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Flame Retardancy of Highly Filled Clay/Polyamide 6 Nanocomposites

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Abstract

To obtain an in-depth physical knowledge of the protective barrier stability and uniformity under fire conditions, we prepared highly filled polyamide 6/organoclay nanocomposites and characterized their thermal and flammability properties. The objectives were to identify a critical composition that is needed to form a stable char with no apertures or cracks and to gain a thorough understanding of the mechanisms of flame retardancy. It was shown that there is no need for higher percentages of clay and even smaller amounts of clay (< 10 wt.%) should be enough to achieve good fire performance. Factors such as incoherency, poor stability, and non-uniformity of the char or the presence of large cracks and formation of island-like structures were insignificant in slowing down the heat release and mass loss rates. Nevertheless, there was no stage during the flammability test where the fire completely extinguished even when the protective layer was stable and free from major cracks/apertures. Based on these results, new insights and approaches to process better flame retardant polymer nanocomposites are discussed.

Keywords: flame retardancy; nanocomposites; polyamide; clay; barrier

1. Introduction

The increasing use of polymers in various fields of engineering and technology is always associated with increasing fire hazards that are detrimental to the environment and human life. In general, depending on the nature of the polymer involved, thermal degradation may occur in different ways. For example, polyamides degrade *via* hydrolysis of the amide bond, homolytic cleavage of C-C, C-N, C-H bonds, followed by cyclization and homolytic cleavage, and finally produce CO, NH₃, nitriles, and hydrocarbons [1, 2]. To improve flame retardancy performance of a polymer, that is higher ignition resistance and minimized flame spread, escape time and containment of flame and combustible/degradation products, the most common approach is to add flame retardant agents [1-3]. Some of these include: phosphorous- [4-6] and boron- [1, 7, 8] based compounds; halogen (brominated or chlorinated) compounds [2, 9, 10]; hydrated fillers (alumina trihydrate, magnesium hydroxide) [11-13]; nitrogen- [14, 15] and silicon- [16-18] based compounds. These flame retardant agents, depending on their nature, act chemically and/or physically in the solid, liquid, or gaseous phase and interfere with combustion during different stages (that is, heating, decomposition, ignition, or flame spread) of the process.

Despite their beneficial effects, there are many negatives in using most of these additives as flame retardants, especially halogen- and phosphorous-based compounds as they generate corrosive and toxic combustion products, like dioxins and furans [1-3, 19]. While hydrated fillers and nitrogen-based compounds are relatively non-toxic, they require high levels of loading (generally, 40-50 wt.%) for adequate flame retardant efficiency [20], which often leads to processing difficulties and deterioration in other critical polymer characteristics, including mechanical and physical properties.

Much attention was diverted on using nanoscale fillers, particularly, layered silicates as flame retarding agents in different polymers [21-33]. It has been recognized that exploitation of the fundamental characteristics of nano-clay (good aspect ratios, large specific surface areas, and excellent cation exchange capacities) in polymers facilitates enhancements in many properties, such as stiffness, strength, dimensional stability, barrier resistance, thermal, optical, and physico-chemical properties, apart from the flame retardant effect. Even at low silicate loading (e.g., 5 wt.%), with no

additional flame retardants in the system, heat release rates (HRR) and mass loss rates were greatly reduced in addition to the delay in burning compared to corresponding neat polymers. The reduction in peak HRR is an important parameter signifying fire safety, as it represents the point in a fire where heat is likely to propagate further (flame spread) or ignite adjacent objects.

By analyzing the combustion chars using electron microscopy and x-ray diffraction, plausible mechanisms for the reduced heat release rates with addition of clay were revealed [21-23, 25-28]. It was suggested that the structure of the nanocomposite collapsed during combustion and a multilayered carbonaceous-silicate structure formed on the polymer surface that insulated the underlying material from the heat flux of the flame and also increased char performance by structural reinforcement. Physically, the silicate-carbonaceous char acts as an excellent insulator and mass transport protective barrier, thereby reducing the heat release rate and delaying the escape of volatile products released as the polymer decomposes. Other mechanisms were also proposed and included: radical trapping effect by paramagnetic iron within the clay [35]; chemical cross-linking of decomposing polymer induced by clay due to long residence times for polymer radicals and some catalytic capability of clays to aromatize hydrocarbons [23, 36]; and at higher temperatures, the inorganic additive would act as a radical scavenger due to adsorption to Lewis acid sites, which might interrupt the burning cycle as these radical species were required to break down the polymer chains to fuel fragments [3, 37].

Despite all these, polymer/clay nanocomposites without any other conventional flame retardant does not self-extinguish until most of the fuel has been burnt, that is, they burn slowly but completely. This means that the protective layer formed during burning on the polymer surface is not uniform/stable and jammed with nanoparticles like a continuous net-like structure or not forming quickly to insulate the underlying material from the flame. It is also shown that in almost all the studies on polymer/clay nanocomposites, the clay layers tend to develop large lateral surface cracks in which vigorous bubbling still occurs. This is a plausible reason why these materials by themselves are unable to meet the existing requirements of the ignition resistance tests (e.g., vertical burning UL94) and hence, many researchers incorporated additional

conventional flame retardants, like phosphorous or bromine, in their recent studies. Therefore, the original concerns of eco-friendliness recur.

