SUSTAINABLE FLAME RETARDANT NANOCOMPOSITES

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ABSTRACT

This paper examines the current state of research into sustainable flame retardants with the work on nanocomposites highlighted. The motivations to move away from halogen-based flame retardants are discussed and a number of life-cycle-assessments are mentioned which set the stage for a similar LCA study of nanocomposite flame retardant products. Additives, such as hydrotalcite and cellulose nanofibrils, are proposed as components of potential future sustainable flame retardant nanocomposites.

Figure 1. A Pop art sculpture outside the National Arboretum in Washington DC depicting the challenges which our current non-sustainable plastics present to the world.

INTRODUCTION

In the current economic and environmental climate it is more critical than ever to develop the tools and information that enable quantitative evaluation of the sustainability of utilizing nanotechnology in products. Environmental concerns over the potential risks that halogenated chemicals pose have been a reality for decades. This is rooted in the persistence, bioaccumulation and toxicity (PBT) associated with specific brominated organic compounds.[1] To respond to this, the flame retardant research community and others began developing non-halogenated flame retardants. Initial non-halogenated research focused on developing new phosphorus based flame retardants. Numerous publications and patents were issued in this area[2] based on phosphorus, [3, 4, 5, 6, 7, 8, 9] aluminium trihydroxide and magnesium dihydroxide, boron[10], siloxane and silica[11].. A more recent class of flame retardants based on nano-additives was also developed in response to the non-halogen FR issue. This later class of FR additives utilize naturally occurring smectite clays (layered silicates), such as Montmorillonite (Mt), Hectorite (Hc), or Laponite (Lp). Incorporation of clay in polymers has been reported to have as much as a 75% decrease in the peak heat release rate (PHRR), as measured in the cone calorimeter.[12] These materials exhibit enhancements in a variety of physical properties at one tenth the loading required as compared to when micrometer size additives are used.[13] However, in practice, i.e., in the patent and archival journal literature, the publications show that the best advantage is found when the clay FR is combined with another non-halognated FR.

The first studies of polymers combined with layered silicates at the nanoscale to form “nanocomposites” was work by Carter et al.,[14] in 1950, which was followed by *in situ* polymerization of vinyl monomers in the interlayer space of Mt by a series or researchers in the early 1960s.[15],[16],[17],[18] . Most of this early work involved intercalated clay polymer nanocomposites (CPN) comprised of much higher loadings of clay mineral (50% mass fraction) than are used today in nanocomposites (5% mass fraction).

Nanocomposites with lower loadings (1mass fraction % to 10 mass fraction %) characterize the type of materials that are the focus of more recent studies. Examples include those disclosed in initial patents in the 1970’s and mid-1980s from General Motors (GM),[19] Imperial Chemical Industries (ICI)[20] and DuPont.[21] The GM patent primarily claims the use of clay minerals as substitutes for antimony oxides, while the ICI patent teaches the use of “delaminated vermiculite” to impart self-extinguishing and charring properties to expanded polystyrene beads. The DuPont patents also discuss the flame retardant properties of CPN, but only as anti-drip additives to formulations heavily filled with conventional flame retardants. The inventors note an increase in char formation, which they attribute to the polyester. Kamigato et al., at Toyota[22] also filed patents on the *in situ* polymerization of styrene, isoprene, vinyl acetate and caprolactam. Although some of these patents indicate that clays nanocomposites enable self-extinguishing properties, or a V0 rating (self-extinguishing in under 10 s) in the UL94 test (Underwriters Laboratories 1996), or they may pass other large scale fire tests such as the UL 910 (Underwriters Laboratories 2001),[23] no other study of the char forming flame retardant properties of nanocomposites appeared in the literature until the mid-1990s.

Groups at NIST and Cornell both reported that polymer nanocomposites ,with no other flame retardant, reduced the parent polymer’s flammability and enhanced char formation. Giannelis et al.,[24] found self-extinguishing properties for nanocomposites when they were exposed to small open flame tests. Researchers at NIST used cone calorimetry and radiative gasification to show that Mt nanocomposites had enhanced char formation and gave up to 75% lower flammability, as measured by reduction in the peak heat release rate (PHRR) or peak mass loss rate.[25] In most cases, the carbonaceous char yield was limited to (2 to 5) mass fraction %; consequently, the total heat release (THR) was not significantly affected. In addition, ignition times were either minimally or not all improved.. However, the unique character of this new approach to flame retardant polymeric materials was the dual benefit of reduced peak heat release rate and improved physical properties, a combination not usually found with conventional flame retardants. A significant number of papers have since been published on this topic, with many shedding light on the flame retardant mechanism .[26, 27, 28, 29, 30, 31, 32, 33, 34, 35]

DISCUSSION*

 Certain commercial equipment, instruments, materials or companies are identified in this paper in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by NIST. The policy of NIST is to use metric units of measurement in all its publications, and to provide statements of uncertainty for all original measurements. In this document however, data from organizations outside NIST are shown, which may include measurements in non-metric units or measurements without uncertainty statements.

