, to aromatic chlorine for the highest temperature decomposition range. However, interference with flame reactions inhibited hydrocarbon oxidation and the conversion of CO to CO₂ and resulted in very smoky, highly toxic fire effluents, rich in products of incomplete combustion. For example, plasticised PVC, which loses about 20% chlorine by mass when burnt, evolves a number of chlorine containing species, including mono- and dichlorobenzenes and other chloro-aromatic and chloro-aliphatic hydrocarbons². It has been reported that, depending on the fire situation, as much as 20% of the chlorine may exist in an organic form in the effluent³. Approximately 70 compounds⁴ including benzene, toluene, xylene, indene, and naphthalene have been identified, but among these hydrogen chloride is of even greater toxicological significance than carbon monoxide, while the other compounds are of lesser significance. Under non-flaming decomposition conditions the irritancy of the mixed effluent has been found to be considerably greater that could be explained on the basis of the hydrogen chloride content, so the additional organic irritants must also be considered.

In addition, halogen flame retardants have been shown to leach out of polymers into the natural environment, where their presence is now ubiquitous, and some are proven endocrine disruptors^{5, 6}. These problems have driven the search for alternative “halogen-free” fire retardants, which include metal hydroxide^{7, 8} and carbonate fillers⁹, phosphorus compounds¹⁰, low melt glasses¹¹, as well as a range of more esoteric materials, such as clay and silica nanoparticles^{12, 13}, carbon nanotubes¹⁴, expandable graphite¹⁵ and metal chelates^{16, 17}. In general, halogen-free fire retardants are much more polymer-specific – while one fire retardant will work well in one polymer, it may not work at all in another. Some of these fire retardants, such as the volatile phosphorus compounds, act like halogens, inhibiting gas phase combustion reactions, while the majority attempt to stabilise the condensed phase through barrier formation, resulting from build up of char or inorganic residue or swelling (intumescence) to create an insulating layer. In many cases these additives are less efficient than halogen-based flame retardants, requiring higher loadings (up to 70% by weight) in order to meet required flammability standards. Thus the commercial development of many of these materials has been dependent on the availability of suitable compatibilising agents, to incorporate the fire retardant additives into the polymer at suitable loadings with adequate dispersion, and polymer processing equipment able to cope with higher melt viscosities associated with higher filler loadings.

Market acceptance of fire retardant formulations is generally based on performance in industry-standard material or product tests. These range from simple limiting oxygen index (LOI) tests (the minimum concentration of oxygen to support downward combustion of a thin strip of material), or Bunsen burner tests (such as the UL-94, quantifying horizontal or upward flame spread along a thin strip of material after ignition), to large-scale specific tests for cables, furniture, wall linings etc. The general term “flammability” can be subdivided into more specific criteria, the most important of which are often considered to be ignitability and heat release rate.

These processes result in condensed phase polymer decomposition, such as random and end-chain scission, chain stripping and char formation; this is followed by heat transfer through the decomposing polymer matrix; volatile production leading to bubble formation and swelling of the condensed phase; and ultimately the release of sufficient quantities of fuel to the gas phase for ignition. Piloted ignition of a polymer occurs when the heat transfer from the flames or other heat source is sufficient to pyrolyse enough fuel for that flame to become self-sustaining. Spontaneous (non-piloted) ignition tends to occur around 200 °C above piloted ignition, after the heat released by non-flaming processes results in the accumulation of a critical concentration of free radicals in the gas phase. The processes leading to ignition are complex, involving heat transfer, by conduction through the polymer, competing with localised surface heating.

Once ignition occurs, the rate of burning will depend on two factors:

1. The rate of flame spread over the surface. Flame spread can be seen as a repeated series of piloted ignitions, and thus the parameters governing ignitability also control flame spread.
2. The rate of penetration of the flame front into the bulk of the fuel. For thermally thin fuels, such as textiles or film this will be insignificant, but for objects with sufficient depth, this will be a controlling factor. The heat flux from the flame will drive the production of volatiles. If the flame is above the material, radiant heat transfer will predominate. If gas phase inhibition occurs, this will result in more soot and hence more radiation and greater heat transfer to the fuel. As the rate of fuel pyrolysis increases, so the heat flux from the flame will increase, leading to a greater peak in the heat release as a function of time.

Mineral fillers

Incorporation of any non-combustible filler will reduce the flammability of a polymer, by reducing the total amount of fuel, the rate of diffusion of oxygen into, and fuel from, the polymer bulk while increasing the heat capacity, thermal conductivity, reflectivity and emissivity. There may also be synergistic or antagonistic catalytic¹⁸ or other surface effects associated with the filler, and effects on the polymer melt rheology¹⁹. In addition, certain inorganic materials decompose endothermically with the release of inert gases or vapour, enhancing the potential fire retardant effect. In order to be effective, the decomposition must occur in a narrow window above the polymer processing temperature, but at or below its decomposition temperature. In practice most of the suitable materials are group II or III carbonates or hydroxides. They have three fire retardant effects, in addition to those of the inert fillers described above.

1. Endothermic decomposition, absorbing heat and therefore keeping the surrounding polymer cooler.
2. Production of inert diluent gases. Flaming reactions require a critical concentration of free radicals to be self-sustaining. If this concentration falls sufficiently, for example by the release of water or carbon dioxide, flame extinction will occur.
3. Accumulation of an inert layer on the surface of the decomposing polymer, shielding it from incoming radiation, and acting as a barrier to oxygen reaching the fuel, flammable pyrolysis products reaching the gas phase, and radiant heat reaching the polymer.

For example, aluminium hydroxide ($\text{Al}(\text{OH})_3$), (which when used as a fire retardant, is commonly referred to as alumina trihydrate (ATH) and formulated as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, even though it is neither an alumina, nor a hydrate²⁰), decomposes to form alumina (Al_2O_3) with the release of water. It breaks down endothermically forming water vapour, diluting the radicals in the flame, while the residue of alumina builds up to form a protective layer.



