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Polymer Modifiers & Additives News

A Publication of Polymer Modifiers and Additives Division of Society of Plastics Engineers

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PMAD Officers Election

PMAD board of directors has held an election in April and the following volunteers have been elected for the positions announced. PMAD congratulates and thanks them for their continued support of our Division.

Dr. Thoi Ho as PMAD Councilor
Dr. Ray Pearson as PMAD Chair-elect
Dr. Dick Grossman as PMAD Treasurer
Dr. Ashok Adur as Communication Committee Chair and Newsletter Editor

PMAD Wine and Cheese Reception at ANTEC, Tuesday April 29

Time: 5:30 to 7:00 pm

Location: Rio Hotel, Pavilion 5/6/7

PMAD will hold a joint reception with Vinyl Division and Engineering Properties and Structure Division (EPSDIV) at ANTEC. Please join us to network with your peers, meet your board members and communicate your views and interests. During the reception, PMAD will introduce our new officers, PMAD challenge winners, and special recognition award winners.

- New Chair and Officers Announcement (Saied)
- PMAD Challenge Award Winners (Ray)
- Special Recognition Award Winners (Kim/Thoi)
- Polyolefin PMAD Scholarship Winners (Thoi)

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PMAD Out-going Councilor

Dr. Ernie Coleman, PMAD's Elected councilor in 2013 is no longer able to continue in this role due to personal reasons. Ernie has recently gone through a surgery and we all wish him the best of health and quick recovery. PMAD has benefited from the long time support and great vision of Ernie over the years. Ernie has been one of the funding members of PMAD and you may find a sample of his contribution in his last report on Page 8.

PMAD also thanks Dr. David Riley, who temporarily acted as Proxy Councilor for PMAD until PMAD board elected Ernie's replacement. David is another funding member and a great asset for PMAD.



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Chairman's Message

This is my final message as PMAD Chair to our colleagues, industry professional, friends, and members of Polymer Modifiers and Additives Division and SPE. It is hard to believe that two years has passed since I took over this role. It has been a privilege to lead our division during this period and my primary goal was to ensure PMAD properly represents our industry and plays an active role in supporting student and academic activities related to polymer modifiers and additives. I would like to thank all my good friends at PMAD Board of Directors who helped us moving in this direction, which resulted in achieving SPE's Gold Pinnacle Award and SPE's Communication Award both in 2013 and 2014.



PMAD Technical Program Committee lead by Thoi Ho for SPE International Polyolefins Conference and by Baris Yalcin for SPE ANTEC has held strong programs in these two years, which was very well received by strong attendance for PMAD Sessions. PMAD Tutorial Sessions organized by Thoi for Polyolefins Conference receives more 100 attendees each year despite being held one day in advance of the main conference. Due to the strong success of our tutorial program, PMAD has started holding a tutorial session in this year's ANTEC Conference. This would allow us to alternate tutorial sessions on the subject of polymer modifiers and additives between Polyolefins Conference

and ANTEC so that we do host a PMAD tutorial every year.

PMAD Education Committee lead by Ray Pearson has held strong PMAD Challenge programs, which saw a growth in student participation. PMAD Challenge program encourages research activities in the field of polymer modifiers and additives and awards students based on their review of technical papers and proposal for continued research. PMAD also continued its support of other SPE student activities.

PMAD has also been looking for other ways to contribute to our industry through improving the technical content of our Newsletter and looking for other conferences and technical programs that PMAD can lead or participate in. We have made some progress, and we will continue working in these directions to enhance PMAD representation of our industry under the leadership of Kim Crane, Ray Pearson, and Thoi Ho as PMAD upcoming Chair, Chair-elect, and Councilor, respectively. I would like to thank you all for your support in the past two years and will continue supporting PMAD as the Past-Chair and Membership Committee Chair.

Saied Kochesfahani

PMAD Chair

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OPTUM® Technology an innovative barrier solution for polypropylene-based materials in food packaging applications

*Sergio Torres-Giner, Alberto Chiva-Flor, José Luis Feijoo-Gómez
FERRO SPAIN, Specialty Plastic Division (PCEM), Almassora, Castellón, 12550, Spain*

Abstract

High-barrier packaging can significantly reduce absorption, desorption and diffusion of gases and liquids to maintain the quality of food. This paper provides technical information on the barrier properties of a new solution based on a passive non-nanosized technology for its use in polyolefin materials. This is interestingly presented as a novel alternative to other new commercial passive fillers such as unmodified or organically modified nanoclays. In particular, the new additive offered better barrier performance during sterilization conditions, in which the water vapor permeability was reduced to about 60% when compared to the unfilled polypropylene film.

