Volume 1, SPRING 2025

Polymer Modifiers & Additives News

A Publication of Polymer Modifiers and Additives Division (PMAD) of Society of Plastics Engineers

TABLE OF CONTENTS

Chairman Message

Dear SPE PMAD Members,

I hope this message finds you well. As we navigate through these challenging times marked by economic instability, I want to extend my heartfelt gratitude for your unwavering dedication and resilience. Our division has always been a beacon of outreach and collaboration, and it is your commitment that continues to drive us forward.

The current economic climate presents significant challenges, but it also offers opportunities for growth and adaptation. We are actively monitoring our investment accounts that support various scholarships we offer. Our focus is on maintaining financial stability while continuing to support our members and their professional development.

In these times, expanding our membership base is crucial. We are launching several initiatives aimed at attracting new members and retaining existing ones. These include enhanced networking opportunities, professional development programs, and exclusive access to industry insights. Your participation and advocacy are vital to these efforts, and I encourage you to share the benefits of PMAD membership within your professional circles.

Education and continuous learning are at the heart of our mission. We are proud to announce the expansion of our scholarships to support members in their pursuit of advanced studies and professional certifications. These scholarships are designed to alleviate financial burdens and empower our members to achieve their career goals. Details on application processes and eligibility criteria will be shared soon.

In closing, I want to thank each of you for your contributions to the PMAD division. Together, we will overcome these challenges and emerge stronger. Your dedication and support are the pillars of our success. Please feel free to reach me directly at Anshuman.shrivastava@geon.com Counting on your enhanced participation and ideas.

Sincerely,
Anshuman

Upcoming SPE Events

Plastics in Composites and Lightweighting

Monday, June 2 — Wednesday, June 4, 2025
Online

Automotive Composites Conf. & Exhibition

Wednesday, Sep 3—Friday, Sep 5, 2025
Novi, Michigan

2025 SPE Annual Blow Molding Conf.

Monday, Sep 8 – Wednesday, Sep 10, 2025
Sheraton Station Square Hotel, Pittsburgh, PA

SPE Color & Appearance Conf. (CAD)

Monday, Sep 15— Wednesday, Sep 17, 2025
Cleveland, OH

SPE TPO 2025 Automotive Conf.

Monday, Sep 29– Wednesday, Oct 1, 2025
Marriott Hotel, Troy, MI

SPE FOAM 2025

Tuesday, Sep 30 — Friday, Oct 3, 2025
Rochester, NY

2025 International Polyolefins Conference—Celebrating the 50th Year!

IPOC 2025 Recap

As the largest polymer conference in the world that is dedicated to polyolefins, the International Polyolefins Conference (IPOC) has gone through its 50th year. This year, the conference had nearly 900 people from all around the globe who participated either in-person or virtually. There are 63 exhibitors and 15 sponsors this year as well.

Conference technical program included almost 130 reviewed presentations, Sunday afternoon tutorials, 2 networking socials and five plenary lectures. As a tradition, there was a student poster competition hosted during the conference as well.

This year, PMAD continued the strong presence with four additive session added to this year's program, moderated by Dr. Hayder Zahalka. It brought up nearly 25 presentations focused on advances in PFAS processing aid replacement, sustainable additives, enhanced performance, and mechanical recycling.

Several new products were launched: 1) Adeka Chemical of Japan introduced a new and novel clarifier for Polypropylene; 2)Daikin of Japan introduced a new and novel PFAS-Free PPA; 3)BP Polymers introduced a new barrier technology 4)Fine Organics of India introduced a specialty "green" slip additive for Polyolefins. The 2026 IPOC conference will again take place at the Galveston Convention Center on February 23-27.

Selected Paper Abstracts

High Performing Fluoropolymer-Free PPA's in a Post-Fluoropolymer World — *Kazuki Sakami, Daikin's Compounds and Additives Business*

Traditional fluoropolymer polymer processing aids (PPA's) have been widely used for many years in polyolefin polymer compositions in food and non-food contact cast, shrink, and blown film applications. This year Daikin commercialized a non-fluorine, silicone-free polymer processing aid (PPA) with equivalent performance to its fluorine-based predecessors that effectively and economically eliminates melt fracture and die lip buildup, and reduces pressure and load, providing desired levels of production efficiency. This presentation provides performance and other key data on Daikin's newly commercialized alternative PPA product, DAHC-101, in comparison to fluoropolymer-based polymer PPA's