It is hence necessary to obtain an in-depth knowledge on the formation and stability of protective barrier under fire conditions to develop environmentally benign (halogen- and phosphorus/phosphate-free) and superior flame retardant polymer/layered silicate nanocomposites. However, this raises some critical questions like whether elimination of major cracks in the char is enough to improve the fire performance or if other mechanisms need to be operative or if additional conventional flame retarding agents must be added? It is also necessary to answer and understand these issues when exposing polymers to fire with regard to both short-term (like UL94 tests) and long-term (like cone calorimeter tests) conditions. To address these specific issues, we prepared highly filled polyamide 6/nanoclay composites and characterized their thermal and flammability properties to identify a critical composition that is needed to form a stable char with no apertures or cracks and to understand the physical flame retarding mechanisms.

2. Experimental work

2.1. Preparation of materials: Polyamide 6 with a trade name of Akulon F 232-D was obtained from DSM Engineering Plastics (The Netherlands). Organoclay having a cation exchange capacity of 90 mequiv/100 g (trade name: Cloisite[®] 30B) was obtained from Southern Clay Products Inc. via Jim Chambers & Associates, Australia. The alkyl ammonium surfactant used in the organoclay was methyl, tallow, bis-2-hydroxyethyl quaternary ammonium chloride. Polyamide 6 pellets and organoclay were oven-dried at 85 °C for 24 h. Then, the desired proportions of the ingredients were mixed and melt-compounded in a Werner & Pfleiderer ZSK-30 twin-screw extruder (L/D = 30, L = 0.88 m). Extrusion was performed within the temperature range of 210-245 °C and a screw speed of 300 rpm. Subsequently, the extruded pellets were oven-dried and molded into standard 100 x 100 x 3 mm³ plates using a Netstal HP1000 injection molding machine with the barrel and mold temperatures maintained at 240 °C and 50 °C, respectively. The holding pressure was 60 MPa; while the holding and cooling times were 10 s and 25 s, respectively. The following materials were prepared using these conditions: neat polyamide 6 (designated A0) and binary

polyamide 6/organoclay nanocomposites with 10 wt.% (A1), 20 wt.% (A2), and 30 wt.% (A3) of organoclay.

2.2. Morphology observations: To study the microstructures of the nanocomposites, ultra-thin sections of ~70-90 nm in thickness were cryogenically cut with a diamond knife in a liquid nitrogen environment at $-100\text{ }^{\circ}\text{C}$ using a Leica Ultracut S cryo-microtome. Sections were collected on the holey formvar/carbon coated 400-mesh copper grids. Then, the thin sections were observed with a Philips CM12 transmission electron microscope (TEM) at an accelerating voltage of 120 kV.

2.3. Thermal and combustion testing: Thermogravimetric analysis (TGA) was conducted on TA Instruments (TGA 2950) from room temperature ($\sim 25\text{ }^{\circ}\text{C}$) to $800\text{ }^{\circ}\text{C}$ at a rate of $20\text{ }^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. The weight loss/temperature curves were monitored. The combustion experiments were performed in a cone calorimeter (CSIRO, Australia) on injection-molded plates at an incident heat flux of $50\text{ kW}/\text{m}^2$. The instrument was capable of recording ignition times, heat release and mass loss rates, specific extinction area, CO and CO_2 yield. All sides of the samples were wrapped in aluminium foil except for the upper face, which was exposed to the heat flux.

2.4. X-ray diffraction: A Siemens D5000 x-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.54\text{ \AA}$) at a generator voltage of 40 kV and a current of 30 mA was used to study the diffraction behavior of the organoclay and nylon 6 nanocomposites. All tests were conducted in the reflection mode at ambient temperature with 2θ varying between 1° and 30° . The scanning speed was $1^{\circ}/\text{min}$ and the step size was 0.05° . XRD patterns were also obtained after combustion testing of the nanocomposites from the surfaces of the residues.

2.5. Characterization of collected residues: In addition to the XRD analysis, optical, scanning (SEM) and transmission (TEM) electron microscopy was used to characterize the residues of the burnt samples. A Philips S-505 SEM and a digital camera were used to examine the flame exposed surfaces to obtain an idea of the continuity of the protective layer, while the cross-sections beneath the surfaces of

combustion residues were observed via TEM to identify the uniformity and thickness of the insulating layer so as to gain insights on the mechanisms of flame retardancy.

3. Results and discussion

3.1. Dispersion and orientation of organoclay

Representative TEM micrographs of polyamide 6/organoclay nanocomposites with different loading of organoclay (A1 to A3) are shown in Figure 1. All micrographs are taken from the cross-section of the injection molded thin plates along a plane normal to the flow direction (indicated schematically in Figure 1). Clay layers at all loadings are well dispersed, finely distributed, and in addition highly oriented in a particular direction. It has been well-recognized that the affinity and compatibility of organoclay with the matrix along with shear stress play a dominant role in determining the extent of delamination of clay agglomerates into individual layers [38-41].

