Marquette University
e-Publications@Marquette

Chemistry Faculty Research and Publications | Chemistry, Department of

4-12-2005

An Introduction to the Use of Fillers and Nanocomposites in Fire Retardancy

Charles Wilkie
Marquette University, charles.wilkie@marquette.edu

Published version. Published as a chapter of a book entitled *Fire Retardancy of Polymers: New Applications of Mineral Fillers*. Eds. Michel Le Bras, Serge Bourbigot, Sophie Duquesne, Charafedine Jama, Charles Wilkie. Cambridge, UK: Royal Society of Chemistry, 2005, pp. 1-15, DOI: 10.1039/9781847552396-00001. Reproduced by permission of the Royal Society of Chemistry.

CHAPTER 1

An Introduction to the Use of Fillers and Nanocomposites in Fire Retardancy

CHARLES A. WILKIE

Department of Chemistry, Marquette University, PO Box 1881, Milwaukee, WI 53201, U.S.A. (charles.wilkie@marquette.edu)

1.1 Introduction

This chapter is to serve as an introduction to the very broad topic of the use of fillers, both well-dispersed and less well-dispersed, in polymers. When the filler is well-dispersed, a nanocomposite results in which a layered material has been separated into its constituent layers and these can either maintain the registry between the layers, an intercalated system, or this registry may be lost, an exfoliated system. When a well-dispersed system is obtained, loadings of 3 to 5% are sufficient to cause a large increase in mechanical properties and a significant reduction in the rate of peak heat release. Conversely, if the layers are not well-separated, or if there are no layers that can be separated, the filler is not well-dispersed and a simple filled system is obtained; typical loadings of 60% or more are required to confer fire retardancy in such systems and this invariably has an adverse effect on both strength and toughness of the composite, which can be ameliorated by judicious use of surface treatments.

1.2 Characterization of Fire Retardancy of Polymers

The evaluation of fire retardancy is carried out by a variety of techniques, most of which do not correlate well with other test protocols. The three most common methods that are used are the oxygen index, the UL-94 test, and cone calorimetry. Oxygen index is an evaluation of the ease of extinction of a fire, how rapidly does the flame chemistry lead to extinction. The measurement consists of determining the minimum concentration of oxygen in a nitrogen–oxygen mixture that will sustain combustion. The more the value of the oxygen index is

above the percentage of oxygen in the air, the better the system is considered to be. This does not mean that a material with a high oxygen index will not burn, the test measures the ease of extinction of the fire. The UL-94 test measures the ease of ignition; in this test a sample is ignited and the time for self extinguishment is determined. The results of this test permit a ranking of the material. The cone calorimeter measures a third parameter, the rate at which heat is released in a fire. In many cases, this is considered to be the most definitive test, but it still does not necessarily correlate with the other tests. From a cone calorimetry experiment, one can obtain the mass loss rate, the total heat released, the quantity of smoke that is produced and the amount of carbon monoxide and carbon dioxide that are evolved.

1.3 Fire Retardant Fillers for Polymers

The major materials that are used as fire retardant fillers for polymers are alumina trihydrate, ATH, ($Al_2O_3 \cdot 3H_2O$) and magnesium hydroxide, MH, ($Mg(OH)_2$).[1,2] There are various forms for both of these materials, both naturally occurring and synthetic, and the reader is referred to references 1 and 2 for information on these forms. These two materials account for more than 50% by weight of the world-wide sales of fire retardants; as much as 400 kt annum^{-1} is currently used. Most of this is low cost ATH that is used in thermosetting resins. The use of ATH is limited to those polymers processed below about 200°C while MH is stable above 300°C and thus can be used in polymers that must be processed at higher temperatures. Their effectiveness comes from the fact that they both decompose endothermically and consume a large amount of heat, while also liberating water, which can dilute any volatiles and thus decrease the possibility of fire. For ATH, decomposition begins near 300°C and consumes 1270 joules per gram of ATH; for MH, decomposition begins at somewhat higher temperature, near 400°C, and consumes 1244 joules per gram of MH. There is some tendency for MH to catalyze the degradation of some polymers; in unsaturated polyester resins it can act as a chain extender, affecting resin rheology. A major use of both ATH and MH is in low smoke, halogen-free wire and cable applications, where there is significant commercial activity.[3]

With some polymers, the resin and the additive might interact, and so one must be aware of these possibilities as these will influence the mode of action.[4] With polypropylene, 60% loading of MH gives an oxygen index of 26, while with polyamide-6, the same loading gives an oxygen index of almost 70.[5] Both the heat capacity of the filler and the endothermic decomposition may affect the fire retardancy. Analysis of the combustion gases produced just above the oxygen index value can enable one to ascertain the relative contributions of the decomposition endotherm and the heat capacity.[2] With polypropylene, polyphenylene oxide, poly(butadiene terephthalte) and acrylonitrile-butadiene-styrene terpolymer, both MH and ATH break down to give the metal oxides, which, when combined with whatever amount of carbonaceous char is formed, provide an effective thermally insulating barrier, leading to fire retardancy.