The focus of this paper is to bring to light the need to develop and evaluate sustainable approaches to flame retardancy. In 2008, the Environmental Protection Agency (EPA) invited a number of research groups to present work where nanotechnologies were preventing pollution. The nanocomposite flame retardant area was identified and incorporated into a special session on case studies. While it is reasonable to propose that substituting clay for polybrominated diphenyl ether (PBDEs) flame retardants might reduce pollution and be called sustainable, the fact is that no quantitative study has ever been done to support this assertion. Life-Cycle-Assessment (LCA) methods are the tools of choice for such an analysis. According to a report from a similar conference in 2006, from the Woodrow Wilson International Center for Scholars, only 2 LCAs, which meet the full scope of an LCA as defined in the ISO standards (ISO14040:2006, ISO14044:2006) have been published on nanotechnology based products as of 2005.[36]

A LCA study of nanocomposites used for automotive applications has appeared, but the issue of flame retardancy was not addressed.[37] However, this LCA study did provide an illustration of how one might approach this type of analysis. This LCA was performed by Lloyd and Lave from Carnegie Mellon University, and was motivated by the view within the auto industry that the use of polymeric components, instead of metal components, in body panels will reduce the mass of an automobile and improve the fuel consumption. Whereas improved fuel consumption is one of the main selection criteria for automotive customers, the manufactures must be able to provide this in a cost competitive manner and without any additional environmental consequences. In addition, the authors of the LCA study acknowledged the additional drivers associated with nanotechnology are the potential reduction in the energy and materials needed to manufacture products, “while improving environmental performance and sustainability.” But, they caution that a broad spectrum of issues must be examined to make a responsible assessment, and “it is important not to compromise safety, cost, or other desired attributes.” They estimated potential economic and environmental impacts for the use of clay-polypropylene nanocomposites, or aluminium, instead of steel in light duty vehicle body panels. As the data in Figure 2 show, although the manufacturing costs for the nanocomposite body panel are currently higher, a significant potential benefit of this approach is in reducing energy use and environmental discharges during manufacturing.

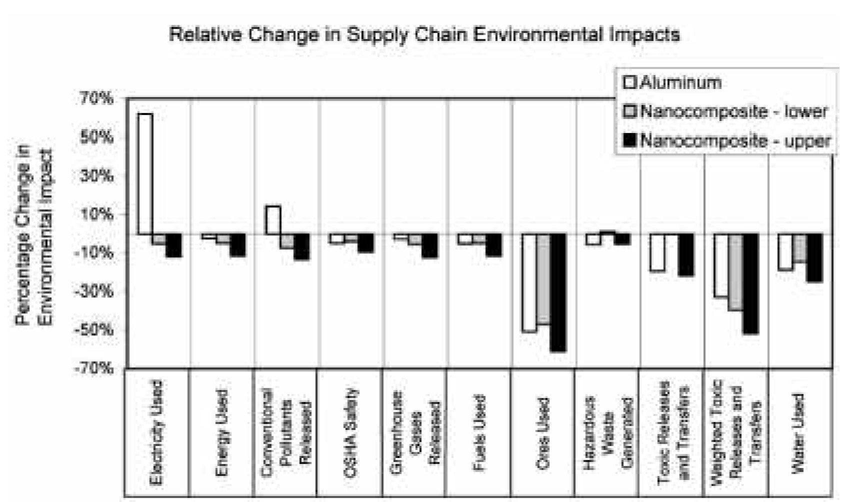

Figure 2. Table from LCA study by Lloyd and Lave[36] showing the higher amount of energy used for aluminium as compared to the range of values expected for energy use during manufacture for the nanocomposite, and the higher pollutants released for aluminium as compared to the range of values expected for that for the nanocomposite.

The authors concluded the use of nanocomposites would increase fuel economy at a low cost, which potentially leads to large economic and environmental benefits, primarily through reduction in the production of CO_2

during the life time of the vehicle. However, since the study was published before the recent world-wide fuel cost crisis they also assert that "U.S. consumers have little interest in greater fuel economy, and so this technology is unlikely to be developed and employed in this application without government intervention." Obviously, changes in the economic situation can radically change the potential that a more sustainable approach will be utilized. The same can be said of how a nanocomposite, or any other new non-halogenated flame retardant products could be approached, i.e., both economic conditions and governmental regulations can be strongly coupled, and can be equally important factors as the environmental realities of the analysis in determining the feasibility of the new approach.