It is worth noting that the heat capacity of organic polymers²¹ vary from 0.9 to 2.1 J K⁻¹g⁻¹, thus the decomposition enthalpy of a fire retardant mineral filler is a factor of 1000 larger – the decomposition enthalpy of 1 g $\text{Al}(\text{OH})_3$ is equal to the heat (q) required to raise the temperature of a mass (m) of 1.5 g of low density polyethylene (LDPE) from ambient temperature to decomposition (400°C) ($\Delta\theta$), assuming constant heat capacity (c) during heating, ($q = m c \Delta\theta$), so $q = 1.5 \times 2.3 \times 375 = 1.29 \text{ kJ}$).

The importance of the three contributions, from endotherm, gas and residue heat absorption has been the subject of some speculation¹⁹. A simplistic analysis by Khalturinskii²², based on work undertaken in connection with the oxygen index test, attempted to quantify the effect of mineral fillers on the LOI. This showed significant enhancement afforded by hydroxides and carbonates over inert fillers. The analysis was based on the heat balance for processes occurring in the condensed phase and gas phase. A term was derived for the LOI as the ratio of the difference between the heat of combustion, minus the heat of gasification, heat capacity of the gas phase fuel, and heat absorbed by the filler, divided by the heat capacity of the surrounding oxygen and nitrogen. (This assumes the sole extinction criteria in the LOI is when the required oxygen is contained in too large a volume of nitrogen to support the flame – neglecting the decreasing proportion of radiant heat transfer which goes back to the fuel as the flame enlarges). Quoting studies of inert fillers, where loadings of 5-20 % have minimal effect on the LOI, he concludes that effective fire retardancy can only be achieved with inert fillers at loadings over 80%. He introduces terms for the heat absorption by the metal hydroxide type fillers, but does not apply the analysis to published data, instead concentrating on the enhanced thermal conductivity on introduction of glass fibres or copper wire.

This work was extended to quantify the three contributions to fire retardancy listed above in a limited report by Rothon¹⁹ of otherwise unpublished work. However, the analysis was only presented for two mineral fillers, aluminium hydroxide ($\text{Al}(\text{OH})_3$) and nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$).

Thermal Effects of Mineral Fillers

The present work concerns an attempt to quantify the four physical contributions to the overall fire retardant effects of mineral fillers as shown in Table 1. In this way, any unexpected effects such as chemical interactions or changes of behaviour resulting from different filler morphologies may be more readily identified. In addition to the decomposition endotherm, the heat capacities of the filler, its solid residue, and its vapour phase products may be estimated for the temperature range over which they exist.

Table 1 Fire Retardant Effects of Mineral Fillers

Effect	How quantified
Diluting polymer in condensed phase	Heat capacity of the filler prior to decomposition
Endothermic decomposition of filler	Heat of decomposition
Presence of inert residue	Heat capacity of the residue after decomposition
Presence of diluent gases	Heat capacity of the diluent gases

However, the heat capacity of any material varies as a function of temperature, and particularly around any phase changes. For a single phase of a pure material this variation has been represented by a polynomial, giving the value of the heat capacity at any temperature. Integrating these values over the temperature range under consideration will give the best value of the heat required to raise temperature over that range. The heat capacity, C_p of a material is given by the Shomate equation^{23, 24}

$$C_p = a + bT + cT^2 + dT^3 + eT^{-2}$$

The heat required to raise the temperature of a known quantity of substance over a temperature range is the sum of the heat capacities at each temperature. This used to be obtained by integration of the Shomate (or equivalent) equation with respect to T , but can also be integrated numerically using a spreadsheet. For example to heat $\text{Mg}(\text{OH})_2$ from 25°C to 300°C (its decomposition temperature), its heat capacity is given by

$$C_p = 84.9 + 0.00744T - 6.89 \cdot 10^{-5}T^2 + 2.66 \cdot 10^{-8}T^3 - 2.17 \cdot 10^6T^{-2} \quad \text{in J K}^{-1} \text{ mol}^{-1}$$

Therefore $C_{p, 298} = 77.2 \text{ J K}^{-1} \text{ mol}^{-1}$ or $C_{p, 298} = 1.32 \text{ J K}^{-1} \text{ g}^{-1}$

similarly $C_{p\ 573} = 1.77 \text{ J K}^{-1} \text{ g}^{-1}$

The heat required to raise 1g $\text{Mg}(\text{OH})_2$ to its decomposition temperature at 300°C is the area under the C_p vs T curve. However, within the errors associated with the approach outlined here, suitable selection of a representative value for C_p will give the heat requirement representative of the whole range. Thus a value of $1.44 \text{ J K}^{-1} \text{ g}^{-1}$ was used here. The same approach was used to determine the energy required to heat the resultant residue (such as MgO) from 300°C to, for example, 600°C , and for the gas phase diluents. Since the water and carbon dioxide will only be present in the gas phase above the filler decomposition temperature, no phase changes need be considered. The decomposition enthalpy of the filler may be determined experimentally, for example from differential scanning calorimetry (DSC), or obtained from the literature.

This approach is deliberately simplistic, allowing more subtle effects to be isolated from the quantifiable physical processes. In particular, the analysis involves the following assumptions:

- The thermal conductivity of the polymer composite is unaffected by the presence of the filler. This is not realistic, particularly if incorporation of the filler results in significant changes to the melt flow behaviour.
- The final temperature reached by the solid residues and the CO_2 and water in the gas phase do not vary significantly from one filler to another. This is discussed further.
- The heat capacity of the filler, and residue is not affected by the presence of polymer.
- The decomposition endotherm of the filler is unaffected by incorporation into the polymer.
- The only effect of the solid residue is its ability to act as a heat sink (in practice it will also change the reflectivity and the absorption of radiant heat).
- The only effect of the gas phase diluent is an absorber of heat, neglecting any effects reducing the free radical concentration below a critical threshold.
- It takes no account of particle size or morphology of the filler, which have been shown to be important in experimental studies.