In a cone calorimetry study, compositions of polypropylene (PP) that contain the same mass of either glass beads or MH have been examined. In both cases the heat release rates were significantly reduced, but the reduction was far greater for MH, even though both materials are considered to be inert fillers.[6] This may suggest that MH is not simply an inert filler. The degradation of MH filled PA-6 and PA-6,6 has been studied and it was found that the presence of MH enhances the degradation of the polyamide.[7] This was attributed to the release of water from the decomposition of MH and its subsequent attack on the polyamide. With PA-6,6, polymer degradation occurred before MH decomposition, while with PA-6 there is better overlap between MH and PA-6 degradations, resulting in enhanced fire retardancy.

With polyethylene, both MH and ATH give the same oxygen index at an equivalent loading level. Conversely, in EVA (30% vinyl acetate content) MH gives an oxygen index of 46 while with ATH the value is 37. It was suggested that this difference is due to the loss of acetic acid from the polymer either delaying water loss (ATH) or accelerating this process (MH).[8]

Another area in which the metal hydroxides excel is smoke suppression. These hydrated fillers not only reduce the smoke release but they also can delay the time at which it is released, and thus provide additional time for escape from a fire.[5] Little work has been done on the process by which smoke suppression may occur, but the best guess is that carbon, from polymer degradation, is deposited on the oxide and this is then volatilized as carbon dioxide, resulting in no smoke.[9] This may be an area in which someone can make a very useful contribution.

As in any fire retardant system, synergy can be useful. Combinations that have been used include ATH with MH (giving an increased range of endothermic decomposition),[10] ATH with red phosphorus (enabling lower loadings),[11] MH with melamine and novolac in PP;[12] several additional examples are given in reference 2.

1.4 Nanocomposites

Nanocomposites are a new class of inorganic materials that only somewhat recently have begun to be used to achieve fire retardancy. The initial discovery is that a polyamide-6clay nanocomposite, containing 5% clay, shows an increase of 40% in tensile strength, 68% in tensile modulus, 60% in flexural strength and 126% in flexural modulus, while the heat distortion temperature increases from 65 to 152°C and the impact strength is lowered by only 10%.[12,13]

The initial work, which was not yet recognized as nanocomposites, actually took place sometime earlier when Blumstein synthesized poly(methyl methacrylate) in the presence of a clay and found that the clay had a templating effect on the formation of the polymer.[14–19] The significance of these observations was not realized for several years and this work has taken on more importance since the advent of the nano era.

Nanocomposites may be produced using several different materials for the nano-dimensional material, including clays, graphites, carbon nanotubes, and polyhedral oligosilsesquioxanes, POSS. Most work to date has been with clays, particularly with montmorillonite clay, an alumina-silicate material. A wide variety of other clays naturally occur, but, for some reason, montmorillonite has been by far the chosen material, probably because interesting results were obtained with this clay.

Surprisingly, graphite has not been more widely used; one concern may be that the *d*-spacing in most organically-modified montmorillonites is in the range of 2 or 3 nm while graphite has a *d*-spacing of about 2 or 3 Å. To form a nanocomposite, the polymer must be able to enter into the gallery space of the nanomaterial, and this may require that this space be large enough to permit the polymer to begin to enter. Graphite does form a number of intercalation compounds in which the *d*-spacing is large. For instance, potassium graphite, KC8 has a *d*-spacing of 5.5 Å and that of graphite sulfuric acid is even larger.[20,21] Possibly, if one begins with an already expanded graphite, a *d*-spacing in the range of 2 to 3 nm at least, that graphite may become more useful as a nano-dimensional material for nanocomposite formation.

Carbon nanotubes are, of course, a newer discovery and they are still quite expensive. There is still some activity in this area;[22–24] the major difficulty with the single wall nanotubes appears to be the need to organically-modify the nanotubes to make them more organophilic, this is probably also a limitation with the graphite system also. The multi-wall nanotubes do not require organic modification for nanocomposite formation. There has been little work on the fire retardancy of nanocomposites using carbon nanotubes.[25–27] The polymers that have been investigated include polypropylene and ethylene/vinyl acetate, EVA, and the reductions in PHRR are comparable to those seen with clays.