It is important to note that unlike spherical nano-fillers, clay platelets due to their 2-D nanostructure exhibit significant orientation differences on any one plane varying from a fully disc shape to a fine layer. Due to their high aspect ratio, during injection molding, only translation motion of clay platelets is possible and rotational motion is generally negligible. So from Figure 1, it is clear that all the clay platelets with their planar dimensions are oriented along the injection molding direction. The high level of orientation even in the mid-thickness regions of the plate is possible owing to the higher clay loading, which induces more shearing among the platelets. The highly oriented planar structure (discs) of clay layers along the sample is important when the sample surface is exposed to fire as the flame retardancy performance of the material heavily depends on how fast the clay platelets can migrate to the burning surface of polymer and cover it, which should be continuous with no openings or apertures. Obviously, the barrier will be most effective if the planar dimensions of the platelets are exposed to the flame surface rather than its orthogonal surfaces.

3.2. Thermal stability

To enhance the compatibility of clay layers with polymers and achieve nanoscale dispersion, it is necessary to modify clay with organic surfactants. This is to replace the interlayer cations by more hydrophobic cations, like ammonium with long alkyl chains and weaken the electrostatic interaction between adjacent clay layers. It is often stated that the presence of clay layers in a polymer enhances its thermal stability and this is attributed to the improved barrier properties and the torturous path for volatile decomposition products, which hinder the diffusion out of the material [42, 43]. However, if the clay layers are organically treated to make them more compatible with the matrix, based on the cation-exchange capacity of clay, the alkyl ammonium surfactant content in organoclay is usually over 30 wt.% [38, 40]. It should be noted that not all clay platelets can be fully ion exchanged due to the natural defects/charge heterogeneities that pre-exist. Therefore, some of the organic surfactant may not be ionically bound and only physio-sorbed onto the clay surface [44]. Additionally, alkyl ammonium organic treatments are thermally unstable and decompose usually from ~200 °C, which is lower than most engineering polymer processing temperatures. Thus, the presence of such a large amount of low molecular weight bound/unbound surfactant may adversely affect the thermal stability and other mechanical properties.

The decomposition of pristine clay and different types of organically treated clays has been well studied and reported [45-47]. Decomposition of pristine montmorillonite starts with the loss (or evolution) of free (absorbed) water residing between the montmorillonite crystallites and interlayer water between silicate sheets comprising the hydration spheres of the cations (before 400 °C). Weakly bound, physio-sorbed water and free water pockets within the aggregate structure evolve at lower temperatures, whereas water within the interlayer and strongly bonded water of hydration (Na^+) evolve at progressively higher temperatures. Then, dehydroxylation of aluminosilicate lattice occurs between 500 and 1000 °C. While even in organoclay, decomposition starts with the evolution of the absorbed water and gaseous species. Though organoclay is considered hydrophobic, due to the alkylammonium cations, it is proposed that water absorption still occurs on the exterior of the aggregates and along the hydrophilic layer edges depending on the environmental conditions [45]. Degradation usually begins at ~180 °C with loss of olefin, and its evolution continues

to 500 °C. The decomposition can cause quick release of fuel early in the ignition process and affect the flammability properties by causing early ignition than the neat polymer. It is also important to note that irrespective of the ammonium surfactant architecture (trimethyl or dimethyl), chain length, surfactant mixture, exchange ratio, or pre-conditioning (washing), the initial onset temperatures for decomposition of the surfactants within the organoclay were reported to be quite similar (~155-180 °C). Dehydroxylation of aluminosilicate was found to occur from 500-700 °C similar to the pristine clay.

Figure 2 shows TGA analysis of neat polyamide 6 (A0) and polyamide 6/organoclay nanocomposites (A1 to A3) in nitrogen. The dispersion/distribution of clay layers or its loading in polyamide 6 did not have any positive effects on the thermal stability of polyamide 6 implying that the barrier properties of delaminated clay layers are not the primary determining factors of thermal stability. Instead, as mentioned above, organoclay containing materials start to decompose earlier than neat polymer. For example, 5% weight loss thermal degradation temperatures of A0 and A1 to A3 are ~471, 451, 422, and 407 °C, respectively. From the DTG curves (Figure 2b), the maximum decomposition temperature is obtained, which also confirms the poor thermal stability of organoclay reinforced materials (A0 ~546 °C; A1 ~535 °C; A2 ~529 °C; and A3 ~525 °C). However, it is important to note that once the thermal decomposition of alkyl ammonium salts in the clay galleries occurs through the Hoffman degradation reaction, the acidic clay site formed on the clay surface will have a direct interface with the remaining polymer [25]. Layered silicates in acid form are generally known to cause hydrocarbon cracking, which will further degrade the polymer [48]. Based on this, it has been shown that if a low fraction of clay layers is added to a polymer matrix, the barrier effect will be predominant; but with increasing loading, the catalyzing effect rapidly rises and becomes dominant, so that the thermal stability of the nanocomposites decreases. Thus, combination of the presence of large quantities of organic content and the catalytic activity of clay seems to be the reason for the poor thermal stability of the nanocomposites.

3.3. Flammability properties

Figure 3a shows representative heat release rate curves of neat polyamide 6 (A0) and polyamide 6/organoclay nanocomposites (A1 to A3). Clearly, nanocomposite even with 10 wt.% of organoclay shows significantly reduced heat release rates (and peak HRR) compared to neat polyamide 6. Among the nanocomposites there seems a slight reduction of heat release rates with increasing organoclay loading, but the differences are not significant. Despite these dramatic reductions in HRR, the total heat released per unit area is somewhat higher (due to the presence of organic surfactant) than the neat polymer. The total heat release per unit surface area (integrated over time) for neat polyamide 6 is $\sim 82 \text{ MJ/m}^2$; while for A1 to A3, they are 94, 100, and 105 MJ/m^2 , respectively. This clearly suggests that the nanocomposites does not self-extinguish even after a protective char is formed until most of the fuel has been burnt out, that is, they burn slowly but completely.

