

Polymers and Fire

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Unwanted fires account for significant losses to life and property. In the UK about 600 lives are lost each year¹, and the cost of unwanted fire has been estimated at about 1% of the UK's gross domestic product². The vast majority of unwanted fires are fuelled by organic polymers, and as manufacturing technology has advanced, there has been a rapid shift from natural polymers (contained in wood, cotton, leather and wool) to synthetic polymers. Synthetic polymers are generally more flammable than their natural counterparts, polyethylene, polypropylene or polystyrene have calorific values comparable to petroleum. However, unlike natural polymers which can only be fire retarded by coatings or other surface treatments, the manufacturing process of most plastic materials is ideal for the incorporation of fire retardants.

Hazards from fire

The flammability of a material is not an intrinsic property, like its density or heat capacity, but is dependent on the fire conditions. The apparent order of flammability of two materials may be reversed if tested under different conditions. Similarly, changing the material composition, for example by the addition of a fire retardant, will also change its reaction to fire behaviour. The incorporation of a nanofiller will reduce the dripping tendency. In one fire scenario, dripping away from a flame will reduce the ignitability, while in another, drips, especially flaming drips, will cause downward flame spread, significantly increasing the fire hazard.

The fire triangle (

Figure 1) demonstrates the interdependence of the material properties with ventilation and heat.

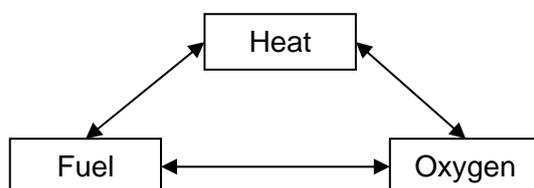


Figure 1 The Fire Triangle

In general, fire growth will be more favourable as the heat flux or oxygen supply is increased, or if the material is more “flammable”. However, excessive ventilation may remove heat from the flame, while additional heat may also result in melting or char formation, each of which could reduce fire growth. This scenario dependence will ultimately favour certain materials under certain conditions. This is the heart of the difficulty in defining flammability, and explains why the materials development

described in the different sections of this book often give apparently inconsistent results when tested under different conditions.

Although recent developments in flammability testing have got closer to addressing the ultimate goal of predicting large-scale fire behaviour from small-scale tests, or even measurements of material properties coupled to models of full-scale fire behaviour, even large scale fires show considerable variation, so there is no universal benchmark against which to judge a material's fire performance.

Fires and Fire Growth

Fire tests focussing on particular fire stages should address the prevailing conditions appropriately. Most fires start from small beginnings. There may be an induction period (involving smouldering) before flaming ignition takes place, then a rise in temperature until ventilation controlled burning takes place (usually 800-1000°C) then a decay as fuel is consumed, shown schematically in figure 2.

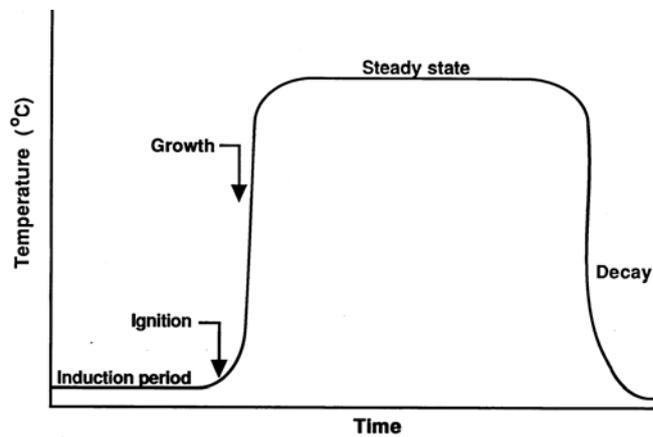


Figure 2 Stages in a fire

During the ignition phase, the impact of heat on a polymeric material causes an increase in temperature. If a sufficiently high temperature is reached then chemical bonds break and volatile fragments are produced. As they are hot, they are buoyant above the surface of the polymer. Once a sufficient concentration is reached, if the products are flammable, then a flame may stabilise. Ignition may either be piloted by a flame or spark, or spontaneous, the latter typically occurring when the polymer surface is 200°C hotter. There will be convected heat above the flame, and radiative heat in all directions, including downwards, shown in figure 3.