Polyhedral oligomeric silsequioxanes, POSS, are a unique class of materials that have the general formula $(RSiO_{1.5})_n$.[28] At least some of the R groups are usually unreactive, as phenyl, methyl, *etc.*, but one can also incorporate one or more reactive groups, *e.g.*, styryl, methacrylate, *etc.* The presence of a polymerizable substituent enables the formation of polymers, either by direct polymerization or co-polymerization with another monomer. The diameter of the POSS is typically on the order of 15 Å and they are, in general, easily incorporated into a polymer matrix. The generalized structure of a POSS system is shown in Figure 1. This consists of substituents R, which are unreactive and provide for compatibilization and solubility, and reactive groups X (only one of which is shown in this figure but more are possible) attached to a chemically and thermally robust hybrid framework. The composition is intermediate between that of silica and silicones; it offers a precise three-dimensional structure for reinforcement at the molecular level of polymers segments.

There has been much less work in fire retardancy with POSS than with clays, one US patent[29] and one paper.[30] The patent shows that POSS significantly reduces the PHRR for a polyether-block-polyamide system (50–70% reduction), for polypropylene (a 40% reduction) and a styrene-butadiene-styrene (SBS) triblock polymer (40–60% reduction). The decrease in the time to ignition,

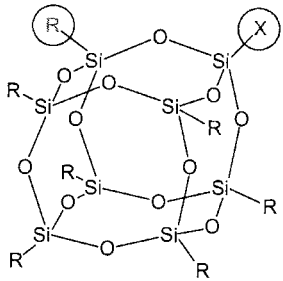

Figure 1 *Generalized structure of a POSS material*

which is common for clay-based systems, is observed for some, but not all, polymers with POSS. For POSS with polyurethane fabrics[30] the reduction in PHRR is about 55%. It appears that POSS materials should be more widely studied as fire retardant systems, since the reduction in PHRR is quite large and the time to ignition shows a more useful behavior.

1.4.1 Preparation and Modeling of Nanocomposites

A nanocomposite is formed by either a polymerization process in the presence of a clay, or similar material, or by blending of the nano-dimensional material with a polymer. At this stage of the discussion, we will speak only about clay–polymer nanocomposites. The clay begins in the form of tactoids with a high aspect ratio – for montmorillonite the length is typically in the range of 100 nm while the width is around 1 nm. Upon formation of a nanocomposite, three possible situations may arise. The clay may remain as tactoids with no penetration of the polymer between the clay layers; this is called either an immiscible nanocomposite or a microcomposite. If the clay is well-dispersed, then either an intercalated or an exfoliated (also known as delaminated) nanocomposite may be formed. Intercalation means that the clay layers maintain their registry while exfoliation indicates that this registry is lost. These situations are depicted in Figure 2.

Vaia and Giannelis have reported on a thermodynamic model for nanocomposite formation by melt blending.[31] This model indicates that the entropic

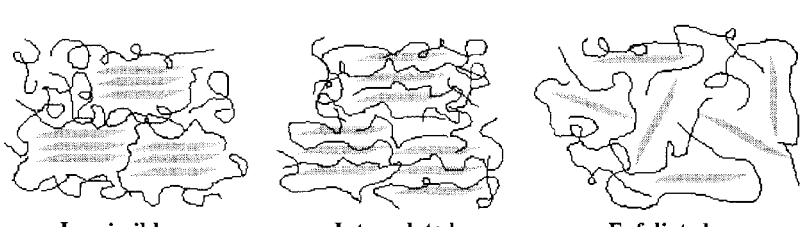

Figure 2 *Depiction of immiscible, intercalated and exfoliated nanocomposites*

penalty for polymer confinement may be compensated by the increased conformational freedom of the tethered chains as the clay layers separate. Complete layer separation depends upon the establishment of very favorable polymer–organically modified clay interactions to overcome the penalty of polymer confinement. The total entropy change is near zero, if complete layer separation is achieved, and the polymer is now not confined.