Revolutionizing Transparency of Polypropylene: A Novel Clarifier for High-Performance PP Applications
— Shinichi Ishikawa, ADEKA Corporation Polymer Additives

ADEKA/AMFINE present an innovative clarifier that dramatically enhances the transparency of polypropylene (PP) through advanced crystalline refinement resulting in unparalleled optical clarity. This Innovation materializes the excellent transparency that surpasses the current benchmarks with significant lower additive dosage, yielding better extraction resistance. Unlike traditional transparent resins such as polystyrene and PET which lose their clarity when heated, PP formulated with this clarifier materializes the excellent transparency with superior heat and chemical resistance, expanding the potential demand of PP as a novel transparent material. PP itself also exhibits lower carbon footprint due to its light weight, lower production energy and recyclability Hence, transparent PP using this technology offers sustainable advantages from a Life Cycle Assessment (LCA) perspective. Through the approval by the US. FDA for safe food contact, this clarifier is ideal for microwaveable food container applications, chemically resistant medical devices, and cosmetic packaging while also creating new opportunities for PP across multiple industries. Today's presentation on our novel PP clarifier will highlight its performance attributes versus current clarifier technology.

2025 SPE ANTEC

With over 500 attendees, ANTEC® 2025 showcased the latest advances in industrial, laboratory, academic, and international work focused on plastics and polymer science. While ANTEC® addressed a range of emerging plastics technologies, processes, polymer research, and new materials, this year also focused on scientific, technical, or industrial problems and their solutions.

Networking:

Monday, March 3: ANTEC kicked off with a Meet and Greet that brought attendees together to mingle, reconnect with old friends, and spark new connections. It was an energy-filled evening with exciting conversations - the kind that could turn into the next big idea!

Tuesday, March 4: Everyone headed over to Victory Brewing for a laid-back evening filled with great food and drinks, and plenty of facetime!

Wednesday, March 5: SPE's Awards Luncheon was an inspiring celebration recognizing the innovators and rising stars of SPE. Everyone honored the achievements of SPE's Fellows of the Society, Honored Service Members, SPE Foundation Ambassador Giving Society, President's Cup recipients, and standout Student Poster winners.

Later Wednesday, students gathered for a blast of a get together, where they participated in a fast and furious game of "find that plastics professional." Then everyone made their way over to an incredible reception hosted by the SPE Injection Molding Division. Whether a seasoned professional or new to the field, this reception was the perfect setting to build connections and celebrate the achievements of the plastics community.

During the Awards Lunch, 3 new Fellows were added as per the announcement made in January. & new Honored Service Member Awards were given out as per the announcement. Unfortunately, no one from PMAD was nominated for either of these awards. SPE Foundation Scholarships were given out and our PMAD was recognized for the donation we made to Student Scholarships along with other donating chapters (divisions & local sections).

Education and Knowledge Sharing:

With five plenaries, two special symposiums honoring Tim Osswald and Michael Sepe, as well as over 180 technical presentations, ANTEC® 2025 provided the perfect blend of plastics and polymer technologies. From sustainability and recycling to extrusion, injection molding and bioplastics, and beyond, there was something for everyone!

This year, PMAD became an off-site sponsor for the first time. PMAD was the Sponsor of the Networking Reception at Victory Brewing, to promote our chapter to broader attendees, and facilitate industry networking.

Join the PMAD!

Help us promote scientific and engineering knowledge sharing related to enhanced performance of polymeric compositions by incorporating modifiers and additives

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FLAME-RETARDANTS FOR POLYPROPYLENE: A REVIEW (SECTION SNIPPETS)