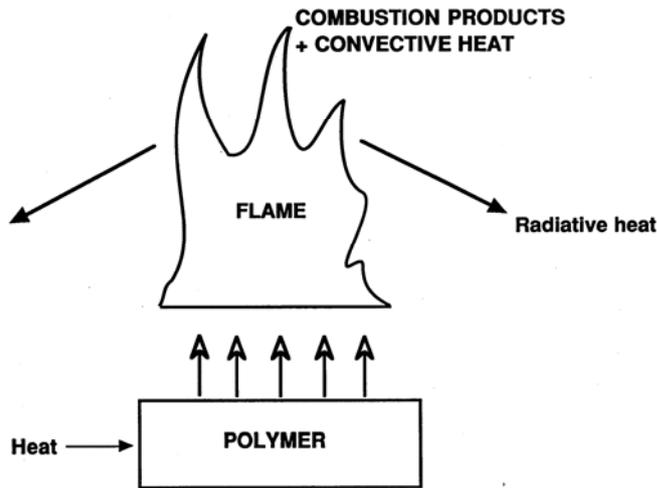


Figure 3 Primary Ignition Process

These heat transfer processes are critical to the ignition and fire behaviour. Once ignited, the fire initially grows by a process of flame spread. The surfaces near the pyrolysis and flame zone are heated and decompose forming more flammable products. The flame spreads by pilot (i.e. flame) ignition of these areas beyond the burning zone. Hence flame spread is essentially a process of repeated ignitions, as depicted in figure 4.

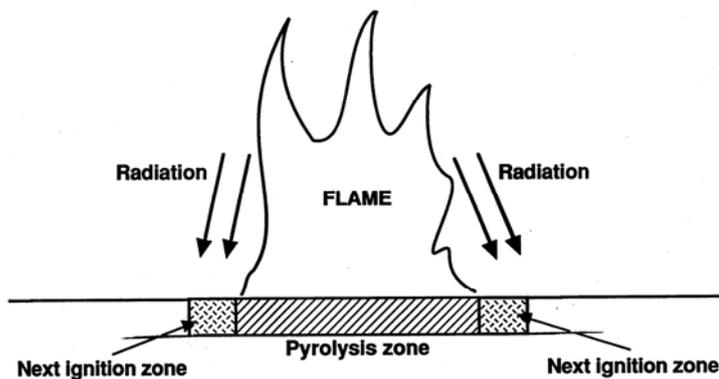


Figure 4 Horizontal Flame Spread (slow)

Horizontal flame spread is relatively slow because the material ahead of the flame is heated only by gas phase conduction enhanced by downward radiation. Upward flame spread (figure 5) is more rapid, because radiative, convective and some conductive heat transfer occurs.

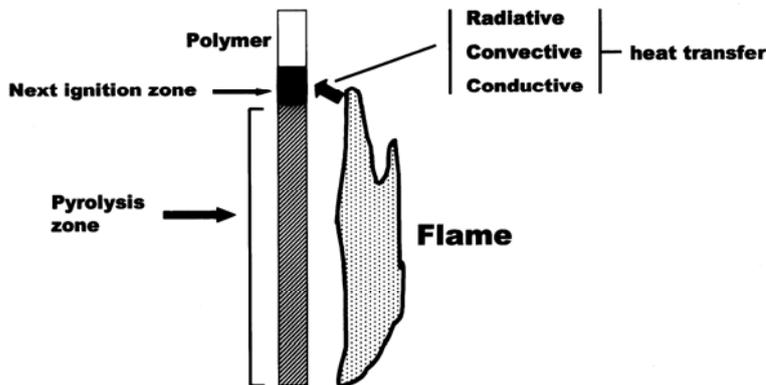


Figure 5 Vertical Flame Spread (Rapid)

During the early growth phase, flaming is normally confined to the item first ignited. As flames become more than about 1 or 2m high, radiative heat transfer to adjacent items becomes important, even to objects several metres away from the flame (figure 6).