Balazs *et al.*[32] have also modeled the behavior of polymer–clay nanocomposites and they have shown that immiscibility occurs for the natural clay and polymers with a degree of polymerization of 100. When the clay is organically-modified, there can be favorable enthalpic interactions between the surfactant and the polymer, which can overcome the unfavorable entropy term and lead to efficient mixing. The formation on a intercalated or exfoliated system depends upon the length of the surfactant chain, the density of the surfactant on the clay, and the molecular weight of the polymer. It appears that if the length of the surfactant and the polymer are similar, then some of the entropic barrier is overcome and this will lead to easier nano-dispersion. When the amount of surfactant increases, the surfactant becomes denser and it becomes more difficult for the polymer chains to penetrate and good nano-dispersion will become more difficult. Finally, if one can produce attractions between the surfactants and the polymer, this highly attractive surface interaction can lead to exfoliation. Thus, one may conclude that the design of the surfactant is extremely important for success in the preparation of polymer–clay nanocomposites.

1.4.2 Organic Clay Modification

The gallery space of a typical clay is hydrophilic, based on the presence of the sodium cations and the alumino-silicate framework of the clay. To permit the insertion of a hydrophobic polymer within this gallery space, one must first render this gallery space organophilic. This is most typically accomplished by ion exchanging the sodium cation for an organophilic ammonium salt; the usual requirement is that there must be at least one long chain or twelve carbons or more on the nitrogen atom of the ammonium cation. As noted above, theoretical studies have shown that an attractive interaction between the surfactant and the polymer greatly enhances the possibility of nano-dispersion of the clay within the polymer. Thus, one should pay careful attention to the type of surfactant that is used. In addition, the thermal degradation of many surfactants begins at temperatures as low as 200°C by the Hofmann elimination, giving an olefin and a tri-substituted ammonium cation.[33,34] The loss of the long chain will frequently eliminate the possibility of nano-dispersion.

Several different counterions have been used to enhance the organophilicity of the clays; the reader will usually think of the 'onium' ion, which is usually taken to include ammonium and phosphonium ions. Brief mention should be made of the single example of a stibonium-substituted clay and its polystyrene nanocomposite.[35] The initial degradation step, which is the loss of the olefin, occurs at slightly higher temperature but the degradation stops at this stage and

there is no loss of the stibine, meaning that the counterion of the clay is R_3SbH^+ and this should impart additional thermal stability to the clay and its nanocomposites. There has been some work in which oligomeric ammonium and phosphonium ions have been used to enhance the interaction between the polymer and the surfactant.[36–40] Three types of oligomers have been examined, styrene, methacrylate and butadiene. For both styrene and methacrylate, copolymers of the monomer with vinylbenzyl chloride, containing about 1 to 2 benzylic chlorides per oligomer, have been prepared and then the benzylic chloride has been used to quaternize an amine, giving a new ammonium salt. For butadiene, the authors used an oligomeric polybutadiene and graft copolymerized vinylbenzyl chloride to the butadiene. Best results were obtained with the styrenic copolymer; exfoliation was observed when this organically-modified clay was melt blended with polystyrene in a Brabender mixer. Even with unmodified polypropylene, an almost exfoliated nanocomposite is formed in the Brabender; it is assumed that complete exfoliation will be obtained if higher shear is applied. With both the methacrylate-modified and the butadiene-modified clays, immiscible materials are usually formed. Quite recently, Zhang has shown that one may use a substituted tropylium ion as the counterion for the clay and produce styrene nanocomposites.[41]

1.4.3 Determination of the Morphology of Nanocomposites

The determination of morphology is usually dominated by two techniques, X-ray diffraction, XRD, and transmission electron microscopy, TEM. XRD enables the determination of the *d*-spacing of the clay. An immiscible system is obtained if the *d*-spacing in the presence of the polymer is unchanged from that of the pristine clay. If the *d*-spacing increases, this indicates that intercalation has occurred. Since the registry between the clay layers is lost in an exfoliated system, no peak is expected. Unfortunately, this same situation will occur if the clay has extensively disordered, so XRD information alone is not enough to identify the morphology. TEM is usually used to address this question, since one can directly image the clay and polymer and identify the type of morphology. This type of measurement is frequently considered to be definitive. One must remember that to obtain one TEM requires only a miniscule piece of material and one cannot be certain that this is representative of the whole. The morphology can only be clearly determined by either sampling enough of the material by TEM so that one has statistical significance or by sampling the bulk of the sample.

A recently reported NMR technique to identify the morphology is based on proton NMR relaxation measurements.[42–44] The relaxation time depends upon the separation between nearest polymer–clay interfaces and the efficiency of paramagnetically-induced relaxation,[45] due to iron that is naturally present in the clay. An immiscible system will have the largest separation and thus the longest relaxation time while an exfoliated system has the smallest distance and the shortest time.