Severine Bellayer, Melvin Dilger, Sophie Duquesne, Maude Jimenez

Polymer Degradation and Stability 230 (2024) 111008

Mode of action of Flame Retardants FRs in PP

3.1. FRs acting mainly in the condense phase

3.1.1. Intumescent flame retardants (IFRs)

An intumescent system swells when heated, forming an insulating foam-like layer limiting heat and mass transfers between the polymer and the flame. It is usually composed of an acid source (a polyphosphate flame retardant PFR, such as ammonium polyphosphate APP, due to its high phosphorus percentage content), a carbon source (charring agent as polyol hydroxyl groups pentaerythritol PER, dipentaerythritol DPER) and a gas source (blowing agent as melamine) to enhance the expansion of the protective layer. The most well-known intumescent formulation is composed of APP, PER and melamine. Intumescent additives are widely used in PP, by forming a protective layer during burning, they limit the dripping occurring during PP combustion (anti-dripping effect) and lower the release of smoke and gases [13,20–23]. However, they have some drawbacks, which can be an issue for some industrial applications. Indeed, for the majority of IFR systems, the total amount of FRs generally reaches 20 to 25 % to be effective either for UL94 or cone calorimeter tests. Moreover, some of the most common intumescent additives (e.g. APP and PER) show a high water sensibility: FRs can migrate to the polymer surface and the fire properties are quickly lost [21]. In order to respond to this water sensitivity issue, some FR fabricants (Clariant with Exolit AP or ICL-PP with Phos-check P30) introduced new water resistant APP products compatible with the polymer matrix. Clariant introduced on the market the Exolit AP 422 and Exolit AP 766 (improved version of Exolit AP 422), which have higher molecular weight and are much more water resistant [21,24]. Encapsulated products such as melamine formaldehyde are also on the market to respond to the water resistance issue [24]. Using other less water sensitive compounds, such as DPER instead of PER, can also be a solution. For several years, many new combinations have been investigated to reduce the percentage of FRs added, to enhance the formation of a protective char and to improve the compatibility between the polymer matrix and FR additives, while keeping the durability toward humidity. Several ways have been used: optimization of the APP/PER ratio, addition of synergists (other PFR, metal oxide or hydroxide) to the basic formulation (APP/PER), and replacement of the APP or PER by other acid source or charring agent.

3.1.2. Nanocomposites

The use of nanotechnology in the flame retardant field has been through a great deal of research since the late 90s. The incorporation of small quantities of nanomaterials leads to a significant reduction in the peak heat release rate (PHRR). Layered silicates, considered the first successful nanometric filler for polymer nanocomposites, were introduced commercially in the early 90's [40,41]. Polymer/silicate nano composites were the first well studied flame-retardant polymer nanocomposites [42,43]. Montmorillonite is a typical flame-retardant nanomaterial, which FR properties are attributed to barrier and catalytic carbonization effects [44–46]. It can be used in polypropylene, as can other types of nanoparticles such as nanotubes, POSS, graphite oxide or metal oxide or hydroxide [8,10,43,47–49]. To obtain flame retardant polypropylene nanocomposites, a good dispersion of the nanoparticles in the polymer matrix needs to be obtained. It is one of the most important parameters to obtain good flame-retardant properties in PP. In fact, nanocomposites with poorly dispersed nanoparticles or too low content of nanoparticles do not form well-structured char and are not able to reduce the combustion rate, whereas nanoparticles form a homogeneous char when they are well dispersed [43,50]. In PP, most of the nanoparticles need to be surface-modified to disperse well in non-polar matrix and act as a heat shield to slow down the thermal degradation of polypropylene. This technology has been considered revolutionary, but although the performance of some nanomaterials has exceeded these of conventional FRs or IFR, nanomaterials have not yet been certified as FRs for commercial applications. The likely reason for this is their excessively high processing cost and/or health and safety concerns. Indeed, the lack of safety studies and data for many nanoparticles will continue to hamper efforts to facilitate their use [51]. Currently, nanoparticles are used in the flame retardant field but it is mostly to reduce the amount of FR agents in polymer composites; nanoparticles are used as synergistic agents to enhance char formation during combustion [52]. Indeed, as we have already seen, a common problem with IFR is that achieving the desired flame-retardant effect often requires a high addition of IFR, typically of the order of 20 to 25 % by weight. Such an addition of IFR compromises the mechanical and processing properties of flame-retardant composite materials. Thus, many works use nanoparticles to enhance the char structure of IFR [23,34,36].

3.1.3. Bio-based FR

Since there is still a tremendous need for new halogen-free, environmentally-friendly flame retardants for PP, it has led to the development and the use of biobased materials [53]. The use of biobased materials is highly attractive due to their low cost, wide availability and ease of access. Among these natural products, chitosan, lignin, cyclodextrin, starch and tannin stand out. Studies have shown that they can be dehydrated and carbonized. The carbonization layer not only forms an external heat and oxygen shield for the polymer matrix, but also prevents flammable and volatile gases generated by the polymer from entering the gas phase, thus preventing flame propagation and achieving a flame-retardant effect [54–57].