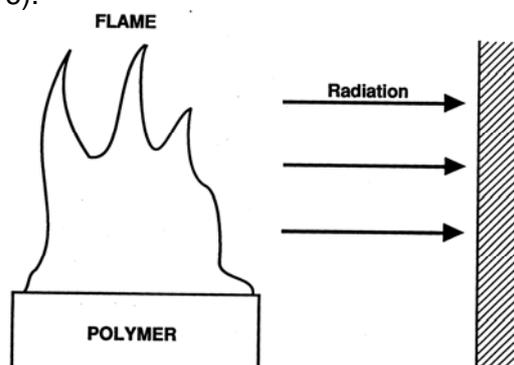


Figure 6 Ignitability at a distance

These items decompose predominantly as a consequence of radiative heat transfer, pyrolyse, and may then spontaneously ignite. As the flame reaches the ceiling, it spreads across it, dramatically increasing the radiant flux to the other objects in the room. These then pyrolyse, filling the room with a flammable, or even explosive fuel air mixture. Once this occurs then the whole room will burn, and flashover is said to occur (figure 7). At this point, the speed of flame spread will be greater than running speed, and the fire can no longer be controlled. Burning will continue until the available fuel is consumed.

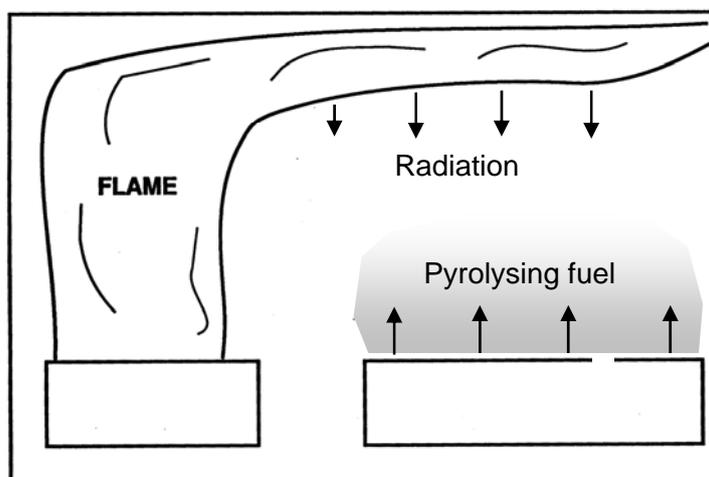


Figure 7 Flashover Conditions

Conditions of each fire stage

In order to simulate the effects of fire for materials development and testing, the test conditions should be related to the appropriate scenario.

- **Ignition:** although unwanted fires may result from spontaneous ignition, as it is more difficult to obtain repeatable results, piloted ignition is generally the preferred scenario to assess the the onset of flaming combustion. This is dependent on the ignition source (flame, cigarette, glow wire etc.), sample size (1 – 10 cm), and ambient temperature.

- **Developing fire:** the continuation of flaming combustion during fire growth involves an external heat flux of around 20 - 60 kW m⁻², which requires larger sample sizes (10 cm – 1 m), ambient temperatures above the ignition temperature (400 – 600°C), with adequate ventilation.
- **Fully developed fire:** the major stage of fire growth involves high external heat fluxes (> 50 kW m⁻²), large sample sizes (1 – 5 m), ambient temperatures above the spontaneous ignition temperatures (> 600°C), and low ventilation. These conditions are not generally easy to replicate on a small scale, and materials which are needed to perform well in developed fires normally need to be tested under these extreme conditions, and may perform differently in bench and large scale scenarios.

Chemical and Physical Processes

The chemical composition of a polymeric fuel, and presence of fire retardants, additives etc., are important in determining the degree to which flammable products will be released as the temperature increases. Untreated natural materials, such as wood, cotton and paper tend to release flammable products and ignite at relatively low temperatures in comparison with synthetic materials (polyethylene, PVC etc). However, the physical nature of the material also plays an important part (sometimes more so than the chemistry) in determining whether a material will reach decomposition temperatures.