As discussed before, TGA results indicate that A0 is more thermally stable than the nanocomposites (A1 to A3). In line with this trend, the ignition of nanocomposites occur earlier than neat polyamide 6 (A3 $\sim 51 \text{ s}$; A2 $\sim 55 \text{ s}$; A1 $\sim 57 \text{ s}$; and A0 $\sim 66 \text{ s}$). The presence of large amounts of low molecular weight organic surfactants in A1 to A3, which thermally decompose earlier than polyamide 6 (that is obvious from Figure 2) seems to be responsible for this behavior. This trend is also observed in carbon nanotube reinforced polymers where it is shown that the radiant flux absorption at infrared wavelengths increases significantly with addition of carbon nanotubes to polypropylene resulting in the radiative ignition delay time that is lesser for the nanocomposite than polypropylene [49]. The mass loss rate curves of all the samples plotted in Figure 3b are also proportional to the heat release rate curves. These results clearly show that the presence of nanoclay layers significantly delays the mass loss rates when compared to the neat polymer.

3.4. Characterization of collected residues

3.4.1. Optical microscopy: Visual observations of the combustion experiments in the cone calorimeter revealed different behavior for neat polyamide 6 and its nanocomposites. Neat polyamide 6 completely melted and was accompanied by severe

bubbling and bursting at the sample surface. At the end of the test, no residue was left behind. In the presence of organoclay, the process of burning was different. At 10 wt.% organoclay, many small, discrete island-like structures were observed after initial formation of numerous small bubbles and bursting at the surface. Even though severe bubbling was not observed, bubbling between island-like structures was clearly seen. In contrast, the residues of polyamide 6 containing 20 and 30 wt.% organoclay appeared to be solid-like and a continuous layer covered the surface during the entire test period. Figure 4a shows the optical micrograph of the residue of A1 where the numerous island-like structures of different sizes along with many cracks/apertures are evident. Also, the microstructure of the residue is coarse with many floccules. With increasing weight percentage of organoclay (20 wt.%), island-like structures and major cracks are greatly reduced indicating that a continuous and homogenized char formation is possible at this organoclay loading (Figure 4b). The microstructure is also fine compared to A1 suggesting a tight packing of ingredients in the char. At 30 wt.% organoclay (A3), the microstructure of the residue is even finer with no major deep cracks of concern (Figure 4c). Moreover, at 10 wt.% organoclay, physically, the char is loose and very easy to break; but at the other two compositions, it is relatively rigid and integrated.

3.4.2. XRD analysis: Wide-angle XRD analysis was conducted for all the collected residues to understand the clay particle structure therein. Before discussing these results, it is important to note that XRD analysis of all the material systems were also performed before burning and it was revealed that except for the peak corresponding to the γ -crystalline phase of polyamide 6 (2θ corresponding to $\sim 21.4^\circ$) in A1 to A3, no other peaks were found in the 2θ range $1-30^\circ$. Figure 5 shows the XRD curves of the combustion chars of A1 to A3 where three major peaks are evident. The first peak at $2\theta \sim 7.05^\circ$ corresponds to an interlayer spacing of ~ 1.3 nm, suggesting that the delaminated/exfoliated nanostructures of clay present prior to burning collapsed in all cases irrespective of the loading. Similar observation (interlayer spacing ~ 1.3 nm) was also reported in many studies in the literature inferring the same nature of the residue irrespective of the matrix (thermoplastics or thermosets) and structure of the original nanocomposite (exfoliated or intercalated) [21, 23, 27, 50]. Taking the thickness of an individual clay layer (completely dehydrated) as 0.7 nm [51], then

~0.6 nm difference corresponds to the carbonaceous layer intercalated into the clay layers. It suggests that this spacing is a thermodynamically stable form of the clay-carbon material produced by thermal degradation.

In general, when the polymer surface temperature becomes sufficiently high, degradation generates pyrolysis products whose majority includes monomer, cyclic oligomers, and small quantities of gas volatiles depending on the polymer. Since, the degradation temperature of the polymer is much higher than the boiling temperature of the monomer, degradation products are superheated and readily nucleate, forming bubbles in the molten layer [27]. The bubbles rapidly rise and expand to the surface if the surrounding polymer layer is a low viscosity melt. This transportation of clay particles pushed by numerous rising bubbles of degradation products and associated convection flow in the melt from the interior of the sample towards the surface has been proposed as a plausible reason for the formation of protective inorganic char on the surface [21, 27]. However, bursting of bubbles at the surface may also push any accumulated clay particles on the melt surface outwards away from the bursting area.