Chitosan (CS) is a natural, biodegradable polysaccharide derived from the deacetylation of natural chitin. It can be extracted from crab, shrimp and mushroom shells [58–60]. The multiple hydroxyl and reactive amino groups in the CS molecular chain make it a positively charged polymer with excellent coordination capabilities, enabling the phosphorylation of chitosan. CS is rich in carbon and can therefore be used as a carbon source for IFR [61–63]. To reduce the quantity of CS, CS can be modified. In their work, Huang et al. replaced the -NH_2 in the CS chain by ammonium polyphosphate to obtain a PP with chitosan-ammonium polyphosphate compound obtained through in-situ polymerization. They obtained a V-1 at vertical at UL94 test [64].

Starch is also used as a derivative for green char formation. The activation temperatures of starch derivatives are considerably lower than the decomposition temperatures of pure starch. The ammonia released by the thermal degradation of the derivative contributes to starch's flame-retardant properties. As a result, starch becomes a promising candidate for sustainable and environmentally friendly flame retardants [65]. In literature, starch-based flame retardants have been modified via surface hydrophobicity to enhance the interfacial compatibility with PP and increase its flame retardant property. A synergistic effect has been obtained with expandable graphite to reach a limiting oxygen index (LOI) value of 33.5 % and a UL-94 V-0 rating [66].

Another class of bio-based material usable for flame retardancy is oligosaccharides, such as cyclodextrin (CD). They are formed by the enzymatic modification of starches and are composed of several glucose units arranged in the shape of a truncated hollow cone. Their simple structure and high thermal stability make them an even better choice for use as carbonizing agents. Among the available CDs, β-cyclodextrin (β-CD) is the most popular and widely used. Ding et al. presented the synthesis of crosslinked β-cyclodextrins hexamethylene diisocyanate (HDI-CD) by reacting β-cyclodextrin (β-CD) with HDI as crosslinking agent at different ratios. HDI-CDs are combined with ammonium poly phosphate (APP) and applied to polypropylene (PP) to form intumescent f lame-retardant composites that can pass UL 94 V-0 evaluation with an LOI value of 32.8 % when the flame retardant load is 28 % by weight [67].

Lignin is also a promising complex organic polymer for flame- retardant properties in polymers. Lignin is a key structural material located in the supporting tissues of most plants [68]. It plays a particularly important role in the formation of wood cell walls. Lignin is used to improve the fire-retardant properties of synthetic polymers because of its excellent thermal properties. Indeed, its decomposition occurs at temperatures between 200 and 500°C, depending on the nature of its production and the chemical modifications of its structure [69,70]. Lignin- and polypropylene-based materials with good fire-retardant properties have been reported in the literature [71,72]. Klapiszewski et al. studied the thermal stability of polypropylene (PP)/silica-lignin composites. The results showed that the incorporation of silica improved thermal stability by increasing the char residue [73]. Flame retardants containing tannic acid (TA) are also an emerging and promising area of research in sustainable fireproofing. TA can be obtained from the seeds, bark and other parts of many tree species [74]. It is a non-toxic, inexpensive and abundant polyphenolic compound that can be characterized by the presence of hydroxyl groups linked to a benzene ring, as well as other groups such as organic acids and sugars [75]. Due to its specific aromatic structure, TA has high chemical and thermal stability [76]. Natural fire resistance is mainly attributed to their phenol-like reactivity. Phenoxy radicals can quench oxygen free radicals when the polymer decomposes during heating. In addition, TA promotes char production during combustion, resulting in the formation of a protective char layer that can block oxygen and heat transfer, as well as the release of flammable gases [77]. Recently, an LDH-based core-shell architecture has been designed using an LDH sheet as the core and a network of tannic acid and phosphazene cross-linked polymers as the shell. In the combustion process, tannic acid (TA) (the carbon source) combined with phosphazene forms an intumescent system which, in synergy with the "tortuous path" effect of LDH, significantly improves the flame retardant properties of PP [78]. Finally, phosphorus-containing biomass such as phytic acid (PA) is also an excellent candidate as a flame retardant. Phytic acid has a phosphorus content of 28 % and is the main source of phosphorus in plant tissues. Found mainly in plant seeds, roots and stems. PA can release phosphorus/polyphosphate during heating, accelerating carbonization of the polymer matrix and forming a protective carbonization layer. In the gas phase, PA decomposes into PO• radicals to capture H• and OH• and HPO• radicals, thus ending the chain reaction and achieving the flame-retardant effect. As a result, PA acts in both the gas and condensation phases and has rapidly become a good candidate for flame retardancy [79]. In literature a bio-based phytic acid salt was prepared through reaction between phytic acid and piperazine. The compound was used at a 18 % rate to formulate flame-retardant poly propylene (PP). The modified PP passed the UL-94 V-0 rating in the vertical burning test, superior to the pure PP [80].