The *thermal inertia* ($\kappa\rho c$) is the product of the thermal conductivity, density and specific heat capacity. It dictates the time for the surface temperature to reach ignition temperature, describing the characteristics of materials according to their heat insulation or heat sink properties. A block of wood is more difficult to ignite with a small ignition source than wood shavings, cellular polymers of inherently combustible compositions (such as polyurethane foam) will burn very rapidly in comparison to their solid counterparts because their heat insulation properties cause heat to be retained at the surface. The thermal inertia is low for insulating materials, and high for heat conducting materials.

Ultimately most fire science and hence most fire testing is focussed on specific protection goals, for good reasons. Common protection goals include preventing sustained ignition, limiting the contribution to fire propagation, or acting as a fire barrier. Most of the better established fire tests try to simulate a specific, realistic fire scenario and monitor a specific fire risk or hazard from a specific specimen within that scenario, rather than to determine the material's properties. Furthermore, the way a specimen responds in a fire, or in a fire test, may make a significant contribution to the overall fire scenario. Hence, three general remarks can be made:

- Comparing the fire behaviour in different fire tests is difficult. Exact predictions often fail because different material properties determine the performance in different scenarios. However, rough correlations or correlations limited to specific classes of materials have been successful.
- Scaling up and down is a key challenge in fire science, since the sample size plays such a major role. Typically, empirical approaches fail to predict fire behaviour satisfactorily; particularly attempts to span multiple orders of magnitude. Advanced predictive models have been developed which are moving towards reliable predictions of fire behaviour.
- The interactions between properties of components and "intrinsic" material properties are complex and variable.

Different polymers decompose in different ways and fire retardants act to inhibit the

decomposition or flaming combustion processes. When a polymer is heated its chains will start to break down, eventually resulting in the formation of volatile fuel molecules. The pyrolysis of a polymer, turning polymer chains of 10 000–100 000 carbon atoms into species small enough to be volatilised, often involves breaking the polymer chain. In some cases, the chain releases groups from its ends most easily, known as *end-chain scission* or unzipping. In others, the chain breaks at random points along its length, known as *random chain scission*. A third process, where good leaving groups attached to the backbone as side chains are lost, is known as *chain stripping*. This is often the preferred mechanism of the fire retardant chemist, especially if the resulting chain may be prevented from undergoing chain scission to form volatiles or lose further substituents, and instead undergo carbonisation resulting in *char formation*. Thus the conversion of organic polymer to volatile organic molecules may follow four general mechanisms. While some polymers fall exclusively into one category, others exhibit mixed behaviour.

This process can be accelerated by chemical attack on the polymer chains, for example by atmospheric oxygen. In the presence of an ignition source, when the concentration of fuel molecules above the surface reaches a critical level, the proportion of their heat of combustion transferred back to the polymer will be sufficient to replace the fuel by further pyrolysis. This is essentially the criteria for piloted ignition. It correlates well with the critical surface temperature for ignition. Once ignition has occurred, a proportion of the heat from the flame will be transferred back to an adjacent non-flaming part of the polymer surface, pyrolysing the polymer and causing a repeat of the ignition process. This results in flame spread across the surface.

Fire Effluent toxicity

Analysis of fire statistics shows that most fire deaths are caused by inhalation of toxic gases¹. While some real life fires may be represented by a single fire stage, most fires progress through several different stages³. Burning behaviour and particularly toxic product yields depend most strongly on a few of factors. Amongst them material composition, temperature and oxygen concentration are normally the most important.

The formation of CO, often considered to be the most toxicologically significant fire gas, is favoured by a range of conditions from smouldering to fully developed flaming. CO results from incomplete combustion, which can arise from:

- Insufficient heat in the gas phase (e.g. during smouldering).
- Quenching of the flame reactions (e.g. when halogens are present in the flame, or excessive ventilation cools the flame).
- The presence of stable molecules, such as aromatics, which survive longer in the flame zone, giving high CO yields in well-ventilated conditions, but lower than expected yields in underventilated conditions⁴.
- Insufficient oxygen (e.g. in underventilated fires, large radiant heat fluxes pyrolyse the fuel even though there is not enough oxygen to complete the reaction).

