

特约专栏

Flame Retardant Design for the Future

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Abstract: Flame retardants have been around for thousands of years, but only in the 20th and 21st century has the science advanced to cover several new chemical classes of flame retardants. Currently there are seven broad classes of flame retardants that are halogen-based, phosphorus-based, intumescent systems, mineral fillers, nitrogen-based, inorganic-based, polymer nanocomposites etc. However, the flame retardants in use today were focused solely on providing fire protection, and were not designed with consideration for how they would be used over long periods of time or how they will be disposed of at the end of their lifetime. With new environmental demands and new potential fire risk scenarios, it will be possible that the seven classes of existing flame retardant chemistry are not sufficient for the future and new efforts in chemical exploration are needed, for example silicon-based flame retardants, transition metal catalysis flame retardants etc. In this paper, what the flame retardants of the future must consider in their design reflecting current environmental concerns and new fire risk scenarios will be discussed. Possible chemistries which show potential for future flame retardants will also be discussed. Finally, the future five principles proposed can help ensure that new flame retardants have little to no environmental impact while maintaining the fire safety our civilization needs.

Key words: flame retardant; flame retardant design; automotive plastics; composite; environmental protection

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未来阻燃剂的设计

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摘要: 阻燃剂已经存在数千年了, 但最近 200 年才发展出一些新化学结构的阻燃剂。目前使用的阻燃剂主要包括 7 种类型, 它们是卤素基、磷基、膨胀体系、矿物填料、氮基、无机物基、高分子纳米复合体系等。现在, 阻燃剂的使用仅仅专注于提供消防, 也没有考虑如何延长它们的使用寿命, 没有考虑如何处理阻燃剂使用结束后的后处理问题。随着将来对环境保护新要求的提升, 以及新型起火原因的出现, 现有的几类阻燃剂显然是不够的, 必须努力开发新型阻燃剂, 例如硅基阻燃剂、过度金属催化作用阻燃剂等。讨论了未来阻燃剂的设计必须考虑的环境保护和新的起火原因等问题, 以及与未来新型阻燃剂有关的潜在化学问题。最后提出了在新型阻燃剂研究过程中, 减少环境污染、保持防火安全的原则。

关键词: 阻燃剂; 阻燃设计; 汽车塑料; 复合材料; 环境保护

1 Flame Retardants of Today

Flame retardants have been used by humanity for centuries, with some of the earliest recorded examples being listed as far back as 850 BC for flame retarding wood. Flame retardants are an ancient and proven concept, but these chemicals have been updated as fire risk changes over time and new chemistry is discovered. Even then, the flame retardant technology used today can be quite old depending upon the specific chemistry. Halogenated flame retardants for example have been with us since the 1930s, and organophosphorus chemistry for flame retardancy had its beginning in the

1950s. This does not mean that these chemistries are too old to use, but rather they have been with us for some time and are proven to work. At present, they may be in need of updating.

Currently there are seven broad classes of flame retardants that the material scientist can choose from for fire safety needs. All of them are commercial, but only five of them are in wide-spread use today. The seven broad classes of flame retardants are halogen-based, phosphorus-based, intumescent systems, mineral fillers, nitrogen-based, inorganic-based, polymer nanocomposites, respectively.

Each of these classes will be discussed briefly in regards to their current use. Comprehensive details on these chemistries, how they work, and how they are used can be found in review papers and books that have been published recently^[1-4]. While I suspect the readers of this article are quite familiar with these flame retardants, the purpose of

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summarizing them in this article is to make the readers aware of what the current regulatory and commercial use is for each flame retardant. Discussing this background will be important for explaining the future of flame retardant chemistry later in the paper.

1.1 Halogen-based

Halogen-based flame retardants in use today are based upon organochlorine or organobromine chemistry. Brominated flame retardants are most common due to their cost-efficiency in chemical synthesis and the fact that they can be useful in a wide range of polymers for an equally wide range of fire safety tests. These flame retardants are available commercially world-wide, but usually are produced by companies which have access to brine (salt water) feedstocks where the halogen can be easily harvested and used.