It appears that cone calorimetry may also be used as a method to sample the bulk. Some of the early work on nanocomposites showed that immiscible systems showed no reduction in the peak heat release rate, PHRR, while intercalated and exfoliated nanocomposites gave significant reductions.[46] In work from these laboratories, we have confirmed this observation and shown that there seems to be a correlation between the extent of nano-dispersion and the reduction in PHRR.

The classic definition of intercalation and exfoliation depends on the XRD and there is a need for new definitions based on other techniques. At this time, one can never be sure how an author is defining the nano-morphology so these terms are somewhat ambiguous.

1.4.4 Utility of Nanocomposites

There are currently believed to be four areas in which nanocomposite formation may be important: permeability, heat distortion temperature, flexural modulus and fire retardancy. A review has covered many of these enhanced properties.[47] The type of nanocomposite is important for some of these properties but unimportant for others. The permeability of a polymer is attributed to the tortuosity of the path that a gas must follow to penetrate a polymer, and the presence of exfoliated clay layers will make the path more difficult and thus lead to a decrease in permeability. It is also felt that exfoliation is an advantage for mechanical properties. However, there appears to be no difference between intercalated and exfoliated polymer–clay nanocomposites for fire properties.

1.4.5 Modeling of Fire Retardancy Due to Nanocomposite Formation

Nyden and Gilman[48] have simulated the thermal degradation of polypropylene that is nano-confined in a graphite matrix. They used graphite for convenience, since they have computational experience dealing with hydrocarbons but not with clays. The model consisted of four chains of isotatic polypropylene, each with 48 monomer units, contained within a graphite sheet of 600 carbons, end-capped with hydrogens. The degradation mechanism for the virgin polymer and the nanocomposite were unchanged in this simulation; the process involves the random scission of the $CH–CH_3$ bonds, followed by β-scission of the backbone to produce secondary free radicals, which then can unzip. Interactions with the graphite layer imparts a degree of stabilization when the graphite layers are separated by 2.8 to 3.2 nm. There is no reason to think that the results would be significantly different if clay were the nano-dimensional material.

1.4.6 Mechanisms by which Nanocomposites Enhance the Fire Retardancy of Polymers

Two mechanisms have been proposed to explain how nanocomposite formation can reduce the PHRR of a polymer. Gilman *et al.*[49] have proposed that the

degradation of the nanocomposite produces a multi-layered carbonaceous-silicate structure that may act as an excellent insulator and also as a barrier to mass transport. Zhu *et al.*[50] have shown that the presence of iron in the clay can lead to some radical trapping reactions that will lower the heat release rate. It appears that at low amounts of clay the paramagnetic radical trapping is effective while the barrier mechanism becomes more important at higher amounts of clay. In a series of papers, Wang *et al.*[51] have shown that the alumino-silicate barrier proposed by Gilman *et al.* does form for both polystyrene and methyl methacrylate nanocomposites. For nanocomposites of poly(vinyl chloride), the surface is covered with carbon. This difference is no doubt due to the different degradation pathways of the polymers; PVC normally degrades to give char while neither PS or PMMA are char-formers.

Gilman *et al.*[49] have found that polystyrene-fluorohectorite nanocomposites do not show a reduced PHRR, even though the same polymer with montmorillonite gives a reduction of more than 50% in PHRR. They note that there is a difference in chemical composition, aspect ratio, and nano-morphology and that they cannot assign the difference to any one of these. In recent work from this laboratory, polystyrene-magadiite nanocomposites have been prepared.[52] Magadiite, like fluorohectorite, is an all silicate material. Again no reduction in PHRR is observed and the differences include the composition, aspect ratio and nano-morphology. With magadiite, the morphology, based on TEM, shows a rather large immiscible component; the improvement in mechanical properties argues that there is also a large intercalated or exfoliated component. Polystyrene-hectorite nanocomposites[53] have also been examined. Here the PHRR shows a reduction, but only at greater than 3% clay. With montmorillonite, a reduction is seen even when the clay amount is as low as 0.1% organically-modified clay. Advances in fire retardancy will require an identification of what causes these various clays to behave differently.

To further complicate the situation, work has been carried out using graphite as the nano-dimensional material. The graphite that has been used is both sulfuric acid-graphite and modified graphite oxides.[54–56] In both cases, the reduction in PHRR is equivalent to the best values that have been obtained with montmorillonite. One may well expect that the nano-morphology, the aspect ratio and, certainly, the chemical composition of graphite are quite different than those of any of the clays, yet the fire retardancy, at least as measured by the reduction in PHRR, is equivalent. This is an additional area of challenge for the FR nanocomposite community to attempt to explain these observations.