Calculation of the physical contribution to the fire retardant effect

Table 2 Physical properties of potential fire retardant mineral fillers

Filler	Formula	T_{decomp} / $^\circ\text{C}$	ΔH_{decomp} / kJ g^{-1}
Aluminium hydroxide	$\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	180-200	1300
Magnesium hydroxide	$\text{Mg}(\text{OH})_2$	300-320	1450
Calcium hydroxide	$\text{Ca}(\text{OH})_2$	430-450	1150
Nesquehonite	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	70-100	1750
Hydromagnesite	$\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$	220-240	1300
Huntite	$\text{Mg}_3\text{Ca}(\text{CO}_3)_4$	400	980
Ultracarb	Hydromagnesite/Huntite 60/40	220-400	1172
Boehmite	$\text{AlO}(\text{OH})$	340-350	560

Table 2 shows a number of metal hydroxide and carbonates as potential fire retardant fillers, together with published estimates of their decomposition temperature ranges and endotherms. In addition to the two most important fire retarding mineral fillers, $\text{Al}(\text{OH})_3$ and $\text{Mg}(\text{OH})_2$, various mixed magnesium and calcium hydroxides and carbonates have been considered. In addition to quantifying their individual suitability as fire retardants, huntite and hydromagnesite are available as naturally occurring mixtures containing different proportions of the two components, which are not easily separated²⁵. This approach allows simple estimation of the fire retardant contributions of different mixtures which are available. One such mixture, of 60% hydromagnesite and 40% huntite is sold as Ultracarb®. The heat absorbed by the filler from ambient to its decomposition temperature was calculated from the representative heat capacity over that range. Similarly the heat absorbed by the inorganic residue was determined from its representative heat capacity from the decomposition temperature to the final residue temperature (e.g. 600°C), for the fraction of 1g remaining in the condensed phase. The heat absorbed by endothermic decomposition was obtained from DSC studies or published data. The heat absorbed by the water or carbon dioxide released to the gas phase is their representative heat capacity from the filler decomposition temperature to the maximum flame temperature (e.g. 900 °C).

These data, together with the average values of heat capacities of the filler, its residue, and its gaseous decomposition products have been used to estimate the heat absorption by the filler (% Filler), the residue (% Residue), the evolved water vapour and carbon dioxide (%Gas) and the decomposition endotherm (% Decomposition Endotherm) shown in Table 3.

Table 3 Relative contribution of heat absorbing effects for potential mineral filler fire retardants

	Relative Contribution Fire Retardant Effects			
	% Filler	Endotherm	% Residue	%Gas
Aluminium hydroxide	9	55	13	23
Magnesium hydroxide	19	56	9	15
Calcium hydroxide	29	55	5	11
Nesquehonite	1	58	12	29
Hydromagnesite	10	56	14	21
Huntite	20	58	9	13
Ultracarb	14	57	12	18
Boehmite	18	46	20	15

In general the figures show broad similarities – in every case, the greatest contribution comes from the endothermic decomposition. The decomposition temperature clearly affects the relative contributions of the heat capacity of the filler, and those of the residue and gas. It can be seen that in some cases, e.g. $\text{Al}(\text{OH})_3$, and $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, the heat capacities of the gas phase products exceeds that of the condensed phase, where for others, e.g. $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ the solid phase contribution is greater. Comparing aluminium and magnesium hydroxide, it is evident that the difference between their relative effects arise from the higher decomposition temperature of $\text{Mg}(\text{OH})_2$, giving a larger contribution to the heat capacity of the undecomposed filler, but a smaller contribution from the heat capacity of the residue that $\text{Al}(\text{OH})_3$, and from the heat capacity of the greatest volume of water vapour released by the

$\text{Al}(\text{OH})_3$ – even though the energy for such a release is almost identical for both fillers. The higher decomposition temperature of calcium hydroxide suggests that it may perform well with polymers of higher thermal stability, although the contribution from the heat capacity of the vapour phase water is the smallest of all fillers in the list. In practice, calcium hydroxide does not perform well, due to the high thermal stability of the carbonate, which forms exothermically, in preference to the oxide¹⁹. Where two separate decomposition processes occur, such as in nesquehonite, which loses water at 100°C and carbon dioxide at 450°C the heat capacity of the intermediate MgCO_3 has been included in the residue contribution, together with MgO . The low decomposition temperature of nesquehonite, and the high volume of volatiles makes this an interesting candidate material for polymers with very low ($\sim 100^\circ\text{C}$) decomposition temperatures. For the hydro magnesite, huntite and Ultracarb mixture, which is often proposed as an alternative to $\text{Al}(\text{OH})_3$, it can be seen that the higher decomposition temperature of huntite gives a greater filler contribution, and overall Ultracarb is intermediate between aluminium and magnesium hydroxides. Boehemite, and nanoboehmite have recently shown²⁶ potential as fire retardant additives, although nanoboehmite is also believed to act in the gas phase as a free radical trap, since its endothermic and overall contributions are too small to justify its wider use as an absorber of heat.

As the data have all been calculated in energy units, the contribution to the individual fillers may also be compared in absolute terms. Figure 1 shows the energy absorption per gram of each of the processes undergone by the filler.