The second peak at $2\theta \sim 20.0^\circ$ (an interlayer spacing of ~0.44 nm) is assigned to the diffraction from the (110) and (020) planes of the montmorillonite crystal, of which planes are both perpendicular to the (001) plane. It was reported by Takahashi *et al.* [52] that the highly uniform orientation of montmorillonite layer along with the orientation of (001) plane of the montmorillonite layer parallel to the film surface was demonstrated by the appearance of (110) and (020) diffraction in the in-plane XRD pattern. While the third peak at $2\theta \sim 27.6^\circ$ corresponds to an interlayer spacing of 0.32 nm and is very close to the ordered graphite spacing of 0.335 nm [53]; and more precisely is the (002) peak for the origami graphite [54]. Therefore, in the presence of clay, after combustion, polymers tend to form a thermally stable organic component possibly having a graphitic structure. It can also be seen that this peak is strong for A2 and A3 with higher loadings of clay than for A1 having a lower clay loading. So, in brief, this multilayered carbonaceous-silicate structure may act as an insulator and mass transport barrier, slowing down the escape of volatile products generated during decomposition.

3.4.3. SEM analysis: Representative SEM micrographs of the top surfaces of residues (which were exposed to flame) of A1 and A3 having different clay loading are shown in Figures 6a-6c. A1, taken on an island-like structure shows the floccules (Figures 6a and 6b); but more importantly, almost all of them are opened up signifying the bursting of bubbles due to not having a stable barrier. So, the transfer of heat and the diffusion of oxygen and combustible gases cannot be effectively prevented leading to a poor flame retardancy of material. While at 20 and 30 wt.% organoclay (A2 and A3), surfaces of the residues are tighter, compactly packed with finer microstructures and with minimum apertures or openings. A representative SEM micrograph is shown in Figure 6c for A3. However, the swelling nature of the microstructure of the char is evident; but the combustible gases generated from thermal decomposition of matrix may not easily break through the charred layer due to the compact and tight packing of the layer.

Nonetheless, the bottom and middle regions of the residues (A1 to A3) still showed evidence of the layers of clay. For example, at 20 wt.% organoclay, Figure 6d shows the SEM micrograph taken from the bottom regions of the residue. This suggests that not all the clay has migrated to the top (surface) upon the exposure of flame pointing to a negative aspect of clay being a flame retarding agent.

3.4.4. TEM analysis: To gain insights into the mechanisms of flame retardancy in these materials, since this knowledge is critical to develop environmentally benign flame retardant materials, TEM examinations (on cross-sections beneath the surfaces of combustion residues) were performed. Figures 7a to 7d show typical low magnification TEM micrographs of residues of polyamide 6/organoclay nanocomposites at various organoclay loadings. In all the materials, large empty spaces below the surface of multi-layered structured barrier (like the neat matrix) are evident, i.e., no individual silicate layers are present except for some aggregated structures. This is attributed to the carbonaceous matter left behind the degradation products, which also suggests that the silicate layers after exposing to flame are not reinforcing the whole char (except for some regions) as reported by others [21]. At 10 wt.% of the rigid phase, although the prevalence of a protective-silicate char at the surface is seen (Figures 7a and 7b), it is very thin ($\sim 0.2\text{-}0.4\ \mu\text{m}$), non-uniform, and broken. This

clearly implies that the migration of all the clay layers from within the sample to the burning surface has not taken place or the rising bubbles may have pushed most of the silicate layers out of the sample.

At 20 wt.% organoclay, the thickness of the protective barrier increased compared to at 10 wt.% (~1-1.3 μm compared to 0.2-0.4 μm at 10 wt.%) though the packing of layers (indicative of char stability) is not perfect and openings can be seen. While at 30 wt.% organoclay, at low magnifications, the protective silicate-rich layer seems to be heavily packed, continuous and uniform. The thickness of the barrier varied from ~1.8-2.0 μm . In addition, high magnification TEM micrographs of the protective barrier in A3 shown in Figures 7e and 7f illustrate the well-ordered multi-layered arrays of silicate-carbonaceous structure formed after combustion. The dark lines represent the silicate layers and the white-grayish spaces represent the carbonaceous matter tightly locked between silicate layers. It also seems that the adjacent silicate layers on any one plane are very closely spaced with hardly any gap between them giving the impression of dark continuous lines. These multi-layered silicates, only very near the surface regions, are effectively reinforcing the carbonaceous matter and improving the char stability.

We have also checked the cross-sections close to the bottom and middle of the residues with TEM and found the presence of numerous clay layers stacked together also confirming that not all clay layers have migrated to the flame surface similar to SEM analysis. This issue of migration of clay layers to the burning surface seems to be a major obstacle in improving the flame retardancy of polymer/clay systems. A representative example is shown in Figure 8 for A3 taken from the middle regions of the residue in contrast to the starting material. When thermal decomposition of the organic surfactant starts, it results in more hydrophilic and thus less compatible clay particles with the resin. Hence, the initial well-dispersed clay layers seem to form aggregated structures. Extended voids in between the aggregated structures are seen, which probably are formed due to the rising bubbles. More discussions on the results and combat methods to improve the fire performance of polymer nanocomposites are given in Section 3.5 below.