Halogen-based chemicals have been under regulatory scrutiny for the past 30 years, with several new regulations banning their use in the US, Canada, and the European Union being published in the past few years^[5]. As some of the chemicals have been around for decades, there are concerns about the persistence, bioaccumulation, and toxicity (PBT) of these chemicals as they continue to be found in the environment^[6-7]. The problem appears to be based upon the fact that most brominated flame retardants are small molecules which can be released from a plastic over time. The newest brominated flame retardants being commercialized in the past 1 ~ 2 years are all polymeric, which is believed to be an acceptable solution to the PBT issues presented by small molecule flame retardants. Polymeric structures are less likely to migrate from a plastic once blended in, and also tend to be less bioaccumulated. These new polymeric additives are currently being produced and evaluated for flame retardant effectiveness and environmental issues.

1.2 Phosphorus-based

This class of flame retardants is composed of both inorganic and organophosphorus compounds. Inorganic phosphorus flame retardants include ammonium phosphate salts and red phosphorus. Organophosphorus compounds include phosphates and phosphonates, as well as some hybrid metal salts of phosphonates which have shown good effectiveness in the past decade. Phosphorus compounds are not as effective in a wide range of polymers as halogen-based flame retardants, but they continue to be advanced to work in more and more plastics. Like halogen-based flame retardants, they are also world-wide available from a wide range of companies, but tend to be more expensive. This cost difference comes from the chemical feedstocks for the flame retardant. In the case of halogen-based, brine is readily available and inexpensive in some countries, while phosphorus feedstocks, usually phosphate minerals, are not commonly found. Further, phosphate minerals are in demand for agricultural needs, and market conditions result in a higher base cost for this class of flame retardants.

Phosphorus-based flame retardants are under some regulatory scrutiny as well but not to the same degree as halogen-based materials. When phosphorus-based flame retardants have been banned, it has been due to specific chemical structures found to be a problem^[5]. It appears that due to the scrutiny shown halogen-based flame retardants that phosphor-

us-based flame retardants will also face a similar level of regulatory review in the future, but that is not clear at this time.

1.3 Intumescent systems

Intumescent flame retardants are a potent class of char-forming flame retardants, and as such have been greatly studied for fire protection needs^[8]. These flame retardants react in response to heat by forming a protective carbon foam on the surface of a material exposed to flame. They can be used as a coating applied to a material surface (like paint on steel) or can be put directly into polymers. Their main limitation is that they activate at temperatures below 200 ~ 240 °C, preventing their use in polymers with high processing temperatures.

This class of flame retardants has not been looked at for regulatory issues as they are systems composed of multiple chemicals. Therefore, it would be individual chemicals in the intumescent system which would be deselected from use, not the entire intumescent system. Since there are many potential intumescent components to choose from, it seems unlikely that this broad class of flame retardants is in any danger of regulatory deselection at this time as the chemist can choose from the other chemicals to make a successful intumescent system. Further, since intumescent materials provide robust fire protection, it seems that this class of materials will continue to be highly studied and used for polymeric material flame retardancy. We can expect that more possible chemicals can be chosen and will become available for commercial use even as some get deselected.

1.4 Mineral fillers

Mineral fillers are composed of inorganic hydroxides and carbonates which endothermically decompose under fire conditions which cool the burning plastic and release non-flammable gases such as water and carbon dioxide. Typical examples include aluminum and magnesium hydroxides, as well as calcium and magnesium carbonates. As the name implies, these flame retardants are typically mined from mineral deposits and used as bulk fillers in plastics to provide fire protection. Some synthetic grades of mineral fillers exist, especially for magnesium hydroxide. These flame retardants are of great utility in wire and cable formulations because they help lower heat release and smoke at the same time. However, they must be used in high loading levels in materials (>50 %, mass fraction) to impart effective flame retardancy. Therefore they typically are used only in flexible polyolefins and other elastomeric materials which can still have good mechanical properties after the fillers have been added. Otherwise this class of flame retardant is used in combination with other flame retardants to help lower smoke release or delay time to ignition.