The reduction in PHRR is different for each polymer and the values for both montmorillonite and graphite systems are shown in Table 1. The differences are striking, for instance with clay-PMMA, the best reduction in PHRR is 25% while polyamide-6 and polystyrene give values in the 60% range. If the mechanism is barrier formation, one would expect that the same barrier would be built in each case and this would be expected to lead to similar reductions for each case. Recent work using TGA/FTIR methods has shown that the clay appears to change the degradation pathway of polystyrene.[57] The degradation of polystyrene proceeds to give a mixture of oligomer and monomer; this is expected based upon the structure, which requires that a secondary and a primary radical

Table 1 *Reduction in PHRR for clay–polymer and graphite–polymer nanocomposites; values taken from references cited in the text. (irradiance level is 35 kW m^{-2} in every case)*

Polymer	*% reduction for clay-polymer nanocomposite*	*% reduction for graphite–polymer nanocomposite*
Polystyrene	57	48
HIPS	40	36
ABS	45	48
Polyamide-6	63	62
Poly(methyl methacrylate)	25	35
PP-g-MA	54	
EVA	47	

be produced upon bond cleavage. These unstable radicals will hydrogen abstract, giving a more stable radical with concomitant formation of oligomer. The degradation process of a PS-montmorillonite clay nanocomposite is changed so that much less monomer is seen, but oligomer is still produced.

1.4.7 Fire Retardancy Due to Nanocomposite Formation

The literature on the fire retardancy of nanocomposites has been recently reviewed[58] and the reader is referred to this review for specific information on polymers that have been studied. In this section, we will only describe the general details of fire retardancy due to nanocomposite formation. Fire retardancy is usually measured by cone calorimetry, particularly the reduction in the peak heat release rate, PHRR. Notably, a nanocomposite in which the clay is well-dispersed, whether intercalated or exfoliated, appears to give the same reduction in the PHRR. However, if one considers that all of the heat from the polymer is eventually released, the nanocomposite does not truly form a permanent barrier but rather an impermanent barrier that still permits the remaining polymer to degrade. It is the opinion of this author that nanocomposites alone will never solve the problem of fire retardancy but they can be a component of the solution. This author advocates the synergistic combination of a clay with some other fire retardant system. In such a system, the role of the clay will likely be to maintain the desirable mechanical properties of the polymer that may be lost by the presence of some other additive. In this case, the type of nanodispersion may be very important and the formation of exfoliated systems may be required to achieve the level of fire retardancy required while maintaining the needed mechanical properties.

One advantage that nanocomposite formation may have for fire retardancy purposes is the improvement in mechanical properties that usually occurs through the formation of the nanocomposite. Many fire retardants are used at very high loadings, which can significantly impact the physical properties of the polymer. Clays may function synergistically with other fire retardants, and the presence of the clay may counteract any deleterious effects from the fire retardant and make these more useful.

The usual measure that is used to evaluate the fire retardancy of nanocomposites is the cone calorimeter, which measures the rate of heat release and mass loss rate, along with smoke and carbon monoxide and carbon dioxide, as a function of the applied radiant energy. The effects that one would like to see are that the time to ignition and the time to peak heat release are increased while the peak heat release rate (PHRR), the total heat released and the mass loss rate are lowered; if one can have every wish, the amount of smoke and CO will also be reduced. In actuality, the peak heat release rate is usually decreased upon nanocomposite formation but the time to PHRR is unchanged and the time to ignition is decreased. Significantly, the total heat released is unchanged, which means that all of the polymer does eventually burn. Nanocomposite formation appears to lengthen the time of burning but none of the polymer is retained. The mass loss rate is somewhat decreased and the smoke is not much changed.

1.5 Conclusion – the Future of Fillers and Nanocomposites in Fire Retardancy

The role of the ATH and MA type filler in fire retardancy is assured, since these are now used on a commercial scale and they are affordable. The rather high price currently charged for modified clays means that the clays must clearly outperform other systems before they will make inroads into the marketplace. It is the opinion of this author that clays alone will not be used as fire retardants but they may be a component of the solution to the problem of fire retardancy. Synergy has been demonstrated between conventional fire retardants and nanocomposite formation in a few cases.[59–62] There will need to be additional investigations of this type to confirm the observations that have been made and to evaluate the different conventional fire retardants that could be used. The advantage that the clay brings to fire retardancy is the improvement in mechanical properties and this means that one can add some other material, the fire retardant, that may cause a deterioration of the mechanical properties. This opens the door to new opportunities with combinations of materials.