Ferro, a leading supplier of specialty plastics, has recently developed **OPTUM®** Barrier masterbatch for a wide range of polymers. This can be incorporated by melt processing in most of the manufacturing processes involved in the developing of single and multi-layer structures in flexible and rigid packaging. In particular this is suitable for food packaging applications in order to increase product protection and shelf-life. Barrier applications can be found, however, in other market segments such as cosmetics, industrial containers and agricultural films, where barrier to oxygen and other gases is also critical.

Introduction

Barrier applications can be found in food and pharmaceutical industries where product shelf life is often directly linked to gas permeability. In these packaging structures, the presence of oxygen barrier resins such as ethylene vinyl alcohol co-polymer (EVOH) and polyamides is key to food quality and safety because it delays the ingress of oxygen, agent responsible for a number of food deterioration processes. Their excellent oxygen barrier properties derive from a high degree of crystallinity and the presence of hydroxyl groups in the polymer structure, which confer them with both high intermolecular and intramolecular cohesive energy and a low fractional free volume between the polymer chains available for the mass exchange of low molecular weight substances (1).

In spite of the low gas permeation, oxygen barrier resins can be adversely affected by high humidity and are liable to undergo an increase of oxygen permeability under a highly humid atmosphere. This deterioration derives from a plasticization effect, i.e. increase of the fractional free volume of the polymer and decrease of the mechanical integrity (2). Generally, oxygen barrier of high humidity dependency structures are adapted to retain their oxygen barrier property by including a protective layer, such as of a polyolefin, having a low water absorption. These multilayer structures are usually made by lamination, co-extrusion, and co-injection processes.

These packages are used to store foodstuffs and they are often subjected to a retort process in which the molded package/container is exposed to excessive moisture as steam at elevated temperatures. It is well known that diffusion of permeants increases exponentially with temperature due to the greater mobility of the polymer chains and with the increase of the free volume of the polymer at higher temperatures (3). This effect leads to lowering of the efficiency of the oxygen barrier resin, an effect called "retort shock" (4). Although this lowering is practically a reversible process, this is a slow process, and in order to meet the expectations of the shelf-life for the food contained in the retorted container the thickness of the oxygen barrier resin layer must be increased or special grades, such as lower ethylene mole percent EVOH, must be used (5). These habitually represent both expensive alternatives and the most economical way to ensure shelf life is still to protect the EVOH layer from the moisture/steam.

Therefore there still remains a need in multilayer structures, to modify the protective layer in order to increase resistance to retort shock. A next generation of materials should be addressed to increase and enhanced the use of oxygen barrier resins when exposed to more aggressive packaging conditions. This paper describes a novel barrier solution based on ultrathin functional fillers to generate high water permeation-resistant polyolefins. The new masterbatch was compared to other commercially available additives for their use in polypropylene extruded films subjected to a steam treatment.

Experimental

Materials

OPTUM® EV-0437BC masterbatch was fabricated using an intermeshing co-rotating twin-screw extruder at FERRO's facilities (Castellón, Spain). The proprietary composition consists of ca. 40% of functional fillers pre-dispersed in a universal polymeric carrier. Following commercial masterbatches based on the following nanoclays were used for comparison: a natural bentonite, an organo-modified (OM) bentonite, and a natural montmorillonite (MMT).

A random copolymer polypropylene (PP), Moplen® RP210G from Basell designed for blow moulding and film extrusion, with melt flow index of 1.8 g/10 min (230°C, 2.16Kg) and density of 0.9 g/cm³ was chosen as a matrix.

Film Extrusion

Composite films were obtained by diluting above mentioned masterbatches at 12 wt.-% in polypropylene. Film extrusion was performed using a Collin E30M single-screw extruder, as depicted in Figure 1. Rotor speed was set at 40 rpm, with a barrel length/diameter of 30 and a flat die exit of 300 mm. The profile of temperatures was set accordingly to provide a melt temperature of 210°C. The cooling temperature of the mandrels was fixed at 40°C and this performed a relation of stretching of 7.2%. Resultant composite films presented ca. 160 µm of thickness.