3.5 Approaches for producing better flame retardant polymer nanocomposites

This study shows that we do not need higher percentages of clay (as the heat and mass loss rates have insignificant differences at all loadings) and even smaller amounts of clay (<10 wt.%) should be enough to achieve significantly delayed heat release and mass loss rates, and reduced peak heat release rates. Factors such as incoherency, poor stability, and non-uniformity of the char or the presence of large cracks and formation of island-like structures are insignificant in slowing down the heat release and mass loss rates. Analogous to this, despite the uniformity, thickness and stability of the protective layer at 30 wt.% organoclay, there was no stage during the cone calorimeter experiment where the fire completely extinguished until most of the fuel was burnt. This indicates uninterrupted supply of oxygen to the burning substances underneath the protective char; it also means uninterrupted diffusion of decomposition products to the ambient. Ideally, for most effective flame retardancy performance, it is beneficial to have a situation where most of the high aspect ratio clay layers quickly migrate to the burning surface of the polymer from inside, with effective coupling between adjacent layers, and not having any apertures (not even finer ones) in order to fully shield/protect the polymer melt. Also, the protective layer should be densely packed so that it has sufficient physical strength not to be broken or disturbed by bubbling. Below are some aspects that should be considered to achieve this beneficial situation and to further improve the flame retardancy performance of eco-friendly polymer/clay nanocomposites.

(a) The presence of large quantities of alkyl-ammonium surfactants acts against the thermal stability of nanocomposites and ultimately affects the fire performance of these materials. To improve the flame retardancy performance of polymer/clay nanocomposites, clay should be modified with thermally stable (like aromatic compounds) surfactants or nitrogen-based compounds. Thermally stable surfactants decompose at higher temperatures than conventional alkyl ammonium surfactants and improve the fire performance of polymer/clay nanocomposites. Nitrogen-based compounds, in contrast, produce nitrogen gas during thermal decomposition and improve the self-extinguishing properties of the nanocomposites; the idea is to stop a fire by blocking oxygen intake, i.e., replacing air by nitrogen and creating an almost inert atmosphere, where the fire would inevitably extinguish. It is, however, important to note that these

approaches are particularly beneficial for short-term fire exposure conditions, like vertical burning UL94 test, which is the major criterion for most of the commercially available fire retardant materials. For long-term fire exposures like cone calorimeter tests, apart from a small delay of ignition and nitrogen gas combating the fire for a while, the benefits obtained from these modifications are very much questionable. Once ignited or the evolution of nitrogen stops, extinguishment is another major concern.

(b) In another approach, addition of small amounts of inorganic additives like low melting glass and zinc borate was thought to improve the coupling of layered silicates [55]. It was assumed that these compounds transform to a partially ceramic-like material and couple all silicate layers to each other upon fire. This in turn effectively provides a continuous coating, physically stabilizing and enhancing the structural integrity of the silicate char to stop the diffusion processes occurring at the surface. However, their effectiveness was not confirmed; thorough testing and understanding are still needed.

(c) It is feasible to have a second layer of defense against fire with another additive apart from silicate layers, which can fill the apertures in the silicate-rich barrier or form additional barriers so that the packing density may be enhanced; that is, using a ternary nanocomposite. This gains further support from recent studies [56, 57] where nanoparticles like polyhedral silsesquioxanes (POSS) and carbon nanotubes are shown to form a protective barrier like clay at the burning surface of the polymer nanocomposites. In particular, with carbon nanotubes, a network jammed structure is reported to form at the burning surface because of the high aspect ratio and entanglement of the tubes. So, a balanced composition of the additives in a polymer seems to be a controlling factor not just for flame retardancy but also for other mechanical and physical properties of the final material.

(d) Flame retardancy performance also depends on how fast the clay layers migrate to the burning surface of the polymer and form an effective barrier. Although it was suggested that the driving forces for the migration of clay particles are the rising bubbles and the convection forces due to the temperature gradient (which may accelerate the migration of clay particles in the direction of the heat source), it is clear

from the above observations that not all the clay layers are migrating to the burning surface resulting in apertures/openings in the char with insufficient thickness, which is a major concern. It is also important to note that no individual delaminated silicate layers are found in the middle/bottom regions of the residue; only agglomerated structures are observed (Figure 8). It seems reasonable to expect that it is hard for the rising bubbles to push these agglomerated structures to the top (burning surface) when compared to individual layers. Furthermore, strong interfacial interactions between polymer and clay layers may hinder the movement of nanoparticles, which delays the formation of a protective barrier on the surface. So, efforts should be made to promote quick migration of clay layers to the burning surface.

In sum, the results of this work clearly reveal the physical significance of the knowledge of multi-layered silicate-carbonaceous barrier, which is quite rare in the literature. These observations have provided new insights and extended our present knowledge of the role of nanoclay layers as flame retardants in polymers. Clearly, % organoclay does not seem to play a determining role in reducing the heat release and mass loss rates. But higher % organoclay reduces the thermal stability of the polymer nanocomposites, which obviously is undesirable. On the contrary, higher % organoclay improves the stability and strength of the char, which is important to combat against fire under all circumstances. Currently, though complete protection of polymer nanocomposites against fire for an indefinite period is difficult, still, it seems reasonable to recommend only lower loadings of organoclay for this purpose. Nonetheless, it is important to realize that the approaches/modifications discussed above in combating fire should be considered and combined with the lower loadings of organoclay as they delay ignition, fire-spread and heat release rates, thereby allowing sufficient time for safety measures to be taken. Finally, it is important to realize that these manipulations of the matrix or addition of other additives/nanoparticles do not bring about degradations of other physical and mechanical properties of the resultant polymer nanocomposites that are required for intended applications.