The high yields of the asphyxiant gas CO from under-ventilated fires are held responsible for most of the deaths through inhalation of smoke and toxic gases, but this under-ventilated burning is the most difficult to create on a bench-scale. For most materials the yields of toxic species have been shown to depend critically on the fire conditions. Figure illustrates the generalised change in toxic product yields during the growth of a fire from non-flaming through well-ventilated flaming to restricted ventilation. Although the toxic product yields are often highest for non-

flaming combustion, the rates of burning and the rate of fire growth are much slower, so under-ventilated flaming is generally considered the most toxic fire stage. Other toxic species include hydrogen cyanide, HCN (the other asphyxiant gas), and incapacitating irritants, causing blinding pain to the eyes and flooding of the lungs and respiratory tracts, inhibiting breathing and preventing escape. The wide variety of these irritants has led to groupings such as acid gases, organo-irritants and particulates, in order to estimate incapacitation⁵. The effect of different fire conditions on the yields of these different toxicants is summarised in figure 8.

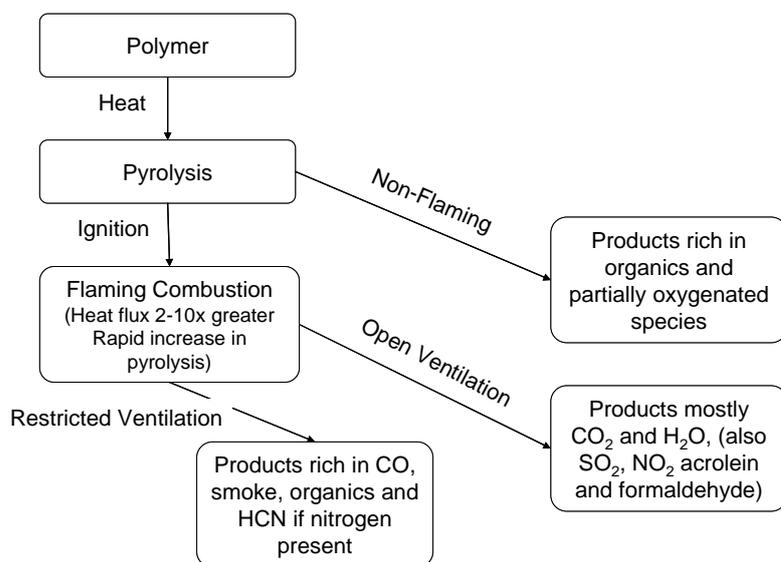


Figure 8 Effect of Fire Stage on Toxic Gas Production

Data from large scale fires^{6,7} shows much higher levels of the two asphyxiant gases (CO and HCN) under conditions of reduced ventilation. It is therefore essential to the assessment of toxic hazard from fire that these different fire stages can be adequately replicated, and preferably the individual fire stages treated separately. Analysis of fire hazard requires data describing the rate of burning of the material, and data describing the toxic product yield of the material. This is best achieved using the steady state tube furnace⁸, in which the air supply and rate of burning are fixed, as the sample is driven into a furnace, and subjected to an increasing applied heat flux. Fire toxicity is also scenario dependent, but using this technique, a clear relationship has been demonstrated between the yield of toxic products (for example in grams of toxicant per gram of polymer) and the fire condition, for a given material composition⁹. A more detailed account of current protocols in fire toxicity testing¹⁰ has recently been published.

Structural Deformation

The increased use of polymer materials to replace structural members, such as the carbon fibre composites used in aircraft bodies, increases the importance of maintaining structural integrity during a fire. In many other cases such as electrotechnical products, the failure of plastic components early on in a fire could radically alter the course of a fire with potentially devastating consequences. As new materials with greater rigidity and structural integrity are being developed, synthetic polymer composites are increasingly being used to replace metal components. Incorporation, for example, of a 1% loading of a nanofiller can have a very large, beneficial effect on these physical properties.