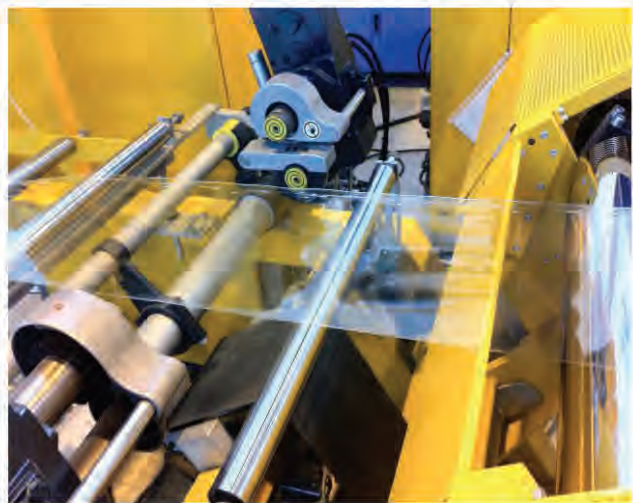


Figure 1. Film extrusion of the composites

Film Characterization

Scanning electron microscopy (SEM) was carried out using a JEOL 7001F microscope with an accelerating voltage of 15 kV. Composite morphology information was obtained from film sections in the extrusion direction.

Thermal behavior was carried out using a differential scanning calorimeter (DSC), model Q100, TA Instrument. Samples were heated from 40°C to 220°C then cooled down to 40°C and heated again at to 220°C at a rate of 10°C/min under N₂ atmosphere. The crystallinity data were obtained from the second heating run.

Steam treatment was carried out on the composite films using a static Steriflow pilot retort Barriquand at 95°C for 25 min. Water uptake on the composite films was determined during retorting. For this, the films were previously sandwiched in a specifically designed permeability cells containing a water absorber. These were then placed inside the retort equipment and water sorption was estimated by means of weight gain through a film area of 48 cm². Tests were done for six specimens in duplicate and averaged.

Permeability experiences were conducted at AINIA laboratory (Valencia, Spain).

Results Composite Morphology

Figure 2 shows the SEM images of the unfilled polypropylene film (left) and the composite film obtained with OPTUM® (right), respectively. In the figure, it can be seen that ultrathin 1 µm-long lamellar fillers are highly dispersed and oriented along the extrusion direction in the polypropylene matrix. This indicates that an effective exfoliation of the platelets into the polypropylene matrix is achieved. These fillers act as impermeable structures for the gas-penetrant molecules, forcing them to follow longer and more tortuous pathways in order to diffuse through the polyolefin film.

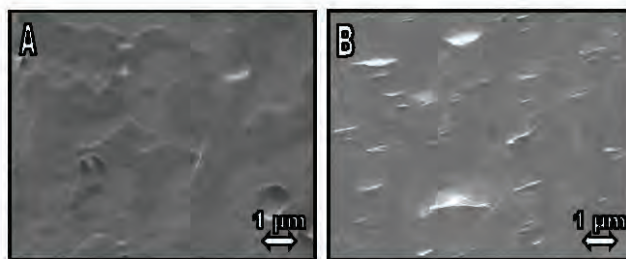


Figure 2. SEM images of the unfilled polypropylene and the OPTUM® composite films.

Thermal Properties

Polypropylene is a semicrystalline, the barrier properties are influenced by the degree of crystallinity and the size and shape of the crystals. From the DSC curves, in Figure 3, the degree of crystallinity fraction can be estimated by relating the enthalpy of fusion (ΔH_m) of the material to the equilibrium heat of fusion of an polypropylene crystal (ΔH_m^0):

$$\chi_c = \frac{\Delta H_m}{\Delta H_m^0} \cdot W_{polymer} \cdot 100 \quad (1)$$

Where ΔH_m^0 is ~ 209 J/g (6) is the enthalpy fusion of 100% ideal polypropylene crystal and $W_{polymer}$ is the weight fraction of the polypropylene in the matrix.