4. Conclusions

To develop environmentally benign and superior flame retardant polymer/layered silicate nanocomposites, highly filled polyamide 6/organoclay nanocomposites were prepared and their thermal and flammability properties characterized. The presence of alkyl ammonium organic surfactant outweighed the effects of fine dispersion and loading (which are important for barrier properties) of organoclay in controlling the thermal stability of the nanocomposites as they were poor when compared to neat polyamide 6. Structural collapse of nanocomposites during combustion and formation of a multilayered carbonaceous-silicate barrier at the polymer surface insulating the underlying material from the heat flux of the flame were key parameters affecting the flame retardancy performance of nanocomposites. Physically, the combustion chars of nanocomposites with 20 and 30 wt.% of organoclay are more uniform, thick, stable, and continuous compared to 10 wt.% organoclay/polyamide 6 in which the char is relatively thin, non-uniform and broken. However, these differences were poorly reflected in the flammability properties of these samples, that is, all nanocomposites significantly reduced and delayed heat release and mass loss rates compared to neat polymer, and no significant differences were found amongst them. Even at 30 wt.% organoclay, there was no time in the flammability test when the fire was completely extinguished. This shows that the formation of a multi-layered carbonaceous-silicate barrier is important in slowing down the heat release and mass loss rates; while the other factors such as incoherency, poor stability, and non-uniformity of the char or the presence of cracks and formation of island-like structures are insignificant.

Based on physical evidences provided in the paper, it seems that complete protection of conventional polymer/organoclay nanocomposites against fire for an indefinite period is difficult to achieve. But it is important that the approaches/modifications discussed in combating fire (that is, by replacing conventional ammonium surfactants; improving coupling of silicate layers in the char, incorporating additional additives as a second layer of defense, and promoting quick migration of clay layers to the burning surface) be considered and combined with a sensible loading of clay to produce better flame retardant polymer nanocomposites.

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References

1. Lomakin SM and Zaikov GE 1999 In *Ecological Aspects of Polymer Flame Retardancy* pp. 107 (VSP BV: The Netherlands).
2. Lu SY and Hamerton I 2002 *Prog. Polym. Sci.* **27** 1661.
3. Zaikov GE and Lomakin SM 2002 *J. Appl. Polym. Sci.* **86** 2449.
4. Stackman R 1981 *Amer. Chem. Soc. Div. Polym. Chem. Polym. Prepr.* **22** 170.
5. Pearce EM 1984 In *Contemporary Topics in Polymer Science* Ed. Vanderburg EJ **Vol. V** pp. 401 (Plenum Press, New York).
6. Moedritzer K 1978 *US Patent* **4 072 653**.
7. Dechirico A, Audisio G, Provasoli F, Armanini M and Franzese R 1993 *Makromol. Chem. Macromol. Symp.* **74** 343.
8. Chigwada G, Jash P, Jiang DD and Wilkie CA 2005 *Polym. Degrad. Stab.* **88** 382.
9. Tjahjadi M and Gallucci RR 1999 *Elastom. Plast.* **31** 205.
10. DeStio P 1991 In *Proceedings of the Conference on Recent Advances in Flame Retardancy of Polymeric Materials* Ed. Lewin M pp. 185 (Stamford, CT, USA).
11. Beyer G 2001 *Fire Mater.* **25** 193.
12. Beyer G 2006 *Polym. Adv. Technol.* **17** 218.
13. Ulutan S and Gilbert M 2000 *J. Mater. Sci.* **35** 2115.
14. Horacek H and Grabner W 1993 *Makromol. Chem. Macromol. Symp.* **74** 271.
15. Weil E and McSwigan B 1994 *J. Coating Technol.* **66** 75.

16. Iji M and Serizawa S 1998 *NEC Res. Dev.* **39** 82.
17. Hsiue GH, Wang WJ and Chang FC 1999 *J. Appl. Polym. Sci.* **73** 1231.
18. Wang WJ, Perng LH, Hsiue GH and Chang FC 2000 *Polymer* **41** 6113.
19. Levchik SV and Weil ED 2005 *Polym. Intl.* **54** 11.
20. Gui H, Zhang X, Liu Y, Dong W, Wang Q, Gao J, Song Z, Lai J and Qiao J 2007 *Compos. Sci. Technol.* **67** 974.
21. Gilman JW 1999 *Appl. Clay Sci.* **15** 31.
22. Gilman JW, Kashiwagi T and Lichtemhan JD 1997 *SAMPE J.* **33** 40.
23. Morgan AB 2006 *Polym. Adv. Technol.* **17** 206.
24. Stretz HA, Wootan MW, Cassidy PE and Koo JH 2005 *Polym. Adv. Technol.* **16** 239.
25. Morgan AB, Chu LL and Harris JD 2005 *Fire Mater.* **29** 213.
26. Zhao C, Qin H, Gong F, Feng M, Zhang S and Yang M 2005 *Polym. Degrad. Stab.* **87** 183.
27. Kashiwagia T, Harris Jr RH, Zhang X, Briber RM, Cipriano BH, Raghavan SR, Awad WH and Shields JR 2004 *Polymer* **45** 881.
28. Zanetti M, Camino G and Mulhaupt R 2001 *Polym. Degrad. Stab.* **74** 413.
29. Wang S, Hu Y, Li Z, Wang Z, Zhuang Y, Chen Z and Fan W 2003 *Coll. Polym. Sci.* **281** 951.
30. Marosfoi B, Matko Sz and Marosi PAG 2006 *Curr. Appl. Phys.* **6** 259.
31. Qin H, Zhang S, Zhao C, Hu G and Yang M 2005 *Polymer* **46** 8386.
32. Nazare S, Kandola BK and Horrocks AR 2006 *Polym. Adv. Technol.* **17** 294.
33. Hao X, Gai G, Liu J, Yang Y, Zhang Y and Nan CW 2006 *Mater. Chem. Phys.* **96** 34.
34. Spadaro G, Dispenza C, Alessi S, Tartaglione G and Camino G 2006 *Adv. Polym. Technol.* **25** 109.
35. Zhu J, Uhl FM, Morgan AB and Wilkie CA 2001 *Chem. Mater.* **13** 4649.
36. Weiss A 1981 *Angew. Chem. Intl. Ed.* **20** 850.
37. Giannelis EP 1996 *Adv. Mater.* **8** 29.
38. Fornes TD, Yoon PJ, Keskkula H and Paul DR 2001 *Polymer* **42** 9929.
39. Lan T, Kaviratna PD and Pinnavaia TJ 1995 *Chem. Mater.* **7** 2144.
40. Kim SW, Jo WH, Lee MS, Ko MB and Jho JY 2002 *Polym. J.* **34** 103.
41. Dasari A, Yu Z-Z and Mai Y-W 2005 *Polymer* **46** 5986.
42. Kotsilkova R, Petkova V and Pelovski Y 2001 *J. Therm. Anal. Calorim.* **64** 591.