Mineral fillers have a good environmental profile when considering how they interact with the environment, and therefore, they are under no regulatory scrutiny at this time. However, the total environmental impact of these additives when they are produced (either by mining or hydrothermal synthesis) has not been studied. These materials have excellent end-of-life properties, but they may have a big carbon footprint when first manufactured. Some more study of environmental impact should be made on these materials, and if

they are found to be increasingly benign for the environment, then more should be done with them.

1.5 Nitrogen-based

This class of flame retardants is used mostly in combination with other flame retardants such as intumescent flame retardants and polyurethane formulations, but sometimes they can be used alone in a few other polymers. Melamine is a good example in which it can be used by itself in polyurethanes, but more often it is combined with other chemicals to form intumescent systems. It is often used as a salt, with examples of melamine cyanurate, melamine phosphate, and melamine polyphosphate being most common. Other nitrogen-based flame retardants include the amine-oxide class of flame retardants, also known as NOR-HALS chemistry, which stands for N-Oxide Hindered Amine Light Stabilizers. These flame retardants were originally used as UV stabilizers, however, when used in polypropylene they cause the polymer to drip away from a flame thus allowing it to pass a flame retardant test. However, NOR-HALS chemistry only affects melt viscosity in flame tests and actually causes heat release to increase for polypropylene matrix. This is due to the fact that it causes the polymer to depolymerize rapidly (increase in mass loss rate) and drip away from the flame. In the event the PP + NOR-HALS system cannot drip away from the flame (the flame is too large) it will burn hotter and faster, thus causing problems in some fire risk scenarios. Therefore, NOR-HALS chemistry should be used with care in select fire risk scenarios; it is not appropriate for use in many other applications.

Other than regulation of Melamine in food supplies, the nitrogen-based flame retardants do not have any regulatory issues for polymer use at this time. Because these flame retardants are not used in high volume, it does not appear that they will be under any level of scrutiny until the other larger volume flame retardants are studied first.

1.6 Inorganic-based

Inorganic flame retardants are a large group of compounds composed of metal or nonmetallic oxides which provide some specific flame retardant benefit in selected systems, but in general are only useful in niche applications or very specific polymers. Silicon oxides, boron oxides, and transition metal oxides are all good examples of inorganic-based flame retardants. Boron oxides for example have great synergists for many flame retardants in many polymers, and silicon oxides tend to help with melt flow issues and create thermally stable chars, but by themselves these two oxides have limited utility. Metal oxides are quite interesting in that they have the potential for unique char formation chemistries, but more study is needed on these materials^[9-10].

Right now, this class of flame retardants is not under any regulatory scrutiny except in cases where metal regulations are present. For example, the Reduction of Hazardous Substances (RoHS)^[11] and Waste Electrical and Electronic Equipment (WEEE)^[12] protocols in place today often require that some transition metals should be removed from use, with some notable examples including Ni, Zn, Cr, Hg, Cd, and Pb. This means that oxides based upon these metals, even if found to be effective flame retardants, would likely not be permitted for use.

1.7 Polymer nanocomposites

Polymer nanocomposite technology is the newest class of flame retardant materials, with the discovery in the early 90s that these materials yield dramatic reductions in peak heat release^[13-15], but are unable to provide regulatory flame retardancy by themselves^[16]. Nanocomposites are of great interest because they bring a balance of properties to the final system-enhanced mechanical properties while still maintaining flame retardant performance. This is noteworthy as most flame retardants decrease mechanical properties once flame retardancy is achieved. Therefore it seems that nanocomposites should have a bright future and build a foundation for new flame retardant chemistries. Specifically they enable flame retardant materials with enhanced properties and lower loadings of flame retardant chemicals.

Even with these attractive features, nanocomposites have not advanced into everyday use. Nanotechnology is under regulatory scrutiny due to unknowns about how the environment or human workers will react to the nanoparticle exposure^[17-18]. Further, despite almost 2 decades of nanocomposite research, there have been very few commercial nanocomposites produced to date. The reasons for this lack of commercialization are not clear at this time. It could be due to the regulatory uncertainty about nanoparticles, or it could be due to the perception that nanocomposites do not work effectively as flame retardants since many companies and researchers found that a reduction in heat release alone is not enough to achieve a passing result in a regulatory test. Whatever the reason, the huge volume of successful literature showing that polymer nanocomposites can bring flame retardant performance while maintaining mechanical properties suggests that this class of materials has potential yet untapped by industry, and hopefully we will see some reinvestment in this technology.