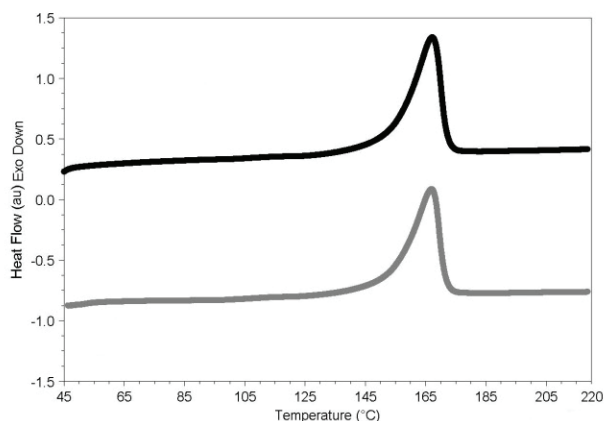


Figure 3. DSC curves of unfilled PP (black) and OPTUM® composite (grey) films.

In terms of the melting temperature and crystallinity, as it is showed in Table 1, the OPTUM® composite does not appreciably produce changes with respect to the unfilled polypropylene.

Table 1. Thermal properties of the films.

Films	T _M (°C)	ΔH_m (J/g)	χ_c (%)
Unfilled PP	167.19	70.93	33.94
OPTUM®	167.83	61.13	33.24

Barrier Properties

The water uptake of the all studied films during the retort process are box plotted in Figure 4. This indicates that the water uptake decreases in all the composite films compared to the unfilled polypropylene.

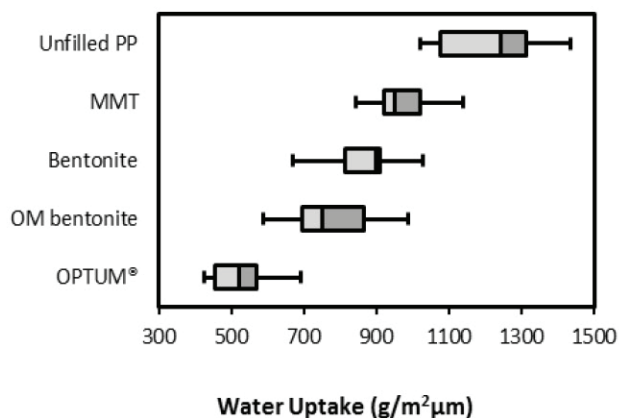


Figure 4. Box plot of the water uptake on the films.

Table 2 gathers the average values obtained from the figure. Highest barrier properties were observed for OPTUM®. In particular, the flow of water vapor decreased ca. 57% compared to the pure polypropylene. This results is consistent with the exfoliated structure of material obtained. This behavior can be attributed to a high orientation and high aspect ratio of the functional fillers with an exfoliated structure to form a more tortuous path at the water vapor diffusion in the film.

Table 2. Average values of water uptake of the PP films.

Films	Water Uptake (g/m ² µm)	Reduction (%)
Unfilled PP	1,219 ± 151	-
MMT	1,020 ± 204	16.3
Bentonite	906 ± 185	25.7
OM bentonite	828 ± 236	32.1
OPTUM®	525 ± 84	56.9

Conclusions

Permeation study during the steam treatment showed that the incorporation of OPTUM® generates a significant effect on the barrier properties of polypropylene. The morphology results showed that the incorporated functional fillers in the masterbatch were properly dispersed in a polymer matrix, obtaining a highly exfoliated-structure composite. Since the crystallinity of the composite is in the order of polypropylene, the decreased of water vapor permeability can be attributable solely to the incorporation of the functional fillers.

Ferro's OPTUM® masterbatch can be incorporated by melt processing in most of the manufacturing processes in flexible and rigid packaging for polyolefins. In particular this is suitable for protecting oxygen barrier resins during thermal treatments such as a retort process. The technology can be also seen as a new alternative to other more expensive high-barrier systems such as coating, multilayers or metallization.


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Keywords: Polypropylene, OPTUM®, barrier properties, food packaging, ultrathin particles.

Acknowledgments

Packaging Technologies Department of AINIA (Valencia, Spain) and particularly Luis Gil are acknowledged for the collaboration and the barrier characterization carried out on the films.