Studying Polymer Decomposition

Thermogravimetric Analysis (TGA) provides a valuable insight into the decomposition behaviour under controlled conditions. The temperature at which significant mass loss occurs during decomposition in air gives an indication of the ignition temperature, as the point when a significant amount of fuel is lost from the polymer. This can be affected by gas phase flame inhibitors, and to some extent, by the production of carbon dioxide on the surface, which will simultaneously reduce the oxygen and fuel concentrations. Once ignition has occurred, the mass loss in nitrogen is more representative of the fuel production rate, since the oxygen concentration under a flame is close to 0%.

Fire Retardant Strategies

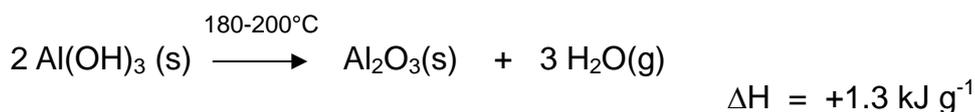
These can be broadly separated into those blocking the fire physically, and those using alternative chemical reactions to stop the material from burning. They are outlined here to set the context for the specific approaches described in detail in the individual sections.

Physical action

There are several ways in which the combustion process can be retarded by physical action:

- * **By cooling** - Endothermic reactions cool the material.
- * **By forming a protective layer** – Obstructing the flow of heat and oxygen to the polymer, and fuel to the vapour phase.
- * **By dilution**. Release of water vapour or carbon dioxide may dilute the radicals in the flame so it goes out.

For example, the most widely used fire retardant, aluminium hydroxide (Al(OH)₃) breaks down endothermically forming water vapour, diluting the radicals in the flame, while the residue of alumina (Al₂O₃) builds up to form a protective layer. Unfortunately relatively large amounts may be needed to be effective (up to 70%) and the freshly formed alumina can lead to afterglow¹¹.



Chemical action

- * **Reaction in the gas phase** - The radical reactions of the flame can be interrupted by a flame retardant. The radical concentration falls below a critical value, and the flame goes out. The processes releasing heat are thus stopped, and the system cools down. However, interfering with the flame reactions often results in highly toxic and irritant partially burnt products, including carbon monoxide, generally increasing the toxicity of the fire gases while reducing fire growth.
- * **Reaction in the solid phase** - The flame retardants work by breaking down the polymer so it melts like a liquid and flows away from the flame (just like trying to light candle wax without a wick). Although this allows materials to pass certain tests, sometimes fire safety is compromised by the production of flammable drops.
- * **Char Formation** - Better solid phase flame retardants are those which cause a layer of carbonaceous char to form on the polymer surface. This can occur, for example, by the fire retardant removing the side chains and

thus generating double bonds in the polymer. Ultimately, these form a carbonaceous layer by forming aromatic rings. Char formation usually reduces the formation of smoke and other products of incomplete combustion.

- * **Intumescence** - The incorporation of blowing agents, causes swelling behind the surface layer, providing much better insulation under the protective barrier. The same technology is used for coatings, for protecting wooden buildings or steel structures.

Polymer Nanocomposites

Polymeric materials containing fillers with at least one dimension of only a few tens of nanometres has opened up an enormous range of possibilities in fire retardant research. Fillers may have dimensions extending over 4 orders of magnitude, and have effects including reinforcing organic char as a barrier layer; providing a catalytic surface for promoting char forming reactions; enhancing the structural rigidity of the polymer; changing the melt-flow properties of the polymer close to its ignition temperature; and providing intimate contact between a fire retardant and the host polymer. Initially investigations involved polymer clay nanocomposites, but more recently investigations have included the use of single and multiwalled carbon nanotubes¹², and other nanoscopic fillers with potential fire retardant properties including layered double hydroxides¹² (or hydrotalcites) aluminium hydroxide¹³ and others.

Types of nanofillers for fire retardancy

Although the effect of polymer clay nanocomposites on fire was first investigated over 2 decades ago, wider study of the full range of sizes, morphologies, chemistries and surface treatments of polymer nanocomposites has only just begun.