1.6 References

1. W.E. Horn, Jr., in *Fire Retardancy of Polymeric Materials*, A.F. Grand and C.A. Wilkie (eds.), Marcel Dekker, New York, 2000, pp. 285–352.
2. P.R. Hornsby, *Int. Mater. Rev.*, 2001, **46**, 199.
3. J. Jow and D. Gomolka, *US Patent 5482990A*, 1996; E. Sezaki, M. Akami and H. Endo, *European Patent 0331358*; Y. Yamamoto and M. Tanmachi, *Japanese Patent 04253748*.
4. P.R. Hornsby, *Macromol. Symp.*, 1996, **108**, 203.
5. P.R. Hornsby, *Fire Mater.*, 1994, **18**, 269.
6. P.R. Hornsby and A. Mthupha, *Plast. Rubber Compos. Process. Appl.*, 1996, **25**, 347.

7. P.R. Hornsby, J. Wang, G. Jackson, R. N. Rothon, G. Wilkinson and K. Cosstick, *Polym. Degrad. Stab.*, 1996, **51**, 235.
8. J. Rychly, K. Vesely, E. Gal, M. Kummer, J. Jancar and L. Rychly, *Polym. Degrad. Stab.*, 1990, **30**, 57.
9. P.R. Hornsby and C.L. Watson, *Plast. Rubber Process. Appl.*, 1989, **11**, 45.
10. G.L. Kirshenbaum, *Kunstst. J.*, 1989, **79**, 62.
11. H. Staendeke, *FRCA meeting*, Spring 1988.
12. E.D. Weil, M. Lewin and H.S. Lin, *J. Fire Sci.*, 1998, **16**, 383.
13. Y. Kojima, A. Usuki, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, J. *Mater. Res.*, 1993, **8**, 1185.
14. A. Blumstein, *J. Polym. Sci.: Part A*, 1965, **3**, 2653.
15. A. Blumstein, *J. Polym. Sci.: Part A*, 1965, **3**, 2665.
16. A. Blumstein and F. W. Billmeyer, *J. Polym. Sci.: Part A-2*, 1966, **4**, 465.
17. A. Blumstein, R. Blumstein and T.H. Vandersppurt, *J. Colloid Interface Sci.*, 1969, **31**, 236.
18. A. Blumstein, S. L. Malhotra and A. C. Watterson, *J. Polym. Sci.: Part A-2*, 1970, **8**, 1599.
19. A. Blumstein, K.K. Parikh, S.L. Malhotra and R. Blumstein, *J. Polym. Sci.: Part A-2*, 1971, **9**, 1681.
20. W. Rudroff, *Adv. Inorg. Radiochem.*, 1959, **1**, 233.
21. G.R. Henning, *Prog. Inorg. Chem.*, 1959, **2**, 125.
22. C.A. Mitchell and R. Krishnamoorti, *Proc. Addit.* 2003, April, 2003.
23. H. Koerner, C.-S. Wang, R.A. Vaia, M.D. Alexander, N.A. Pearce and H. Bentley, *Proc. Addit.* 2003, April, 2003.
24. C.A. Mitchell, J.L. Bahr, S. Arepalli, J.M. Tour and R. Krishnamoorti, *Macromolecules,* 2002, **35**, 8825.
25. G. Beyer, *Fire Mater.*, 2002, **26**, 291.
26. T. Kashiwagi, E. Grulke, J. Hilding, R. Harris, W. Walid and J. Douglas, *Macromol. Rapid Commun.*, 2002, **23**, 761.
27. T. Kashiwagi, E. Grulke, J. Hilding, J. Shields, R. Harris, W. Awad and J. Douglas, *Abstract of 9th European Meeting on Fire Retardancy*, September, 2003.
28. G. Li, L. Wang, H. Ni and C. U. Pittman, Jr., *J. Inorg. Organmet. Chem.*, 2002, **11**, 123.
29. J.D. Lichtenhan and J.W. Gilman, "Preceramic additives as fire retardants for plastics," *US 6,362,279 B2*, issued March 26, 2002.
30. E. Devaux, M. Rochery and S. Bourbigot, *Fire Mater.*, 2002, **26**, 155.
31. R.A. Vaia and E.P. Giannelis, *Macromolecules*, 1997, **30**, 7990.
32. A.C. Balazs, C. Singh, E. Zhulina and Y. Lyatskaya, *Acc. Chem. Res.*, 1999, **32**, 651.
33. W. Xie, Z. Gao W-P. Pan, R. Vaia, D. Hunter and A. Singh, *Polym. Mater. Sci Eng.*, 2000, **83**, 284.
34. J. Zhu, A.B. Morgan, F.J. Lamelas and C.A. Wilkie, *Chem. Mater.*, 2001, **13**, 3774.
35. D. Wang and C.A. Wilkie, *Polym. Degrad. Stab.*, 2003, **82**, 309.