While these seven classes of flame retardants are likely to continue to be used for some time, recent events suggest that there is a need to look at flame retardant design again. This time, design criteria must consider not only solving a fire protection need, but also the lifetime and environmental impact of the flame retardant.

2 Flame retardants for addressing environmental issues

In general, the Western World (North America, Western Europe) has a phobia of chemicals in general, perhaps rightfully due to the significant environmental events occurred in the past. Two notable events that instilled this chemical phobia were the Great Smog of 1952 in London, United Kingdom^[19], and the Cuyahoga River catching on fire in 1969 near Cleveland, Ohio, USA^[20]. Water catching on fire due to incorrect chemical disposal and numerous deaths due to emissions will capture the public's attention. As our society has progressed, we have made great strides and improvements towards balancing technology and environmental protection in response to events like the ones above, but interestingly the detection technology for pollutants has far outstripped the advances in environmentally benign plastics and

chemical development. We can now detect picograms of chemicals in the environment, and due to this ability, we are discovering new scientific phenomena, specifically that some chemicals used as flame retardants can be quite widespread. The detection is also finding that in some cases, specific flame retardants can be persistent, bio-accumulative, and toxic (PBT), which has led to calls for their deselection from use. These PBT effects, combined with extensive regulatory schemes in the EU to address electronic wastes and register chemicals, has led to the regulatory banning of some brominated flame retardants, with chemical phobia starting to roll over to give all flame retardants a bad name. In May of 2012, a wide-ranging article was published by the Chicago Tribune in the US^[21], and from this it appears that an entire chemical class of flame retardants may be up for deselection, as flame retardants appear to have lost both political battles and in the court of public opinion.

A lot of scrutiny has been given to halogenated flame retardants. The EU has been investigating the PBT issues of this class of chemicals for quite some time now, and over the past 20 years the issue has been discussed and debated in the US and Canada as well. In the past years, though, the most amount of change has occurred; flame retardants that have been in use for decades are no longer going to be allowed for use by the end of 2013 and 2014, depending upon the exceptions allowed by national regulators. Even with some regulatory exceptions, the extended use time for these flame retardants will likely be for one or two years at most. Two brominated flame retardants being deselected are brominated diphenyl ethers and hexabromocyclododecane (HBCD). In 2006, pentabromodiphenyl ether and octabromodiphenyl ether were voluntarily withdrawn by the last major manufacturer of these chemicals (Great Lakes Chemical Corporation, Part of Chemtura) and regulated heavily in the US by the Environmental Protection Agency (EPA), thus ensuring that there would be no new major use of these chemicals^[22]. In 2012, all brominated diphenyl ethers have been voluntarily withdrawn by the main flame retardant manufacturers and also placed under EPA regulatory control for phase-out and banning of import or use in the US^[23]. These rules effectively eliminate the use of these flame retardant additives in any new product sold in the US, but this flame retardant will still effectively be in use in whatever existing products still contain that flame retardant. The other brominated flame retardant being deselected, HBCD, which is used mostly for expanded polystyrene foam insulation, has also been selected for phase out in the US^[24] and Canada^[25]. So in just one year, two widely used flame retardants have been voluntarily withdrawn by the manufacturers and also put under regulatory bans. This is quite a change for flame retardant molecules which have been under scrutiny for decades at this point.

The path forward for flame retardants of the future is to consider their environmental impact early in the design of the chemistry. This is easier said than done since many of the environmental chemical models which predict PBT properties are still weak in predictive accuracy. Therefore the following principles may need serving as an initial hypothesis for future flame retardant design. Specifically, these proposed concepts may need to be studied by flame retardant chemists to see if

they are valid ways of addressing environmental impacts until such time as the PBT models are better at predicting environmental impact. The reliance on the models is important here, as the alternative is to do the full range of environmental tests for each and every chemical made before commercial use, which can be a R&D cost well into the millions of US \$, and would be a cost that would effectively slow technological development to a near stop. However, the inability of the models to predict performance is not an excuse to ignore environmental impact in flame retardant design, and so we must start somewhere. Based upon known facts about flame retardants in the environment today and how they likely got there as well as their PBT impact, we can propose the following guiding principles for new flame retardant design.