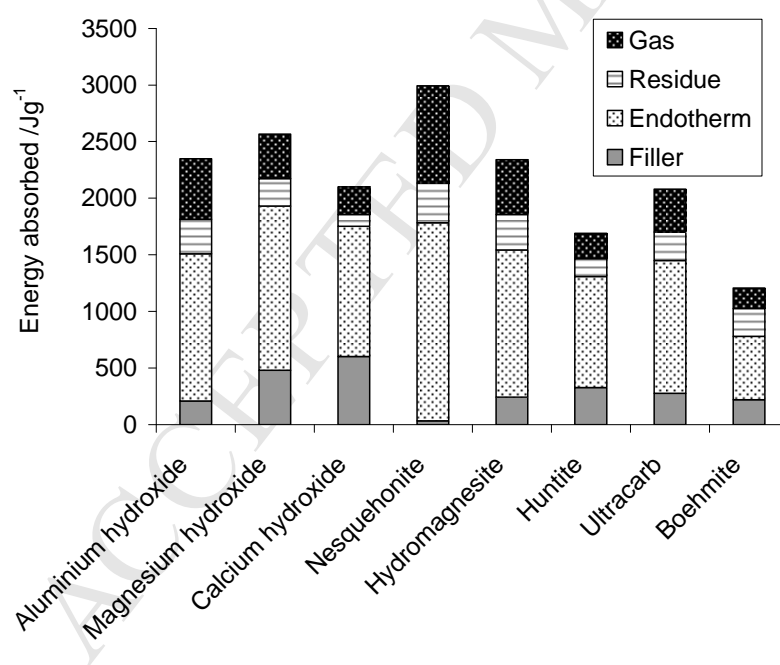


Figure 1 Absolute estimation of heat absorbed by potential fire retardant mineral fillers

The higher decomposition temperature of magnesium hydroxide and particularly the greater contribution of the filler, increase its energy absorbing capacity by about 250 J g^{-1} , compared to aluminium hydroxide, while the lower endotherm and smaller volatile heat capacity of calcium hydroxide also indicates inferior potential as a fire retardant. The large endotherm

and higher vapour heat capacity of nesquehonite suggest its potential as a superior fire retardant additive, except that it decomposes at such a low temperature. The behaviour of hydromagnesite is very similar to that of aluminium hydroxide, where the smaller endotherm and vapour heat capacity of huntite reduce the apparent fire retardant potential of the Ultracarb mixture below aluminium hydroxide. In practice, the Ultracarb mixture is often found to outperform either hydromagnesite, or aluminium hydroxide as a fire retardant. This has been ascribed to the platy morphology of huntite, reinforcing the barrier properties of the residual layer²⁷. The much lower energy absorbing capacity of boehmite, together with reports²⁸ of its successful application as an additive fire retardant, suggest that other mechanisms must also be operating.

It is evident from figure 1 and table 3 that endothermic decomposition accounts just over half of the fire retardant effect for the mineral fillers considered. For the example of LDPE and $\text{Al}(\text{OH})_3$ considered earlier, the total heat absorbed by 1g of filler could otherwise have heated almost 4g of LDPE to its decomposition temperature.

Sensitivity of solid and gas phase temperatures

One assumption, used by Khalturinskii²² and Rothon¹⁹, and also used here is that the temperature of the residue will always be 600°C and the temperature of the gas phase will always be 900°C. This has been discussed qualitatively by Rothon. To test the sensitivity of this assumption, the calculations were repeated using residue temperatures of 500, and 700°C and gas phase temperatures of 800 and 1000°C, shown in Figure 2.

It can be seen from Figure 2 that both these assumptions have only a minor influence on the contributions of the heat absorption by contributions in the gas phase and residue.

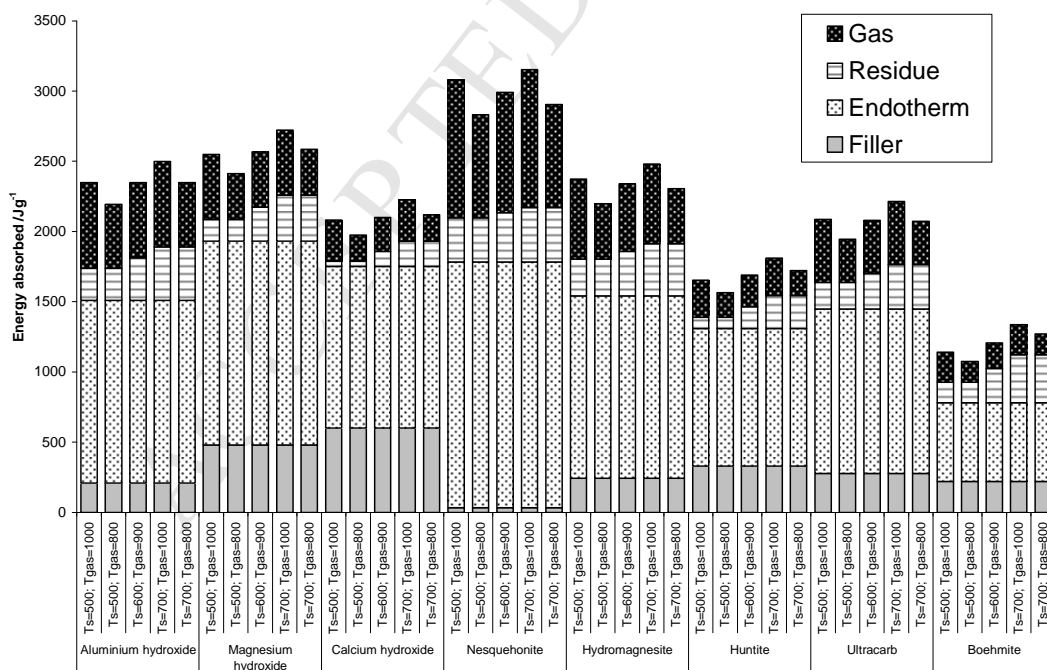


Figure 2 Comparison of Temperature estimates for residue and gas phase

The filler decomposition temperature will be increased when it surrounded by molten polymer. For example, ATH normally decomposes at 190°C, whereas, when in an ethylene-vinyl acetate copolymer (EVA) in a common cable industry formulation, water does not start to be lost until the temperature reaches 250°C²⁹. The loss of water can also have a deleterious effect, rupturing protective layers formed, for example, by the cross-linking of the conjugated polyene in EVA/ATH composites³⁰.