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PMAD Councilor Report

SPE Council Meeting of November 14 and 15, 2013

Ernie Coleman

The SPE Council met on November 14 and 15, 2013 in San Diego, CA. There were two major topics: elections and membership. Dick Cameron a long time personal friend was chosen chair elect. I know him to be an open minded innovator who will lead SPE in growth. Along with Dick we have Scott Owens as Senior VP and Jamie Gomez as VP. These are more strong leaders and SPE is fortunate to have them. These elected officers along with council and current SPE members are working with Executive Director De Vos on growth of SPE membership.

The following is my personal understanding of current membership problems. Many companies are finding that current employment conditions are such that funding or encouraging individual memberships in professional organizations such as SPE are not essential. This is short sighted in terms of employee growth and plastics industry expansion. We are all sales people who know the benefits of plastics and will teach others. Our source of information that we can openly discuss is the SPE and its technical data resources.

This failure of many companies in our industry to encourage membership in professional organizations such as SPE makes it difficult for SPE to recruit young members. Young members of our wonderful industry have to be shown how to grow in the industry. Personal mentors along with management encouragement are a necessary part of the process. Right now, many companies are failing in this important employee training activity.

SPE is reaching out to young members as never before with the Next Generation Committee. ANTEC 2014 in Las Vegas will be different. In order to make the professional meeting entertaining as well as educational there will be a race or form of a treasure hunt based on plastics and related sciences that ties into physical locations in the city of LV. This brave experiment will include special "T" shirts so we will know that this activity is occurring. Funding for this new activity will be generated by donations. The modest goal is \$20,000.

SPE has talked about doing something about young members for a long time. Now we are doing something. Like many current SPE members I am over 65 and I do not know many of the likes and dislikes of the under 30 age group. I do know that SPE like many other professional organizations is not currently meeting the needs of this group and therefore we need to change our approach. Well, that is happening.

The Student Activities Committee awards travel money at ANTEC and this insures that the student is present. This year at ANTEC there will be the usual poster sessions, student lunch

and something else (a plant tour) besides the fun race mentioned above. About \$39,000 was raised from Sections and Divisions to pay for these youth related activities. Another good suggestion for keeping young members comes from the Sections and Divisions Committees. The idea is to make room on the boards for appointed members to serve for one or two years and then stand for election or move on to another position.

The hard facts of membership are that SPE retains about 73% of members and this is not enough to maintain current membership of about 14,000. New members and continuing members minus loss of members lead to an annual loss of membership of about 31%. This is not new and it must be reversed. Younger members may not like the current SPE web page. Last year money was approved for an upgrade to the web page. This is ongoing and accounts for financial losses in 2013.

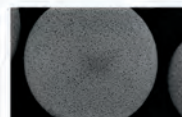
The SPE income base is mostly membership but other sources are important. TOPCOM income is being reviewed and there will be changes. Section and Division rebates are also under review and in all likelihood will be reduced. Growth in international membership and different international currencies are included in the financial reviews. All international SPE members will be charged a fair price for membership.

As your councilor I will keep an eye on all these issues and make sure that Divisions and Sections are treated reasonably. Changes are coming and PMAD must be prepared to grow as SPE changes.

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HOW TO IMPROVE (PHOTO)OXIDATIVE STABILITY OF FLAME RETARDED POLYOLEFINS

Rudolf Pfaendner, Fraunhofer Institute for Structural Durability and System Reliability, Division Plastics, Darmstadt, Germany

Abstract

Flame retarded polymers are mainly used in long-term applications. However, many flame retardants including halogen free products reduce the oxidative and photo-oxidative stability of polymers and polyolefins. Strategies to provide formulations of improved (photo)oxidative stability are reviewed and two successful possibilities are shown. Key additives for filler type flame retardants and nanocomposites are filler deactivators or coupling agents. There, the class of glycidyl methacrylate copolymers extends decisively the long-term thermal stability and moreover enhances the mechanical properties. Another class of selected multifunctional additives is based on NOR-Azo compounds and provides flame retardancy and light stability in one molecule.