36. S. Su, D.D. Jiang and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **83**, 321.
37. S. Su, D.D. Jiang and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **83**, 333.
38. S. Su, D.D. Jiang and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **84**, 279.
39. S. Su, D.D. Jiang and C.A. Wilkie, *Polym. Adv. Tech.*, 2004, **15**, 225.
40. S. Su, D.D. Jiang and C.A. Wilkie, *J. Vinyl Add. Tech.*, 2004, **10**, 44.
41. J. Zhang and C.A.Wilkie, *Polym. Degrad. Stab.*, 2004, **83**, 301.
42. D.L. VanderHart, A. Asano and J.W. Gilman, *Macromol.*, 2001, **34**, 2001, 3819.
43. D.L. VanderHart, A. Asano and J.W. Gilman, *Chem. Mater.*, 2001, **13**, 3781.
44. D.L. VanderHart, A. Asano and J.W. Gilman, *Chem. Mater.*, 2001, **13**, 3796.
45. S. Bourbigot, D.L. VanderHart, J.W. Gilman, W.H. Awad, R.D. Davis, A.B. Morgan and C.A. Wilkie, *J. Polym. Sci.: Part B: Polym. Phys*, 2003, **41**, 3188.
46. J.W. Gilman, T. Kashiwagi, M. Nyden, J.E.T. Brown, C.L. Jackson, S. Lomakin, E.P. Giannelis and E. Manias, in *Chemistry and Technology of Polymer Additives*, S. Al-Malaika, A. Golovoy and C.A. Wilkie (eds.), Blackwell Scientific, Oxford, 1999, pp. 249–265.
47. M. Alexandre and P. Dubois, *Mater. Sci & Eng.*, 2000, **R28**, 1.
48. M.R. Nyden and J.W. Gilman, *Comp. Theor. Polym. Sci.*, 1997, **7**, 191.
49. J.W. Gilman, C.L. Jackson, A.B. Morgan, R. Harris, Jr., E. Manias, E.P. Giannelis, M. Wuthenow, D. Hilton and S.H. Phillips, *Chem. Mater.*, 2000, **12**, 1866.
50. J. Zhu, F.M. Uhl, A.B. Morgan and C.A. Wilkie, *Chem. Mater.*, 2001, **13**, 4649.
51. J. Wang, J. Hao, J. Zhu and C.A. Wilkie, *Polym. Degrad. Stab.*, 2002, **77**, 249; J. Du, J. Zhu, C.A. Wilkie and J. Wang, *Polym. Degrad. Stab.*, 2002, **77**, 377; J. Du, D. Wang, C.A. Wilkie and J. Wang, *Polym. Degrad. Stab.* 2003, **79**, 319; J. Du, J. Wang, S. Su and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **83**, 29.
52. D. Wang, D.D. Jiang, J. Pabst, Z. Han, J. Wang and C.A. Wilkie, *Polym. Eng. Sci.*, 2004, **44**, 1122.
53. D. Wang, B.N. Jang, S. Su, J. Zhang, X. Zheng, G. Chigwada, D.D. Jiang and C.A. Wilkie, this book, chapter 5.
54. F.M. Uhl and C. A. Wilkie, *Polym. Degrad. Stab.*, 2002, **76**, 111.
55. F.M. Uhl and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **84**, 215.
56. F.M. Uhl, Q. Yao and C.A. Wilkie, *Polym. Deg. Stab.*, submitted.
57. S. Su and C.A. Wilkie, *Polym. Degrad. Stab.*, 2004, **83**, 347.
58. D. Wang and C.A. Wilkie, in *Fire Behaviour of Composite Materials*, G. Gibson and A. Mouritz (eds.), Kluwer Press, 2005 in press.
59. G. Chigwada and C.A. Wilkie, *Polym. Degrad. Stab.*, 2003, **81**, 551.
60. X. Zheng and C.A. Wilkie, *Polym. Degrad. Stab.*, 2003, **81**, 539.
61. M. Zanetti, G. Camino, D. Canavese, A.B. Morgan, F.J. Lamelas and C.A. Wilkie, *Chem. Mater.*, 2002, **14**, 189.
62. G. Beyer, *Fire Mater.*, 2001, **25**, 193.