4. PP FRs acting in the gas phase (free radical generators)

4.1. Halogenated FRs with synergists

Halogenated FRs are very effective in PP but not environmentally friendly. Some synergists, such as antimony trioxide, ATO are also considered as an environmental threat. In order to have a less impacting FR system, NOR 116 could replace antimony trioxide. A formulation containing 0.5 % NOR 116 and 14.5 % of decabromodiphenyl ether has been reported to show a V0 rating at UL94 test and improve the UV resistance and long- term stability of PP, but also to lower the smoke density during combustion, while maintaining the mechanical properties of PP [19]. NOR 116 also shows a good synergy with the tris(3-bromo-2,2-bis (bromo methyl)propyl)phosphate (TBBPP), it reduces the release temperature of HBr (a gas phase active flame retardant) below the decomposition temperature of PP. HBr is thus released when PP decomposes, leading to a much more effective inhibition effect [37,81].

4.2. PFRs with synergists

PFRs are still considered as environmentally friendly FRs, that can act in gas and/or condensed phase, with a favored phase according to the oxidation degree. Lot of PFRs, mainly acting in gas phase, are commercially available (Aflammit PCO 900 (Fig. 7), pentaerythritol di- phosphate, Al or Ca hypophosphite…) and can access V0 rating at UL 94 test or good LOI values. However, they usually need to be added at high loading to be effective. For example, the Aflammit PCO 900 from Thor used alone at a loading of 5 % increases slightly the LOI from 19 % for neat PP to 21 % and leads to a small decrease of pHRR (1635 to 1434 kW.m^2). Pentaerythritol di-phosphate from great Lakes reaches a V0 rating with a loading of 19 % in PP [21]. The use of synergists is needed to improve the fire performances of PFRs and reduce the quantity of additives.

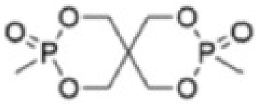

Fig. 7. Aflammit PCO 900.

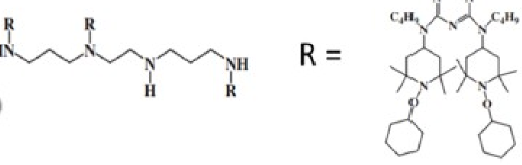

Fig. 8. Flamestab NOR 116.