Filler Morphology

Traditionally, particles with a platey morphology, and especially montmorillonite have been investigated, as it was generally assumed that these would most easily assist in the formation of a barrier layer. The influence of nanocomposite formation and the different mechanisms of breakdown of different polymers make generalizations regarding filler morphology difficult. In some cases fillers with aspect ratios greater than 1000 have been successfully deployed for enhancement of fire retardancy. For example, a clay filler with a mean diameter of 25 μm has been used commercially to reduce the flammability of cable sheathing materials¹⁴.

Filler Coating and Dispersion

In order to produce properly dispersed polymer nanocomposites, it is generally necessary to add a compatibilising agent, such as a surfactant to the polar filler surface in order to insert it between the polymer chains. In partially ionic polymers, such as nylon, dispersion is much easier than in hydrophilic, crystalline polymers such as isotactic polypropylene (PP). In these cases it is generally necessary to attach a grafting agent, such as maleic anhydride onto the polymer to ensure adequate dispersion. While the mechanical properties of the polymer depend on adequate dispersion at ambient temperatures, the fire behaviour is a function of the dispersion of the nanofiller in the molten bubbling polymer. In many cases, the

surfactant will have decomposed, leaving the polar nanofiller. There has been intense speculation as to whether this results in incompatibilisation, and migration of the filler to the surface, or whether the preferential loss of the first few hundred nanometres of polymer results in accumulation of filler at the surface. In some cases no fire retardant effect is observed without adequate dispersion. In others it is evident, suggesting that dispersion occurs in the molten, decomposing, bubbling polymer.

Effects of nanofiller composition on thermal decomposition burning behaviour

In a study of the evolution products from nanocomposites made from polyethylene, ethylene vinyl acetate and polystyrene, with organically modified clays, single and multi-walled carbon nanotubes and layered double hydroxides¹², it was found that the relative amounts and the identity of the degradation products are changed when both well-dispersed cationic and anionic clays are used, but there is no difference in the degradation products when carbon nanotubes were utilized. When the nano-dimensional material is not well-dispersed, the degradation products are not changed. Unlike clays, polymer-layered double hydroxide nanocomposites give reasonably good reductions in peak heat release rate even when nano-dispersion has not been obtained. These data suggest that the enhancement in the fire behavior must be, at least in part, due to different mechanisms for montmorillonite, layered double hydroxides and carbon nanotube-based nanocomposites.

Conclusions

Fire is a complex process and no two real fires are identical. In developing materials with enhanced fire safety, such as lower ignitability, lower heat release rates during burning, and lower fire toxicity, it is essential to relate the desired properties to the end use scenario. This is normally the role of regulators to select appropriate test methods in order to protect people and property from the most likely fire scenarios.

The thermal decomposition of polymers is a complex process, which may follow a number of different routes, depending on the material and the conditions. Polymers burn by breakdown of their long chain structures, releasing fuel into the gas phase, where flaming combustion can occur. The mechanism of breakdown is often unique to a particular polymer, and in general, flame retardant methods cannot be directly exported from one polymer system to another. Fire retardants may be classified by their mode of action (physical or chemical; condensed phase or gas phase; char forming or intumescent etc.) or by their physical or chemical structure.

Polymer nanocomposites are an important new class of materials, offering thermal and mechanical properties not evident in their parent polymers, with great potential for fire retardancy. Some of their physical properties, for example the typically massive increase in viscosity modulus, may cause processing problems preventing large scale production using conventional extruders. The incorporation of additives, which have dimensions ranging over 4 orders of magnitude, has a range of physical effects, such as barrier layer formation, loss of compatibiliser, migration to the surface, inhibition of bubble movement and the reduction in the flow of the molten polymer. In addition, a number of chemical effects have been observed, including catalysing decomposition reactions, promoting graphite formation, and altering the decomposition pathway, which has been seen to influence the decomposition behaviour. The recent approach of preparing conventional fire retardants in nanoscopic form increases the range of chemical effects. The degree of dispersion has often been cited as a pre-requisite for improved fire behaviour (typically a shorter time to ignition but a lower peak of heat release rate), but this is certainly not always the case. The controlling parameter is the degree of dispersion at the point of ignition, rather than in the cold polymer, since either the compatibiliser may decompose, reducing the degree of dispersion, or the nanofiller may disperse under the more extreme agitation within the decomposing polymer. Measurements of rheological properties as a function of temperature have been shown to be an effective tool for demonstrating this.