(1) Flame retardant chemists should partner with environmental scientists to understand chemical transport mechanisms in the environment. By gaining the understanding of what chemical groups promote rapid transport of chemicals through the food chain or into soil/water streams, the chemist can try to avoid certain chemical groups which may cause environmental damage.

(2) Use of reactive flame retardants over non-reactive flame retardants is to be encouraged. By having the flame retardant react into the polymer during production, there is less likelihood of the flame retardant coming out of the polymer and getting into the environment during its lifetime.

(3) Use of polymeric flame retardants over small molecule flame retardants. Large molecular weight polymers have been found to be less accessible by living organisms and so have an automatically lower PBT profile when compared to small molecules. Therefore polymeric flame retardants should be a starting position for new chemistries if possible.

(4) Simple test protocols for flame retardant leachability alongside small-scale flammability tests. Flame retardant chemists should look to simple extraction, weatherability, and environmental exposure tests to see how their flame retardant reacts in a polymer over time. While it may have great flame retardant potency within days of synthesis in the lab, how does it hold up over time? By making this a new standard test alongside thermal analysis, chemical analysis, and flammability tests done today, the scientist is likely to have a better idea about the durability of their new flame retardant, and, how likely it is to leave the polymer over time. This can give some common-sense insight into PBT issues. If the material easily migrates from the polymer and does not degrade rapidly, it may be quite persistent and from there, some simple bioaccumulation and toxicity tests can be run to see if this is an issue or not, and if so, then the scientist can quickly go back to chemical redesign. Likewise, if the material degrades too quickly, it may not be appropriate for fire safety use in a durable good, but might be useful in a disposable good. Understanding chemical persistence early in the research project will save time and R&D resources later.

(5) Consideration of product lifecycle in flame retardant design. Along with item #4, another practical test to run in new experimental work would be to think about how the product containing the new flame retardant will be dealt with at the end of its lifetime. Would it be incinerated, recycled, or let to biodegrade in the environment? If incineration, does

the chemistry have a potential to form species of emission concern which cannot be dealt with easily through high temperature incineration (example, NO_x , SO_x)? If recycled, how does the flame retardant hold up in the plastic after multiple regrind & recycle events? If biodegradable (the flame retardant is believed to be environmentally benign), how does the flame retardant product hold up via standard composting techniques? Does the chemical degrade safely or does it react with the polymer decomposition products to create something of concern?

These five proposed experimental guidelines are a starting point to consider and readers are encouraged to come up with their own experimental guidance should they have data suggesting a more important experimental design parameter exists when compared to the ones listed above. Regardless of the guidelines or experimental protocols chosen, flame retardant chemists must start considering environmental impact in their product design. Failure to do so will result in the inability to come up with new commercial products, or worse, a gap in flame retardant solutions available for use when all existing flame retardants have been banned from use due to real or perceived PBT issues. Finally, we must learn from the mistakes of the past. Failure to learn from these mistakes will result in us repeating them, and we do not need another London Smog event, or another Cuyahoga River Fire event either. For chemistry to regain its trust of the citizenry, we must embrace environmental needs in our research to design for a sustainable and safe future for ourselves and future generations. Further, we must not only have environmentally friendly flame retardants, we must also consider new fire risks that the new flame retardants would protect against.

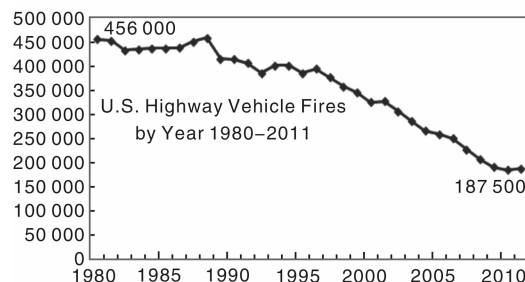
3 Flame retardants for automotive and composite fire safety

Flame retardants must be designed to meet specific fire tests which address specific fire risk scenarios. Therefore flame retardants of the future may need considering not only environmental needs, but also new fire risks. Listed below are some potential new fire risk scenarios which may result in new tests and therefore new flame retardant chemistries.