Introduction

Flame retarded polymers are mainly used in long-term applications whereas antioxidants, light stabilizers and other additives provide the requested lifetime. However many flame retardants influence the oxidative and photo-oxidative stability of polymers often in a negative way resulting in early failure and loss in value. On the other side insufficient (photo)oxidative stability of the flame retardant itself may reduce the flame retardance performance over time. With regard to (photo)oxidation the polymer and the flame retardant may degrade independently, there might be a direct interaction between the polymer and the flame retardant causing acceleration or retardation and there might be an indirect interaction through the influence on the stabilizing additives. Moreover secondary chemical processes during use like hydrolysis may result in degradation products influencing the overall stability of the polymer formulation.

Many non-halogen flame retardants act as typical polymer filler and have to be used in high loadings. Therefore, these molecules “disturb” the polymer compound and influence the rheological properties during processing, the mechanical properties, e.g. acting as nucleating agent, and the visual appearance of the final product. Furthermore it is well known that filler interactions reduce the stability of the polymer which is even more critical if nano-sized materials are applied. Therefore, depending on the type of flame retardant

selected, the polymer substrate and the intended application adjusted stabilizer systems have to be developed [1].

The influence of classical bromine containing flame retardants such as tetrabromobisphenol A or brominated diphenyl ethers on polymers is well documented. The bromine compounds are less thermally stable than most polymers. Therefore, the dehydrobromination already occurs during processing and can be suppressed by the addition of heat stabilizers from the PVC heat stabilizer range. Photooxidation of polypropylene, polystyrene and polyethylene (HDPE, LDPE) is accelerated in the presence of decabromodiphenylether [2, 3] as the fire retardant decomposes quickly under irradiation into free radicals which attack the polymer. Furthermore, hindered amine light stabilizers (HALS) are deactivated through the formation of an amine salt with HBr, preventing the oxidation of HALS to the nitroxyl radical which is mandatory in the stabilization process. The resulting aminium salt is less thermally stable than the corresponding amine and may be easier degraded during processing [4].

In many applications halogen containing flame retardants are replaced nowadays through halogen free alternatives, which open up new challenges with regard to (photo)oxidative stability of the flame retarded polymer formulations.

Filler type halogen free flame retardants and nanocomposites

A substantial flame retardant class comprises inorganic fillers such as $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, $\text{Mg}(\text{OH})_2$, and more recently layered silicates or other nanocomposites. Also organic flame retardants (melamine cyanurate, melamine polyphosphate etc.) act often like filler type materials as these are insoluble in the polymer and are distributed in particles throughout the matrix. Inorganic fillers show, independent of the structures, experimentally a negative effect on the (photo)oxidative stability of the polymer, however to a various extent depending on the chemical structure and the source. Mainly interactions between the stabilizer and the filler and adsorption/desorption mechanisms are responsible for this influence. The surface area of the filler and pore

volumes, surface functionality, hydrophilicity, thermal and photosensitisation properties of the filler, transition metal ion content (manganese, iron, titanium) have been defined as potential elements of the interaction [5]. Mechanodegradation through the filler forms additional radicals during processing resulting in increased consumption of stabilizers. Furthermore, efficient stabilization of polymers will be even more complicated when additional to natural inorganic fillers other materials such as carbon black or pigments such as TiO₂ are incorporated in the formulation.

To cope with the negative impact of fillers on the photooxidative stability so called filler deactivators or coupling agents have been suggested to modify the filler surface. Suitable additives range from typical filler coatings (stearic acid, stearates), oligomeric epoxides, silanes, titanates to functional polymers (e.g. polypropylene-graft-maleic anhydride or polypropylene-graft-acrylic acid). Excellent results with regard to the oxidative stability of filled polymers can be achieved by using amphiphilic modifiers such as acrylates with long carbon chain side groups [1].