Behaviour in Standard Fire Tests

The aim of any fire retardant chemist must be to improve the fire safety of the material under development. However, given the infinite range of possible scenarios and the need for demonstrable standards of fire behaviour, the performance of materials in standard reaction to fire tests is generally assumed to reflect improvements in fire safety. The most important parameters in selecting mineral filler remain the suitability of the decomposition temperature to the polymer, the compatibility of the filler with the polymer, and the total energy absorbed by the filler before and after decomposition, (shown in Figure 1). The discussion below focuses on the effects of the other contributions to the fire retardant behaviour of mineral fillers in three most common standard flammability assessments.

Limiting Oxygen Index (LOI)

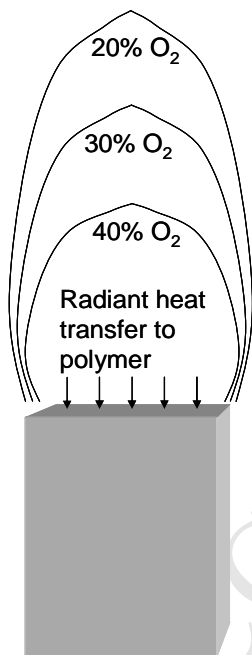


Figure 3 The LOI test showing the swelling of the flame and consequent decrease in radiant heat transfer to the polymer with oxygen concentration decreasing from 40 to 20%.

The LOI is essentially an ease of extinction test – a flame will only propagate down the polymer sample if the radiant heat transferred from the flame to the polymer is sufficient to vaporise enough fuel to replace it. As the oxygen concentration is decreased, the flame is diluted by nitrogen, increasing in size, and also reducing the radiant heat transferred to the polymer, until it is so large, the concentration of the flame propagating free radical species falls below a critical threshold, and the flame goes out. This is illustrated in Figure 3 for three

oxygen concentrations. If the test is run in high oxygen concentrations, a small, very intense white flame is observed.

The endothermic decomposition of the filler and the heat capacity of both the filler and its residue will all increase the amount of heat needed to vaporise the same amount of fuel, while the presence of gas phase flame diluents (water or carbon dioxide) will also tend to swell the flame, and reduce its temperature, reducing the proportion of heat transferred back to the polymer. Therefore the different contributions to fire retardant behaviour will all contribute to the increase in LOI, and thus be indistinguishable. However, the incorporation of any filler material in easily depolymerisable materials (which drip, improving their LOI) reduce the LOI.

Rothon^{19, 31} and Hornsby³² have reported a lack of correlation of LOI to other tests when applied to mineral fillers which they attribute to the key structural role played by the filler residue in the LOI. In particular, significant inexplicable differences were observed in the LOI, for example, between calcium carbonate and glass beads, or when the residue was tapped off the tip of the burning polymer, although in both instances little difference was observed in the UL94 tests.

Rothon¹⁹ observed that although the oxygen index test appears fairly well understood, its relevance to other tests is not well founded, and these other tests are themselves poorly understood in terms of filler effects. He attributes the difference to the smaller portion of heat fed back to the polymer in the LOI from the flame, shown in Figure 3, compared to other tests.

In addition, correlations were usually worse with very fine particle sizes. This was attributed to sintering of the particles, providing a more resilient residue structure, capable of shielding (by re-emission) the polymer from much of the flame's radiation.

Work on $\text{Al}(\text{OH})_3$ has shown the strong reversibility of the dehydration reaction, such that with larger particle sizes water released inside the particle recombines with the reactive surface of the freshly formed alumina³³. If escape of water is hindered sufficiently (for example by the high viscosity of the polymer melt) it has been found that partial decomposition product boehmite is formed nearer the middle of the particles. This effect increases with particle size³⁴. Industrial sources report the use of nanoboehmite as a fire retardant, citing free radical trapping properties.

Bunsen burner test UL 94

Although widely regarded as the simplest of flammability tests, the UL 94 horizontal and vertical tests involve several interacting physical processes which are inadequately reflected in the final classification of HB, V-2, V-1 and, for the best performance, V-0. As the flame propagation is either horizontal (HB) or vertically upward (V), flame dilution, and hence flame dilation is likely to have a smaller effect than energy absorption through endothermic decomposition or solid phase heat capacity, since a greater portion of the heat of combustion is fed back to the polymer. Unlike the LOI, dripping can be disadvantageous in the UL 94 test; flaming drips limit the classification to V-2 at best. Solid phase fillers and residues will almost always reduce dripping. Endothermic decomposition with release of water or carbon dioxide must coincide with fuel release to be effective in flammability

reduction – in the UL 94 test, once the first flame is extinguished, it is followed by the second 10 second application – after which the heat capacity of the protective residue may make the most important contribution.

Cone Calorimetry

Results from the cone calorimeter increasingly dominate reports of the efficacy of fire retardant systems, although it features in few regulatory requirements. A detailed description of its use for assessment of fire retardant behaviour has been given elsewhere³⁵. Unlike the LOI, the effects of dripping are negligible, since the solid/liquid sample is contained within a foil tray. The key flammability parameters obtained from cone calorimetry are the time to ignition (TTI), and the heat release rate per unit area (HRR). As flame spread can be viewed as a series of repeated ignitions, surface spread of flame is likely to be controlled by the time to ignition. The overall heat release rate (\dot{Q}) is the most important parameter controlling the fire growth rate. In the cone calorimeter and other standard protocols, only the heat release rate per unit area (HRR) is measured, since surface spread of flame is prevented by the small sample size (100 x 100 mm). However, uncontrolled fires spread across surfaces as well as penetrating into them, and the overall heat release rate (\dot{Q}) is the product of the heat release rate per unit area (HRR) and the burning area (A). If the speed of flame spread is assumed constant (v_f) and the fire spreads as a growing circle (of radius r), the heat release rate will increase in proportion to the square of time³⁶.

$$\dot{Q} = A \times \text{HRR} = \pi r^2 \times \text{HRR} = \pi v_f t^2 \quad \text{so } \dot{Q} \propto t^2$$

Fire safety engineers frequently refer to this as a “ t^2 fire”. Thus a major limitation of cone calorimeter data is that the only indication it gives of flame spread rate is through the time to ignition parameter.