3.1 Automotive plastics

The fire safety standard that regulates plastics for automotive applications is Federal Motor Vehicle Safety Standard # 302 (FMVSS 302), which is a simple horizontal burn flame spread test. This test was created in the 1970s to simulate cigarette ignition scenarios and has not been significantly changed since its creation. In the 1970s, a typical car would have, at most, 30 kg of plastic throughout the entire vehicle, all of which would have had to pass this simple test. Today there is much more plastic (150 kg or more) present in a car, and this plastic serves a valuable purpose in mitigating corrosion/rust damage and improving fuel efficiency (light-weight materials-better miles per gallon performance). This increased level of plastic also presents a significant fire risk; in the event of a post-crash fire or other accidental ignition more intense than a cigarette, the plastic is not flame-retarded to a level that allows enough time to escape the burning

vehicle^[26]. In light of this information, there have been several calls to change the standard over the past few years, with only minor success. So automotive plastic fire safety is an unmet need, but until a new fire safety standard is decided upon, it is hard to know what type of flame retardant performance will be required. Today, most plastics with no additional flame retardant at all will pass the FVMSS 302 test. The test of tomorrow will be based upon a fire risk scenario which is to be determined. If we look at the fire losses for automobiles today in the US, it appears that there may not be an immediate problem (Figure 1), but the situation requires vigilance in case the fire losses begin to increase in the near future. However, as automotive sales and use increase in China, there may be more of a need for automotive fire safety there than in the US. As of January 2013, production of cars in China was set to be more than that of the European Union, and further, most of those cars appear to be for domestic Chinese use, not export^[27]. Depending upon how cars are driven in China and the potential fire risk scenarios, Chinese specific flame retardant regulations are required, but country specific regulations typically fail due to the global nature of automotive manufacturing. Specifically, it is rare that an industry will tailor materials for just one market given the large R&D cost associated with doing so. Still, there is the potential for new flame retardants in automotive plastics that material scientists should look into.



Source: Fire Loss in the United States during 2011, Michael J. Karter, Jr., NFPA, September 2012 and previous reports in the series.

Fig. 1 Car loss fire statistics from NFPA ([http://www.nfpa.org/itemDetail.asp?categoryID=953&itemID=29658&URL=Research/Fire % 20statistics/The% 20U. S. % 20fire% 20problem&cookie_ test = 1](http://www.nfpa.org/itemDetail.asp?categoryID=953&itemID=29658&URL=Research/Fire%20statistics/The%20U.S.%20fire%20problem&cookie_test=1))

Complicating this situation further is the fact that automobile fire risk scenarios are in flux as new propulsion technology comes on line. The fire risk from a tank of gasoline igniting in a crash event is more different than the fire risk observed with an electric car, in which electrical short circuit or battery explosion may be the issue. The battery explosion issue from lithium ion batteries, however, may be resolved if other battery technology such as the lithium-air battery becomes commercial in the coming decade. Cars powered with natural gas or hydrogen have more of an explosion hazard than fire hazard, and fuel cells present both flame spread (from liquid fuel) and explosion risks. All of these points to a significant unmet need for fire safe materials in automobiles, but until the fire risk scenarios can be positively identified and regulators can design tests to meet those scenarios, it will be hard to see how this need will be met in the future.

If the goal of flame retardancy to meet the above topic is to give more time to escape, then very likely the flame retardants will need to reduce flame spread and heat release rate at the same time. Low smoke and toxicity may also be needed to meet new regulations, and so char forming flame retardants and flame retardants which lower heat release while lowering smoke may be required. However, if the fire risk scenario is one requiring protection from blast protection (from battery explosions), then fast-acting intumescent and/or blast containment chambers may be needed rather than flame retarding more of the plastic in the electric car. In the future we are likely to see a range of fire scenarios-electric cars, gasoline cars, and alternative fuel (methane, H_2 , fuel cell) cars, and therefore multiple solutions may be required.