Layered silicates have been extensively evaluated as flame retardant components [6, 7], but the stabilization of the resulting “nano”-fillers implies additional challenges. Again layered silicates from natural sources (e.g. montmorillonite) contain metal ions as contaminants, which will act in the same way as in other fillers but are more homogeneously distributed and, therefore, will be more crucial to the polymer stability than metal ions in micro sized fillers. An indication of the long-term thermal stability of stabilized nanocomposites based on layered silicates may be gained from OIT (oxygen induction time) measurements. Already there, it is quite obvious that conventionally stabilized nano sized materials are rather limited in thermal stability, e.g. Polypropylene (PP) nanocomposites containing 5 % organically modified natural montmorillonite or synthetic fluorohectorite and 15 % compatibilizer (maleic anhydride grafted PP), stabilized with 0.05 % phenolic antioxidant (AO) and 0.05 % phosphite (P), achieve only a life time of 1.8 minutes (fluorohectorite) or 2.3 minutes (montmorillonite) at 190 °C. With a proper stabilization including filler deactivators the OIT value can be prolonged to more than 90 minutes (Table 1). Key factor for this improvement is the combination of phenolic antioxidants, phosphite processing stabilizers and reactive molecules of selected glycidyl or dianhydride structures. With similar systems the long-term thermal stability can be raised again to values of unfilled materials, however a higher stabilizer loading is mandatory [8].

Table 1. Oxidative Induction Time (ASTM D 3895-80) of PP Nanocomposites

Stabilizer	Stability [min] at 190 °C
0.1 % AO/P	2.3
0.3 % AO/P	7.5
0.5% AO/P + 0.5 % Diepoxid	80-92
0.5 % AO/P + 0.5 % Tetracarbonsäuredianhydrid	46.6

As glycidyl groups proved to be efficient as filler deactivator, several additional structures on that basis were tested. By choosing glycidyl groups containing copolymers not only the thermal stability (OIT) but even more the mechanical properties of nanocomposite formulations can be improved [9]. At somewhat increased antioxidant level (phenolic antioxidant (AO) and phosphite (P) 1:1) the oxidative stability can be multiplied by adding the selected copolymers based on styrene-acrylate-glycidyl methacrylate copolymers (copo, Table 2). At concentrations above 1 % of the copolymer the mechanical properties are enhanced as shown in the values of tensile impact strength.

Table 2. Oxidative Induction Time (ASTM D 3895-80) and mechanical properties of PP nanocomposites

Stabilizer	Stability [min] at 190 °C ASTM D 3895-80	Tensile impact strength [kJ/m ²] ISO 8256
0.2 % AO/P	13.3	128
0.5 % AO/P	30.3	n.d.
0.2% AO/P + 0.3 % copo	19.9	n.d.
0.5 % AO/P + 0.3 % copo	61.5	128
0.5 % AO/P + 1.0 % copo	82.4	132
0.5 % AO/P + 2.0 % copo	96.6	178

Moreover these copolymers adjust the long-term stability of other critical additives. For example, the thermal stability of stabilized PP is reduced from 672 h to 326 h at 150 °C through the addition of only 1 % carbon nanotubes. The initial stability is regained through combination with 1 % of glycidylmethacrylate copolymer [10].

Multifunctional additives to provide flame retardancy and polymer stability

Radical generators as synergists in flame retarded polymers have been used in combination with brominated flame retardants for decades. However, due to the low thermal stability of radical generators under the usual polymer processing conditions the use was limited to selected applications e.g. in polystyrene foams. The need to find efficient halogen free flame retardants resulted inter alia in the discovery and commercialization of hindered amine light stabilizers based on alkoxyamines (NOR-HALS). NOR-HALS provide flame retardancy of polypropylene and polyolefin fibers, non-wovens and films. Due to the sterically hindered amine structure these molecules combine flame retardancy, inherent light stability and long-term thermal stability. These alkoxyamine flame retardants can be used alone [11] or in combination with other flame retardants [11-15]. It is even possible to incorporate further flame retardant active structures chemically in one molecule e.g. in phosphorus containing alkoxyamines [16].

The performance of the NOR molecules depends on their structure i.e. the capability to degrade into nitroxyl plus alkyl or aminyl plus alkoxy radicals. Through formation of radicals a fast degradation of the polymer chain is induced and flame retardancy is achieved by removing the substrate from the flame [17-19]. On the other hand, the formed radicals are involved in the free radical chemical reactions during the combustion process. Furthermore, alkoxy amines can interact with brominated flame retardants and facilitate the release of bromine, consequently increasing the overall FR performance. Therefore, it is possible with NORs to design flame retardant polyolefin molding compositions with lower levels of halogenated flame retardants and, in addition, to eliminate antimony trioxide.