The complexities of fire behaviour, and the difficulties in quantifying that behaviour in a scenario independent way, compound the problems of understanding the thermal decomposition of polymer nanocomposites. However, the large number of empirical studies to have produced encouraging results provides evidence that the future of fire retardancy will follow the nanocomposite route, even if it is not possible to predict which type of nanofiller; in terms of chemistry, morphology, compatibilisation and dimensions ranging over 4 orders of magnitude; and what degree of dispersion and filler loading are required for optimum performance. The fact that nanofillers uniquely improve physical properties, while almost all other fire retardants worsen them, suggests that until such optimisation has been reached, and the vast numbers of experiments required to achieve it has been undertaken, fire retardant formulations will be based on a combination of nanofiller and conventional flame retardant.

References

- 1 *Fire Statistics* United Kingdom 2005, Office of the Deputy Prime Minister: London, April 2007.
- 2 *The cost of fires - A review of the information available*, Home Office Publications Unit, UK, 1997.
- 3 ISO TS 19706:2004 Guidelines for assessing the fire threat to people.
- 4 T. R. Hull, J. M. Carman and D. A. Purser, Prediction of CO evolution from small-scale polymer fires, *Polymer International* 49, 1259-1265, (2000).
- 5 ISO 13571:2007, Life-threatening components of fire - Guidelines for the estimation of time available for escape using fire data.
- 6 P.Blomqvist, and A.Lonnermark, *Characterization of the Combustion Products in Largescale Fire Tests: Comparison of Three Experimental Configurations*, *Fire and Materials*. 25, 71-81, (2001).
- 7 B.Andersson, F.Markert, and G.Holmstedt, *Combustion products generated by hetero-organic fuels on four different fire test scales* *Fire Safety Journal*, 40, 439-465, (2005).
- 8 T R Hull, J M Carman and D A Purser *Prediction of CO evolution from small-scale polymer fires*, *Polymer International* 49, 1259, (2000).
- 9 A.A.Stec, T.R.Hull, K.Lebek, J.A.Purser, D. A. Purser, The Effect of Temperature and Ventilation Condition on the Toxic Product Yields from Burning Polymers, *Fire and Materials* 32, 49-60, (2008).
- 10 T R Hull and K T Paul, Bench-Scale Assessment of Combustion Toxicity – A Critical Analysis of Current Protocols *Fire Safety Journal*, 42, 340-365 (2007).
- 11 T.R.Hull, R.E.Quinn, I.G.Areri and D.A.Purser, *Combustion toxicity of fire retarded EVA*, *Polym. Degrad. Stab.* 2002, 77, 235-242.
- 12 M.C.Costache, M.J.Heidecker, E.Manias, G.Camino, A.Frache, G. Beyer, R.K.Gupta, and C.A.Wilkie, *The influence of carbon nanotubes, organically modified montmorillonites and layered double hydroxides on the thermal degradation and fire retardancy of polyethylene, ethylene-vinyl acetate copolymer and polystyrene*, *Polymer*, 48, 6532-6545, 2007,
- 13 K Daimatsu, H Sugimoto, Y Kato, E Nakanishi, K Inomata, Y Amekawa, and K Takemura, *Preparation and physical properties of flame retardant acrylic resin containing nano-sized aluminum hydroxide*, *Polymer Degradation and Stability* 92, 1433 -1438, (2007)
- 14 T.R. Hull, D. Price, Y. Liu, C. L. Wills and J Brady, *An investigation into the decomposition and burning behaviour of Ethylene-vinyl acetate copolymer nanocomposite materials* *Polymer Degradation and Stability* 82 (2003) 365–371