4.3. NOR

Some Anti-Oxidants (AO), such as Hindered Amine Light Stabilisers (HALS) and more specifically N-alkoxy hindered amines (NOR) have also demonstrated FR properties. The NOR is a common light stabilizer used to improve polymers durability. In fact, polymers are sensitive to heat, light and oxygen: when auto-oxidation process occurs, free radicals are generated, which leads to further degradation cycles of the polymer, producing ketone carbonyl, hyperperoxides accelerating the degradation cycle. This irreversible degradation has a huge impact on the polymer properties [37]. Anti -oxidant agents are used to inhibit or delay the polymer degradation by reacting with the free radicals or hyper peroxides formed during the degradation, thus increasing the polymer life-time [37,38]. The AOs have the capacity to form free radicals easily to inhibit the initiation or the propagation of oxidation. The first ones having realized that N-alkoxy hindred amines (NOR) can act as potential flame retardant by itself were inventors from Ciba Specialty Chemicals (now BASF). They introduced the first commercial product on the basis of N-alkoxyamines (NOR) in 2000 under the trade name Flamestab NOR 116 (Fig. 8). This product has the capacity to easily form several free radicals (aminyl, alkoxy, nitroxyl, alkyl radicals) that can react with the HO and H produced during the polymer decomposition [13,37,38]. Aminyl and alkoxy radicals act both in the gas phase, by radical inhibition [18,82,83]. NOR is suitable with a wide range of PFRs. According to the literature, 5 % of aluminum hypophosphite and 7.5 % of melamine hydrobromide provide a V2 rating at UL-94. These percentages can be decreased to 1 % for aluminum hypophosphite and 1.5 % for melamine hydrobromide by adding 0.2 % of a synthetic NOR (NORSM similar to Tinuvin 123 (Fig. 10)). This formulation has a V2 rating but the time of combustion decreases, from 16.1 s/3.5 s (t1/t2) to 7.3 s/3.4 s [39]. However, several combinations for PP including halogenated FRs, PFRs (hypophosphite) and NOR are claimed in patents [84–87]. For example, a combination of 0.25 % Tinuvin NOR371, 3 % Aluminum hypo phosphite and 3 % Decabromodiphenyloxide allows reaching a V0 rating at UL-94 test [85]. Unfortunately, the hypophosphite can decompose into phosphine over time and lose its FR properties[21,39,85] but the combination with NOR enhances the stability over the time and the fire performance. Solvay also developed an encapsulated Ca hypophosphite to limit the decomposition of phosphine over time [21]. NOR 116 shows a strong synergy with phosphonates and especially with Aflammit PCO 900, THOR. Aflammit PCO 900 can be combined with NOR 116, providing a non-dripping behavior as showed in the literature [28,85–87]. The interaction between the Aflammit PCO 900 and the NOR 116 can form a slight char but not enough to protect the PP. Different kinds of NOR are commercialized such as Tinuvin 123 or 152 from BASF. They can be synthesized but they are not all equally effective [37,82,83]. In recent works, different NORs have been synthesized to understand how to improve the effectiveness of the NOR. The effectiveness strongly depends on three properties, i.e. thermal stability, decomposition products and mechanisms, as well as reactivity of the radicals generated (the more stable the radicals are, the more effective they will be) [82]. The modification of the substituents (the R = formula group attached to the oxygen) can improve the stability of the radicals generated. For example, 2 % of a synthetic NOR T-TEMPOC (Fig. 11) incorporated in a PP film (0.2 mm) was tested in the “thin material vertical burning test” condition (VTM, a similar test to the vertical burning test except that the material is wrapped around a mandrel before clamping it to the stand, the flame application is 3 s) and provides a VTM-0 rate and increases the LOI up to 27 % [83]. Fig. 9. Degradation of Aluminum hypophosphite. Fig. 10. NORSM. Fig. 11. NOR T-TEMPOC. NOR can also be directly combined with phosphorus compounds to synthesize new phospho-substituted NOR with good flame retardancy [88]. NORs can be synthesized in many forms and they are very effective synergists with both halogenated FRs and PFRs. Their capacity

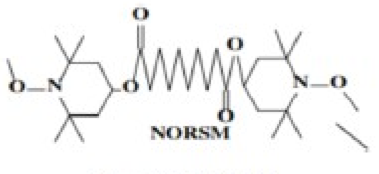

Fig. 10. NORSM.

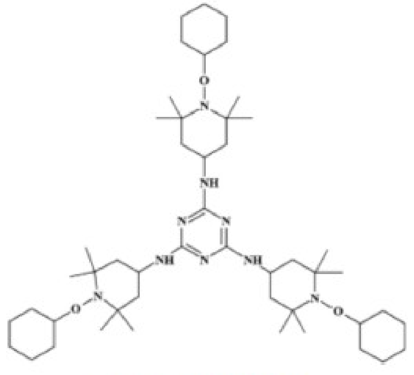

Fig. 11. NOR T-TEMPOC.

to generate quickly free radical scavengers strongly enhances their fire performance and decreases the amount of FR needed to reach good results. However, NORs usually have a low thermal stability. Thus, recent research focuses on the synthesis of oxyimides, which show better stability compare to usual NORs. These oxyimides were tested in combination with PFR. The patented results show that the incorporation of phosphonate (Aflammit PCO 900) (between 6 % and 8 %) and 2 % or 4 % of the synthesized oxyimides in PP can lead to a V0 rating at UL-94 test [84,89].