The issues associated with performing a LCA of a product flame retarded using a nanocomposite, or another non-halogenated flame retardant, as compared to a halogen based flame retardant, are somewhat complex. However, the LCA reported by Lloyd and Lave[36] provides an example of how the evaluation of a nanocomposite flame retarded products might be performed.

In addition, several LCAs of various flame retardant products (television sets, wire and cable, and sofas), performed at Swedish National Testing and Research Institute (SP), can also be used to provide insight as to how to structure such an LCA[38]. The unique information that these LCAs offer is the inclusion of the effect of accidental fires on the LCA, something not usually included in most LCAs.[39] In the 2000 SP study of halogenated flame retarded versus non-flame retarded television sets[40] made of high impact polystyrene (HIPS), a similar approach to that taken by Lloyd and Lave was used, i.e., the incorporation of the effect of a different additive on the gasses released into the environment. However, instead of CO_2 emission savings, the SP researchers found *reduced* emissions from incineration of recycled TV sets *with* halogenated flame retardants as compared to those without any flame retardant. Furthermore, they pointed out that since TV sets with halogenated flame retardants had a V0[41] rating (self-extinguishing in 10 s), which "essentially removes the risk of TV fires" the societal cost of using no flame retardant in the TV sets is 165 TV fires per million TVs or 160 deaths and 2000 injuries per year in the European Union. Additional distinctions from the SP study include the fact that the halogenated FR HIPS performed better in ageing and recycling studies than the non-FP HIPS, and the FR in the HIPS did not bloom (phase separate to the surface) during tests.

Nanocomposites have been found to prevent blooming[42], which may reduce environmental release of any additive present in the nanocomposite product. This raises another unique aspect of nanocomposite based FRs. Specifically, there is a lack of environmental health and safety (EH&S) data on nanoparticles, which is required information for for many of the inputs of an LCA. Mechanism of release into the environment over the life of the product, toxicity, effect nanoparticles have on the combustion gasses formed during accidental burning or during incineration, are some of the areas where research is needed so the necessary data can be produced and made available to enable companies to perform meaningful LCAs. This challenge is particularly daunting not only when natural nanoparticles, such as clays, are considered, but when engineered nanoparticles are included. Engineered nanoparticles are man-made, using multiple techniques, and often post processed so the number of different varieties of a given nanoparticle can be huge. Furthermore, since many engineered nanoparticles have only been prepared recently very little is known about their EH&S properties, in addition to the economic feasibility of manufacturing them. This is relevant to the nanocomposite FR approach since in the last several years many nanoparticles have been found to have flame retardant properties, such as, layered double hydroxides (LDH),[43] carbon nanofibers,[44] and carbon nanotubes.[45]

One approach which may simplify developing sustainable FR additives is to utilize nanoparticles where a significant amount of favorable EH&S data is already available. Some of the nanoparticles that may fall into this category include: LDH, and cellulose nanofibrils (see Figure 2). LDH (Aluminum hydroxide magnesium hydroxide carbonate (hydrotalcite)) and cellulose are approved by the US Food and Drug Administration (FDA) for contact food.

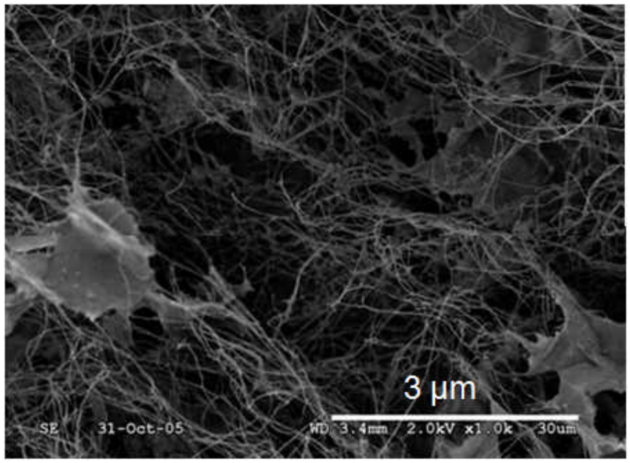

Figure 3. SEM image of dried microfibrilated cellulose prepared from dissolving pulp with enzyme treatment. (Source: Henriksson, Licentiate thesis, KTH, Stockholm, Sweden, 2004).

CONCLUSIONS

In the current economic and environmental climate it is more critical than ever to develop the tools and information to enable quantitative evaluation of the sustainability of utilizing nanotechnology in products. This is true for nanoparticle based flame retardant products as well. However, only a hand full of LCAs has appeared that address some of the issues which must be included. A lack of EH&S data on many nanoparticles will continue to hamper the effort to perform complete LCAs. This suggests that the international research community must gather the necessary EH&S data, while at the same time investigate approaches utilizing materials currently know to have favourable EH&S attributes if nanotechnology is going to actually be successfully used in commercial products.

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