3.2 Structural composite fires

Fiber reinforced polymer composites are increasingly being used to replace metal to gain fuel savings (train, aircraft, buses, ships) as well as to achieve improved durability in applications where metals are prone to rust or corrosion damage. The improvement in fuel efficiency and material durability are well worth the price of the composite, but, fire protection of fiber reinforced composites continues to be a challenge, especially when the composites are used in structural (load-bearing) applications. A polymer composite can structurally fail well before it ignites, and will begin to soften and deflect once the glass transition temperature (T_g) is reached. Therefore fire protection of polymer composites must consider flame retardancy of the polymer itself and fire protection barriers which prevent the composite from reaching T_g . This requires new flame retardant approaches to make fire protection in the outer barriers of the composite, and also to utilize flame retardants increasing T_g .

Today intumescent flame retardants are used to protect steel from temperature increase that would cause them to soften and fail, and it makes sense to consider using intumescent coatings for composites. Some work has been done on the use of co-polymerized intumescent coatings for composites, and the results suggest this approach has great potential applications^[28-30]. Intumescent paints could also be applied to composites, as well as infrared reflecting mirrors^[31], but additional flame retardants may be needed under these coatings. Flame retardants which provide thermal insulation and/or provide endothermic cooling for the polymer would be appropriate chemistries to consider as for in future flame retardants for composites. Finally, some sort of structural reinforcement may be needed so that when the polymer softens, there is a thermally resistant structure in place to help carry load until the flame retardant can activate or until the flames/fire can be extinguished. It is not clear what this secondary structural reinforcement would be made out of, but this may be a role for polymer/metal/ceramic hybrid composites to fill.

4 Possible new flame retardant chemistries

With new environmental demands and new potential fire risk scenarios, it will be possible that the seven classes of ex-

isting flame retardant chemistry are not sufficient for the future and new efforts in chemical exploration are needed. Listed below are some chemistries which have showed potential over the past few years and may be worth additional study in the future.

4.1 Silicon-based flame retardants

Not including polymer nanocomposites, there have been some interesting reports on silicon based flame retardants which suggest there may be more roles for this chemistry in the future. Silicas have been found to reduce mass loss rate and form glassy chars in select systems^[32-34], while silicones also seem to have effectiveness at producing glassy surface chars which prevent further thermal damage^[35-38]. There have been also some reports that micron-thin plasma deposited silicon oxide barriers on the surface of a plastic will yield delays of time to ignition^[39]. Forming silicon oxide surface chars, or any other glassy based ceramic, should yield superior fire protection as these ceramics tend to be thermally insulating and cannot be burned away compared to carbon-based chars. The trick to getting them to work is having the silicon forming compounds be already on the surface of the part, having them quickly migrate to the surface early in the burning process, or having them part of the polymer chemistry such that as the polymer burns, the silicon-based glassy char is formed immediately. Some possible concepts to achieve this include: ① low melting glass precursor additives: silica + borate + phosphate combinations; ② preceramic resin chemistry incorporated into polymer backbones; ③ silicone polymers copolymerized or blended with commodity polymers.

Silicon based chemistry appears to be fairly environmentally benign, although there are some concerns with nanoparticle silicas that need to be addressed^[40-41]. Still, silicon based flame retardants look to be a useful system to study in the future.

4.2 Transition metal catalysis

The d-elements, occupied a large portion of the periodic table, have not been extensively studied for flame retardant performance. There have been some reports on transition metals enabling char formation and heat release reduction^[42], but no systematic study of these elements for flame retardancy has been undertaken so far. What makes transition metals attractive for flame retardancy is that with the right ligand chemistry, these metals may be able to quickly form C-C bonds during burning, thus helping convert flammable polymers into thermally stable carbon char. Because transition metal flame retardants capable of this bond formation are likely to be catalytic, they could enable the creation of flame retardant materials which have a low loading of flame retardants, and therefore they have better mechanical properties and may be more easily recyclable. However, because there has been very little study on these flame retardants to date, it is hard to say if this potential is real or not. Still, with a wealth of transition metal chemistry available for elevated temperature bond formation, metals look to be a possible flame retardant of the future. Some possible future solutions worth investigating would be:

- Using metal oxides known to catalyze aromatic bond

formation in intumescent formulations (for better carbon char thermal durability).