4.4. Azoalkanes (AZO)

Due to great effectiveness of the NOR, several nitrogen free radical generator compounds were investigated to improve flame retardancy, such as azoalkanes (AZO), AZONOR and triazenes. The AZO (Fig. 12) are the cleanest and most convenient source of alkyl free radicals. The cleavage of the CN bound from AZO or triazenes releases alkyl radicals and also aminyl radicals for the triazenes, that trap the radicals formed by the decomposition of the polymer (H ◦ cleavage of C N bound, N_2 and HO). Following the is also released and dilutes the gas phase [19,90–92]. AZO compounds (Fig. 12) were compared to NOR 116 according to DIN 4102 part 1 classification B2. 0.5 % of AZO decreases the burning time from 100 s for neat PP down to 8s, whereas sample containing 0.5 % NOR 116 decreases the burning time down to only 22 s. Unfortunately, AZO presents less affinity with brominated FR (tris(tribromoneopenthyl) phosphate (TBBPP)), 14 % of TBBPP and 0.5 % AZO lead to a “no rating” classification whereas with 0.5 % of NOR 116 a V0 rating was reached. Alone, at low concentration in thick PP, the AZO compounds are more efficient as flame retardants than NOR 116, but less effective as UV stabilizer [19]. The AZO compounds (Fig. 12) have a good affinity with PFR (melamine phenyl phosphonate). For example, an amount of 20 % of PFR in PP led to a V2 rating whereas the addition of 1 % of AZO in presence of 17 % of PFRs led to a V0 rating. Moreover, AZO has a non-dripping behavior but is less effective than bis AZO (Fig. 12). When bis AZO is added at 0.5 % loading in a 200 μ m pressed PP film, no drop is observed under the DIN 4102 part 1 classification B2 test and the weight loss is only 1.9 % instead of 3.8 % when AZO is used [19].

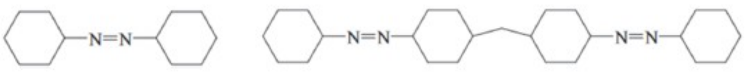

Fig. 12. AZO (left) and bis AZO (right) molecules.

4.5. Combination of AZO and NOR

In order to take advantage of both NOR and AZO properties, they were combined in one molecule (AZONOR) (Fig. 13) to improve both the fire performances and the UV stability [38,82]. AZONOR improved the flame retardancy compared to both NOR116 and AZO: following the DIN 4102–1/B2 test method, the burn length and the weight loss have significantly decreased in presence of 0.5 % of different AZONOR compounds (Fig. 14) [82,93]. Moreover, the stability after artificial weathering was improved and the fire performances were almost preserved [38]. The AZONOR loaded at a few percentages (0.5 %) in PP film provides a much better flame retardancy and UV stability than AZO or/and NOR. The use of AZONOR is claimed in a patent for thin PP (film) and injected PP [93].

4.6. Triazene

Due to the good flame retardant properties of the AZO, other nitrogen-based molecules were investigated, such as triazenes. Triazenes were compared to NOR 116 and tested using the DIN 4102–1 test. The results obtained showed no drop igniting the paper and a faster extinction time when triazene is added. “Triazene (3)” shows a shorter burning time and burning length than “triazene (4)”. This may be explained by a faster decomposition time for “triazene (3)” and an increased dripping behavior. As for AZO, triazenes loaded alone in small quantities in a PP film provide better fire properties than NOR 116 [19, 82,94].

4.7. Disulfides and sulfenamides

Sulphur free radical generators were also investigated. Nitrogen based free radical generators are not the only one that provide this kind of mechanism and fire performance. Sulfur compound such as disulfide (DIS) or sulfenamide have shown good flame retardancy. The cleavage of S-S or C-S and S-N (for sulfenamide) bounds forms free radicals reacting with the radicals released from the polymer degradation The stabilization of the formed radical is important to obtain better flame retardancy [19,95]. For example, the DIS3 (Fig. 16) has electron withdrawing substituents (nitro and carboxylic acid) at the aromatic rings that remove electrons from the aromatic system and stabilize the disulfide bond. DIS3 added at 0.5 % in PP showed better results compared to 0.5 % of Flamestab NOR 116 and the others Disulfides when DIN 4102–1 test is used. The formulation with DIS3 has a less average burning length and time (53 mm and 10s) compared to that containing NOR 116 (78 mm and 11s) [19,95]. Sulfenamides also have been recently investigated to explore new sulphur FRs. The sulfenamides are active during the thermal decomposition of PP (between 250 and 360°C (Fig. 17). Some can produce residues at 700°C) before combustion C after TGA analyses and all sulfenamides synthesized and tested at DIN 4102 passed the B2 rating at low loading (0.5–1 %). Moreover, the most effective sulfenamides can decrease by 3 the average damaged length and by 4 the average burning time [96].