The time to ignition will be a function of the time taken for the surface temperature to reach the critical value for ignition. This depends on the thermal inertia of the material (the product of heat capacity, thermal conductivity and density); on the absorption of radiation, dependent on the absorptivity and emissivity of the sample; all of which will change on incorporation of a filler, though only the heat capacity and the decomposition endotherm of the filler, contributing to the heat capacity, have been included in this simplified analysis.

After ignition, the heat release rate per unit area increases to a peak value (pHRR), an important parameter controlling fire growth, provided the fuel has significant thickness, and the rate of burning increases as it penetrates into the bulk of the material. At the pHRR, adjacent flammable articles are most likely to have their own critical heat fluxes for ignition exceeded, and thus ignite, contributing to the conflagration. However, this mode of burning is essentially penetrative, with the flame front moving towards the fuel above the gas-polymer interface. In this case, the physical presence of the filler residue will exert a greater influence on the burning behaviour (seen as a dramatic reduction of pHRR) through its heat capacity, its absorption and emission of radiation and its physical blocking of the route from fuel to

flame. Thus a polymer containing a mineral which formed a coherent residue would be expected to show a HRR curve like that of a char forming material (such as wood) rather than that of a normal thermally thick burning³⁵. This is shown in Figure 4. In this case the endothermic release of diluent gas may be counter-productive, encouraging greater flow of the protected fuel through the filler residue towards the surface, as the filler decomposes and gas release from below disrupts the protective layer.

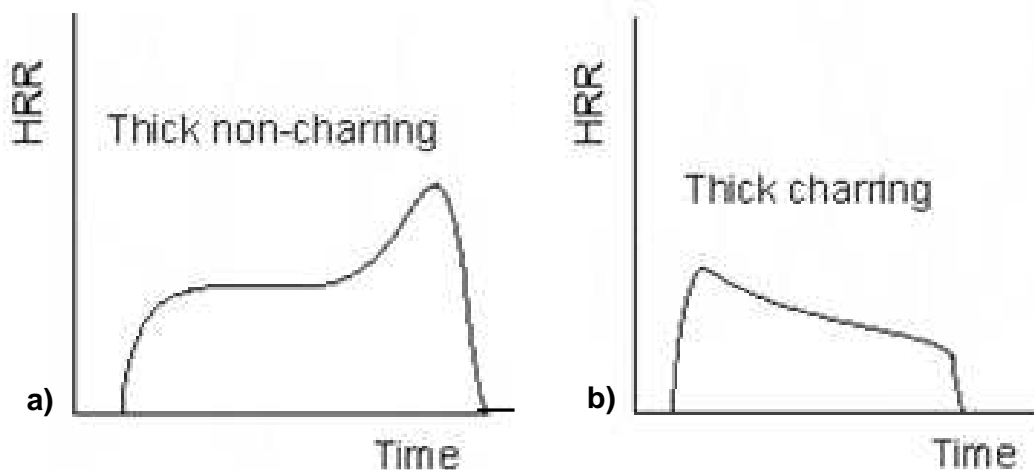


Figure 4 Idealised Heat release curves for a) thermally thick non-charring and b) thermally thick, charring materials.

In a study in the effect of nanoparticulate fillers, Scharrel³⁷ concluded that their major effect as fire retardants was to absorb and re-emit radiation, and this effect increased with increasing surface temperature (following Stefan's Law) $\propto T^4$. While the conclusions of Scharrel's work are controversial, the capacity of fine or ultrafine particles to reach high temperatures, where they become highly effective radiation shields (as absorbers and re-emitters) has a obvious bearing on the present work. However, other sources cite different reasons for the particle size effect³⁸.

It is worth noting that while the burning behaviour of polymers containing mineral fillers will be modified, not all these effects will be evident in the cone data. It has been observed that the particle size effect, evident in the LOI and UL 94 is less evident in the cone calorimeter³⁹. The time to ignition will be delayed, and the peak heat release rate may be delayed and smaller than if the same mass of polymer was burned in the absence of the mineral filler, but the total heat released and hence the effective heat of combustion will not be reduced by the heat absorbing effects of the filler (typically twice the decomposition endotherm). This arises through the use of oxygen depletion calorimetry, which relates the heat release to the oxygen consumption as 13.1kJ of heat released per gram of oxygen consumed. Any endothermic effects, which would be seen by a thermometric device, or in a real fire, will not be observed using oxygen depletion calorimetry. This is an artefact of the technique and corrections need to be incorporated into measurement of total or effective heat of combustion, wherever oxygen depletion calorimetry is used to assess fire performance of materials containing endothermically decomposing mineral fillers.

Conclusions

Mineral fillers are an important class of fire retardant with many inherently sustainable attributes, including cleaner manufacture, reduction in polymer (hence hydrocarbon) use, no reported environmental hazards, and no adverse effect on the biggest causes of death and of injury in fire, smoke and toxicity⁴⁰. The influence of hydrogen chloride on carbon monoxide yields has been reported elsewhere⁴¹ together with a comparison of the toxicity of low smoke zero-halogen (LSZH) and PVC cables. The toxic effluents from 6 LSZH cables and 4 PVC cables were determined, and the relative toxicity (as a proportion of the lethal dose, calculated as fractional effective dose according to ISO 13344) was 0.05 ± 0.01 for the LSZH cables and 0.23 ± 0.05 for the PVC cables. Mineral fillers are more difficult to incorporate into a polymer and to achieve the required level of fire retardancy than halogenated flame retardants, so better understanding of the details of their mode of action is required. Mineral filler fire retardants decompose endothermically with the release of non-flammable gases, leaving a solid residue. It has been shown that the decomposition endotherm typically contributes just over half of the heat absorbing fire retardant effect. It is well established in the field of fire retardancy that specific interaction between polymer, fire retardants and other components can have a significant impact on the flammability of the polymer composite, and this simple analysis did not consider any of these more subtle effects. The work has shown the difference in the magnitude of the solid and gas phase heat requirements of mineral fillers, though these are strongly influenced by the decomposition temperature of the filler. In terms of selecting the optimum mineral filler for a particular polymer, the perceived wisdom is to match the decomposition temperature of the filler to that of the polymer. However other features, such as coherence of the residual layer, and its ability to re-emit thermal radiation are also of clear and obvious importance.