- Incorporating monomers into polymers where the char formation metal catalyst is connected as a pendant group.

- Polymeric ligands containing transition metal catalysts which can be melt-compounded into other polymers.

Returning to the environmental issues associated with flame retardants, some metals known to be highly toxic (Ni, Cr, Cd, Hg, Os, etc.) should be avoided for future research considerations.

5 Conclusions

The current situation for flame retardants is one of great change, with several older flame retardants being deselected from use due to PBT concerns. Indeed, flame retardants as a class of materials are under a lot of regulatory scrutiny, although some chemistries appear to have better environmental profiles than others. Because of the environmental issues, it is clear that flame retardant chemists need to adapt new approaches to developing flame retardants, including:

- (1) Partnership with environmental scientists in flame retardant chemistry design.

- (2) Focusing first on reactive flame retardants which can be incorporated directly into the polymer structure.

- (3) Use of polymeric flame retardants over small molecule flame retardants.

- (4) Screening for flame retardant leachability and durability early in flame retardant development.

- (5) Consideration of product lifecycle in flame retardant design.

These future five principles should help ensure that new flame retardants have little to no environmental impact while maintaining the fire safety our civilization needs. However, these principles may not be enough, and the flame retardant chemist should pay attention to changing fire risk scenarios as well as new chemistries to be successful in the future. Predicting the future is an impossible activity, but we can project a possible path to follow in the future by learning from the knowledge of today, and the mistakes of the past. We know that environmental pollution is a problem, and we know that some flame retardants, even if successful at preventing fires, do have other problems that they bring. Rather than ignore the problems, let us learn from them and come up with something better. What is proposed in this paper is a place to start based upon what we know about flame retardants and their environmental issues today, and new chemistries which likely will have promise in the future. It is the hope of the author that this paper is of use to the reader, and may serve as a useful guide for future research.

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浙大造出世界最轻固体材料

浙大高分子系高超教授的课题组制造出一种超轻物质，取名“碳海绵”。它是目前世界上已知的最轻固体材料。这一成果被权威科学杂志《自然》在“研究要闻”栏目中重点配图评论(2013年2月28日的第494期404页)。相关论文2月18日在线发表在材料科学界权威的学术杂志《先进材料》(Advanced Materials)上。

高超教授说，“碳海绵”是一种气凝胶——世界上最轻的一类物质，它的内部有很多孔隙，充满空气。

2011年，美国科学家合作制造了一种镍构成的气凝胶，密度为 0.9 mg/cm^3 ，是当时最轻的固体材料。把这种材料放在蒲公英花朵上，蒲公英茸毛几乎没变形。

高超课题组这些年一直从事石墨烯宏观材料的研发。他们用石墨烯制造出了气凝胶——“碳海绵”。“碳海绵”每立方厘米重 0.16 mg ，比氢气还要轻，约是同体积大小氢气重量的两倍。从目前公开的报道看，“碳海绵”是世界上最轻的固体。

在浙大实验室，有不少大小不等的“碳海绵”，大的像网球，小的像酒瓶塞，灰不溜秋，摸上去很有弹性。

高教授说，“碳海绵”可任意调节形状，弹性也很好，被压缩80%后仍可恢复原状。它对有机溶剂有超快、超高的吸附力，是已被报道的吸油力最强的材料。现有吸油产品一般只能吸自身质量10倍左右的液体，而“碳海绵”能吸收250倍左右，最高可达900倍，而且只吸油不吸水。

“碳海绵”这一特性可用来处理海上原油泄漏事件——把“碳海绵”撒在海面上，就能把漏油迅速吸进来，因为有弹性，吸进的油又挤出来回收，碳海绵也可以重新使用。另外，“碳海绵”还可能成为理想的储能保温材料、催化剂载体及高效复合材料，有广阔前景。

(来源：人民网)