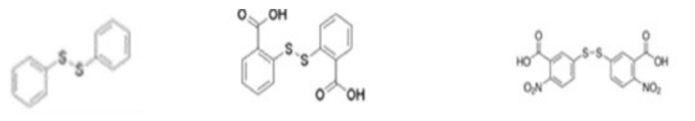
1,1'-Disulfanediyldibenzene (DIS1) / 2,2'-Disulfanediyldibenzoate (DIS 2) /Acide5,5'-dithiobis-(2-acide nitrobenzoïque) (DIS 3)

Figure 16 Disulfide compounds

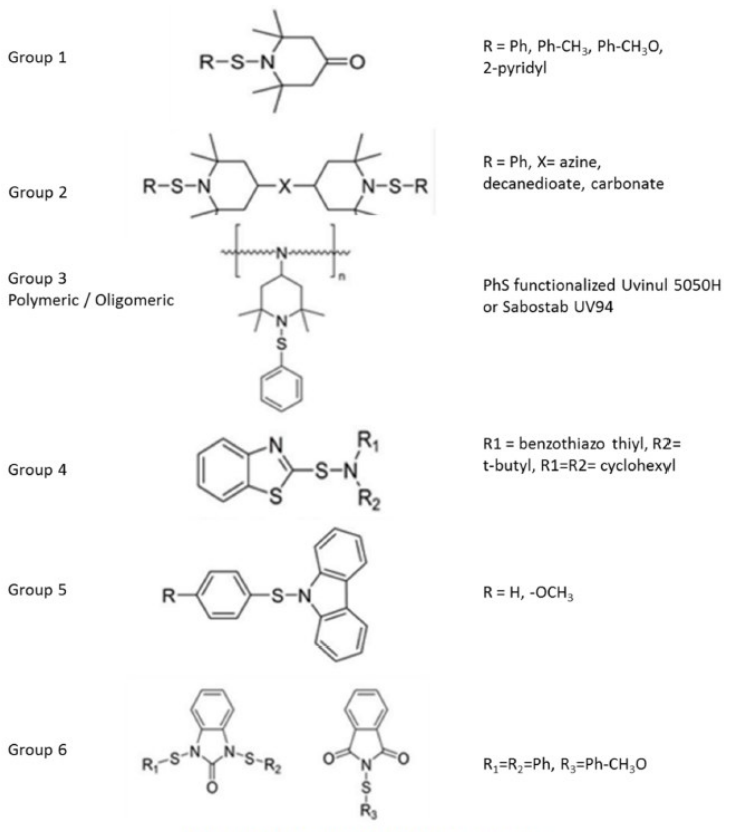

Fig. 17. Sulfenamide N-S and sulfenimide S-N-S radical generators.

In order to go deeper in the investigation, sulfenamides have been combined with other FR compounds. Sulfenamides have a good synergy with Aflammit PCO 900, the incorporation of 15 % of Aflammit PCO 900 led to a V2 rating but adding 1 % of sulfenamide provided a V0 rating. The amount can be decreased down to 8 % of Aflammit PCO 900 and 1 % of sulfenamide, still providing a V0 rating. The inhibition action of both FRs shows a good synergystic effect and allows to change the numbers of drops, the viscosity and temperature, thus decreasing the flammability [97]. Sulfenamides can also improve the performance of an intumescent system. Indeed, adding 25 % of a mix of APP/PER at ratio 3/1 in PP is “no rated” at UL-94 test, but by adding only 0.5 % of sulfenamide to this system a V2 rating was obtained. Moreover, sulfenamide does help to decrease the heat release and smoke production. Sulfenamides have been seen to be the most effective when added in combination with a cyclic di-phosphonate (such as Aflammit PCO 900), this combination provides a V0 rating with a low percentage of additives (9 %) [97].

For References details, please go to:
Polymer Degradation and Stability *230 (2024) 111008*

This learning forum is served to provide education in the area of plastic additives and modifiers. If you have any interesting topic you would like to share or you have any specific area you would like to learn from the forum, please reach out and we would like to hear from you. Thank you!

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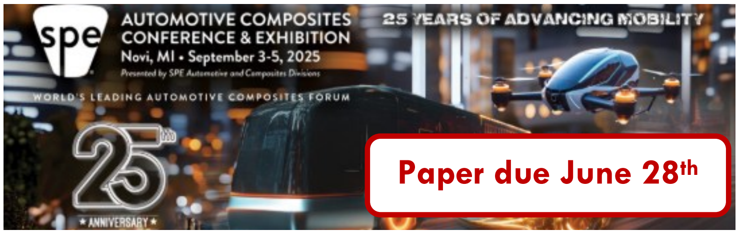
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