43. Burnside SD and Giannelis EP 1995 *Chem. Mater.* **7** 1597.
44. Morgan AB and Harris JD 2003 *Polymer* **44** 2313.
45. Xie W, Gao Z, Pan WP, Hunter D, Singh A and Vaia R 2001 *Chem. Mater.* **13** 2979.
46. Greene-Kelly R 1957 In *The Differential Thermal Investigation of Clays* Ed. Mackenzie RC pp. 140 (Mineralogical Society, London).
47. Zhu J, Morgan AB, Lamelas FJ and Wilkie CA. *Chem Mater* 2001; 13: 3774.
48. Weiss A 1981 *Angew. Chem. Intl. Ed.* **20** 850.
49. Kashiwagi T, Grulke E, Hilding J, Groth K, Harris Jr RH, Butler K, Shields JR, Kharchenko S and Douglas J 2004 *Polymer* **45** 4227.
50. Gilman JW, Jackson CL, Morgan AB and Harris Jr RH 2000 *Chem. Mater.* **12** 1866.
51. Sonobe N, Kyotani T and Tomita A 1988 *Carbon* **26** 573.
52. Takahashi S, Taniguchi M, Omote K, Wakabayashi N, Tanaka R and Yamagishi A 2002 *Chem. Phys. Lett.* **352** 213.
53. Reznik D, Olk CH, Neumann DA and Copley JRD 1995 *Phys. Rev. B* **52** 116.
54. Ebbesen TW and Hiura H 1995 *Adv. Mater.* **7** 582.
55. Gyoo PM, Venkataramani S and Kim SC 2006 *J. Appl. Polym. Sci.* **101** 1711.
56. Fina A, Abbenhuis HCL, Tabuani D and Camino G 2006 *Polym. Degrad. Stab.* **91** 2275.
57. Kashiwagi T, Du F, Winey KI, Groth KM, Shield JR, Bellayer SP, Kim H and Douglas JF 2005 *Polymer* **46** 471.

Figure Captions

Figure 1. TEM micrographs showing fine dispersion quality and oriented nature of clay layers at all loadings: A1 ~10 wt.%; A2 ~20 wt.%; and A3 ~30 wt.%. All the micrographs are taken from the cross-sections of injection-molded plates normal to the flow direction as schematically shown.

Figure 2. (a) TGA and (b) DTG plots of neat polyamide 6 (A0) and binary polyamide 6/organoclay nanocomposites at different weight percentages of organoclay (A1 to A3).

Figure 3. Flammability properties of A0 and A1 to A3 evaluated with a cone calorimeter at an incident heat flux of 50 kW/m²: (a) heat release rates and (b) mass loss rates.

Figure 4. Digital photographs of the residues left after combustion test at an incident heat flux of 50 kW/m² for: (a) A1 – polyamide 6/organoclay (90/10); (b) A2 – polyamide 6/organoclay (80/20); and (c) A3 – polyamide 6/organoclay (70/30).

Figure 5. X-ray diffraction patterns taken on the top surfaces of the residues left after the flame test at an incident heat flux of 50 kW/m² for A1 to A3.

Figure 6. SEM micrographs taken at the top (a to c) and bottom (d) surfaces of the residues left after the flame test at an incident heat flux of 50 kW/m² for (a and b) A1; (c) A3; and (d) A2. The white arrows in (a) point to some of the opened floccules.

Figure 7. (a to d) Low magnification TEM micrographs of cross-sections beneath the top surfaces of combustion residues of (a and b) A1; (c) A2; and (d) A3. (e and f) High magnification images of multi-layered silicate-carbonaceous structure in A3. The holey formvar film underneath the sections can also be seen in some cases.

Figure 8. TEM micrograph of the cross-section beneath the middle surface regions of combustion residue of A3 showing large numbers of aggregated structures with voids in between. The holey formvar film underneath the section can also be seen.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8