Different tests for quantifying flammability focus disproportionately on particular aspects of burning behaviour. Thus, the LOI, which shows the least correlation to other tests, seems to be more strongly influenced by the presence and resilience of the inorganic residue; only the side effects of the endotherm decomposition, not the endotherm itself, are quantified in cone calorimetry (the time to ignition may be delayed and peak heat release lowered and delayed by endothermic decomposition of the filler, but the measured value of the total heat release, or effective heat of combustion will be unaffected by the endothermic event. This analysis is limited in its scope, and some effects of filler, such as the reduction of dripping (UL94) and action as a radiant heat shield the inorganic residue (cone calorimeter), are not included.

It might be that the greatest value of simple models, such as the one presented here, is to observe deviations from the predicted behaviour in order to identify other properties, obscured by the physical effects of the filler, which also contribute to (improvements in) the burning behaviour. For example, the superior performance of mixtures of huntite and hydromagnesite compared to aluminium hydroxide, or the unexpected fire retardant performance of the micro and nano-boehmites.

Acknowledgements

One of us (AW) would like to thank the Centre for Fire and Hazard Science at the University of Central Lancashire for provision of a studentship.

References

- 1 *The Global Market for Flame Retardant Chemicals*, BCC Research, Stamford CT, 2009
- 2 Paul, K.T.; Feasibility Study to Demonstrate the Potential of Smoke Hoods in Simulated Aircraft Fire Atmospheres: Development of the fire model, *Fire and Materials*, **1989**, 14, 43-58
- 3 Lebek, K.; Hull, T.R.; Price, D.; Products of burning rigid PVC burning under different fire conditions, *Fire and Polymers: Materials and Concepts for Hazard Prevention*, ACS Symposium Series No.922, p334-347, Oxford University Press, 2005.
- 4 Huggett, C.; Levin, B.C.; Toxicity of the Pyrolysis and Combustion Products of Poly(vinyl Chlorides): A Literature Assessment, *Fire and Materials*, **1987**, 11, 131-42.
- 5 de Wit, C. A.; An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, 46 (5), 583-624.
- 6 Shaw, S. D.; Blum, A.; Weber, R.; Kannan, K.; Rich, D.; Lucas, D.; Koshland, C.P.; Dobraca, D.; Hanson, S.; Birnbaum, L.; Halogenated flame retardants: Do the fire safety benefits justify the health and environmental risks? *Reviews on Environmental Health* **2010**, 25(4):261-305.
- 7 Hull, T. R.; Price, D.; Liu, Y.; Wills, C. L.; Brady, J., An investigation into the decomposition and burning behaviour of Ethylene-vinyl acetate copolymer nanocomposite materials. *Polymer Degradation and Stability* **2003**, 82 (2), 365-371.
- 8 Rothon, R. N.; Hornsby, P. R., Flame retardant effects of magnesium hydroxide. *Polymer Degradation and Stability* **1996**, 54 (2-3), 383-385.
- 9 Rigolo, M.; Woodhams, R. T., Basic magnesium carbonate flame retardants for polypropylene. *Polymer Engineering and Science* **1992**, 32 (5), 327-334.
- 10 Price, D.; Pyrah, K.; Hull, T. R.; Milnes, G. J.; Ebdon, J. R.; Hunt, B. J.; Joseph, P., Flame retardance of poly(methyl methacrylate) modified with phosphorus-containing compounds. *Polymer Degradation and Stability* **2002**, 77 (2), 227-233.
- 11 Bourbigot, S.; Le Bras, M.; Leeuwendal, R.; Shen, K. K.; Schubert, D., Recent advances in the use of zinc borates in flame retardancy of EVA. *Polymer Degradation and Stability* **1999**, 64 (3), 419-425.
- 12 Hull, T. R.; Stec, A. A.; Nazare, S., Fire Retardant Effects of Polymer Nanocomposites. *Journal of Nanoscience and Nanotechnology* **2009**, 9 (7), 4478-4486.
- 13 Schmaucks, G.; Friede, B.; Schreiner, H.; Roszinski, J. O., *Amorphous Silicon Dioxide as Additive to Improve the Fire Retardancy of Polyamides*. Chapter 3 in *Fire Retardancy of Polymers – New Strategies and Mechanisms*, Hull T.R. and Kandola, B.K. (Eds) Royal Society of Chemistry: Cambridge, **2009**; p 35-48.

-
- 14 Bourbigot, S.; Samyn, F.; Turf, T.; Duquesne, S., Nanomorphology and reaction to fire of polyurethane and polyamide nanocomposites containing flame retardants. *Polymer Degradation and Stability* **2010**, *95* (3), 320-326.
 - 15 Li, Z. Z.; Qu, B. J., Flammability characterization and synergistic effects of expandable graphite with magnesium hydroxide in halogen-free flame-retardant EVA blends. *Polymer Degradation and Stability* **2003**, *81* (3), 401-408.
 - 16 Wang, D. Y.; Liu, Y.; Wang, Y. Z.; Artiles, C. P.; Hull, T. R.; Price, D., Fire retardancy of a reactively extruded intumescent flame retardant polyethylene system enhanced by metal chelates. *Polymer Degradation and Stability* **2007**, *92* (8), 1592-1598
 - 17 Wang, D. Y.; Liu, Y.; Ge, X. G.; Wang, Y. Z.; Stec, A.; Biswas, B.; Hull, T. R.; Price, D., Effect of metal chelates on the ignition and early flaming behaviour of intumescent fire-retarded polyethylene systems. *Polymer Degradation and Stability* **2008**, *93* (5), 1024-1030
 - 18 Hull, T. R.; Quinn, R. E.; Areri, I. G.; Purser, D. A., Combustion toxicity of fire retarded EVA. *Polymer Degradation and Stability* **2002**, *77* (2), 235-242.
 - 19 Rothon, R. N., Effects of Particulate Fillers on Flame Retardant Properties of Composites, Chapter 6 in Rothon R. N. (Ed) *Particulate-Filled Polymer Composites*, 2nd Edition, Rapra Technology, Shawbury, UK, **2003**.
 - 20 Horn, W. E., Inorganic hydroxides and hydroxycarbonates: Their function and use as flame retardants, Chapter 9 in *Fire Retardancy of Polymeric Materials*, Ed Grand, A. and Wilkie, C.A., Marcel Dekker, New York, 2000.
 - 21 Stoliarov, S. I.; Safronava, N.; Lyon, R. E., The effect of variation in polymer properties on the rate of burning. *Fire and Materials* **2009**, *33* (6), 257-271.
 - 22 Khalturinskii, N. A.; Berlin, A. A., On reduction of combustibility of polymeric materials. *International Journal of Polymeric Materials* **1990**, *14* (1-2), 363-379.
 - 23 Shomate, C. H. High-temperature Heat Contents of Magnesium Nitrate, Calcium Nitrate and Barium Nitrate. *J. Am. Chem. Soc.* **1944**, *66*, 928-929.
 - 24 NIST chemistry webbook, <http://webbook.nist.gov/chemistry/>.
 - 25 Hollingbery, L. A.; Hull, T. R., The thermal decomposition of huntite and hydromagnesite-A review. *Thermochimica Acta* **2010**, *509* (1-2), 1-11.
 - 26 Zhang, J.; Ji, Q.; Zhang, P.; Xia, Y.; Kong, Q.; Thermal stability and flame-retardancy mechanism of poly(ethylene terephthalate)/boehmite nanocomposites, *Polymer Degradation and Stability*, **2010**, *95*, 1211-1218.

-
- 27 Hollingbery, L. A.; Hull, T. R., The fire retardant behaviour of huntite and hydromagnesite - A review. *Polymer Degradation and Stability* **2010**, *95* (12), 2213-2225.
- 28 Laachachi, A.; Ferriol, M.; Cochez, M.; Lopez Cuesta, J. M.; Ruch, D., A comparison of the role of boehmite (AlOOH) and alumina (Al₂O₃) in the thermal stability and flammability of poly(methyl methacrylate). *Polymer Degradation and Stability* **2009**, *94* (9), 1373-1378.
- 29 McGarry, K.; Zilberman, J.; Hull, T. R.; Woolley, W. D.; Decomposition and Combustion of EVA and LDPE alone and when Fire Retarded with ATH, *Polymer International* **2000**, *49*, 1193-1198.
- 30 Zilberman, J.; Hull, T.R.; Price, D.; Milnes, G.J.; Keen, F., Flame Retardancy of Some Ethylene-Vinyl Acetate Copolymer-Based Formulations, *Fire and Materials*, **2000**, *24*, 159-164.
- 31 Ashley, R. J.; Rothon, R. N., Use of inorganic fillers to reduce the flammability of polymers. *Plastics Rubber and Composites Processing and Applications*, **1991**, *15* (1), 19-21.
- 32 Hornsby, P. R.; Watson, C. L., A study of the mechanism of flame retardation and smoke suppression in polymers filled with magnesium-hydroxide. *Polymer Degradation and Stability* **1990**, *30* (1), 73-87.
- 33 Souza, S.P.; Souza, S.H.; and Toledo S.P. Standard Transition Aluminas. Electron Microscopy Studies, *Materials Research* **2000**, *3*, 104-114,
- 34 Sobolev, I.; Woychesin, E.A., *Alumina Trihydrate*. Chapter 16 in Handbook of Fillers for Plastics, Ed Katz H.S. and Milewski, J.V., Van Nostrand Reinhold: New York, 1987.
- 35 Scharrel, B.; Hull, T. R., Development of fire-retarded materials - Interpretation of cone calorimeter data. *Fire and Materials* **2007**, *31* (5), 327-354.
- 36 Celzard, A.; Fierro, V.; Amaral-Labat, G.; Pizzi, A.; Torero, J., Flammability assessment of tannin-based cellular materials. *Polymer Degradation and Stability In Press, Accepted Manuscript*. 2011
- 37 Scharrel, B.; Weiß, A., Temperature inside burning polymer specimens: Pyrolysis zone and shielding. *Fire and Materials* **2010**, *34* (5), 217-235.
- 38 Hughes, P.; Jackson, G. V.; Rothon, R. N., Particle morphology effects on the performance of PMMA filled with aluminum hydroxide in a variety of fire tests. *Makromolekulare Chemie-Macromolecular Symposia* **1993**, *74*, 179-183.
- 39 Herbert, M. J., *Aluminium hydroxide for non-halogen compounds*. Proceedings of Flame Retardants '94, Interscience: London, UK, **1994**, 59-71.
- 40 Hull, T. R.; Wills, C. L.; Artingstall, T.; Price, D.; Milnes, G. J., *Mechanisms of smoke and CO suppression from EVA composites*. 2005; p 372-385.
- 41 Hull, T. R.; Stec, A. A.; Paul, K. T.; Hydrogen Chloride in Fires, *Fire Safety Science*, **2008**, *9*, 665-676.