With the knowledge of the formation of specific radicals from NORs, molecules were targeted to provide an even higher concentration of radicals, e.g. Azo alkanes [20, 21], Triazenes [22] and combining NOR chemistry and Azo chemistry [23-25]. A typical structure of the latter approach is shown in Figure 1.

The flame retardant performance of Azo-NOR was tested in polypropylene films according to DIN B 4102-B2 (Table 3). Compared to the commercial NOR (BASF Flamestab NOR 116) Azo-NORs pass the test at much lower concentrations, i.e. already at 0.5 % loading. Moreover a synergistic effect of Azo-NORs with other flame retardant classes such as halogens, inorganic hydroxides or phosphorus compounds was found.

Table 3. Performance of Azo-NOR flame retardants

Flame retardant at 0.5 %	Weight loss [%]	Burn length [mm]	Pass/fail
Control (No FR)	100	190	fail
Commercial NOR	49	80	fail
Azo-NOR of Figure 1	5	27	pass

In addition the flame retardancy of PP formulations containing Azo, NOR and Azo-NOR compounds were tested through artificial weathering. As expected NOR additives contribute to light stability and extend the lifetime of the polymer under photooxidative conditions. Again the NOR-Azo molecules outperform the classical NOR. Even after 2000 hours of artificial weathering the mechanical properties and the flame retardancy are unchanged and the DIN 4102 B-2 test is passed.

Conclusions

Most flame retardants influence the (photo)oxidative stability of the polymer substrate directly through acceleration of the degradation process or indirectly by interacting with the antioxidants and light stabilizers. To improve the oxidative stability of filler type flame retarded polymers and nanocomposites, filler deactivators preferably based on glycidyl methacrylate copolymers in combination with classical antioxidants guarantee processing and long-term thermal stability. Radical generators are a growing class of flame retardants and flame retardant synergists with promising performance in polyolefins. In this area Azo-NOR compounds provide in addition to flame retardancy at low loadings, light and long-term thermal stability.

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PMAD Program at ANTEC 2014

MONDAY PM (April 28, 2014) – PMAD SESSION		
SESSION TITLE : FUNCTIONAL POLYMER MODIFICATION		
CONTROL ID	Author/ Affiliation	PAPER TITLES
KEYNOTE	Ronald Becker/Addivant	Polymer Stabilizers: Response to the Polymer Market and Solutions to Today's Opportunities
1886779	Adur, Ashok/ Vertellus Specialties	Using ZeMac® Copolymers To Upgrade Virgin Nylon Performance
1885793	Saffar, Amir/ Ecole polytechnique de Montreal	Development of Polypropylene Microporous Hydrophilic Membranes by Blending with Acrylic Acid grafted Polypropylene.
1869753	Rosen Kligvasser, Jasmine/ Technion-IIT, Haifa, ISRAEL	Controlled Migration of Antifog from Flexible Polyethylene Films
1873761	K. Akkapeddi/ Graham Packaging Co.	Some physico-chemical structural factors affecting the performance of oxygen scavenging additives in PET
1871146	Senturk-Ozer, Semra/ Polymer Dynamix	Novel Plasticizer Alternative for Polyamide Polymers
1886632	Flaris, Vicki/ Bronx Community College of CUNY	Antimicrobial Effects of Polymer Blended Triazole Derivatives

TUESDAY AM (April 29, 2014) - VINYL/PMAD CO-SESSION		
SESSION TITLE : NEW DEVELOPMENTS IN VINYL		
CONTROL ID	Author/ Affiliation	PAPER TITLES
1883379	FROM VINLY DIVISION	and Reactivity in the Chlorination of PVC Model Compounds in Radical Complexing Solvents
1886293	FROM VINLY DIVISION	Test Method Development for Outdoor Exposure and Accelerated Weathering of Vinyl Siding Specimens
1890310	FROM VINLY DIVISION	Comparison of High-Solvating and General Purpose Plasticizers on PVC Dry Blending Dynamics
1888559 (INVITED)	Lane G. Shaw/ Huber Engineered Materials	Effect of Ground Calcium Carbonate Particle Size Distribution, Milling Method, And Impurities On Abrasion Properties In Highly Filled Formulations
1871176	Qian, Zheng/ Polymer Dynamix LLC	Novel Development Flame Retardant Additive for Environmentally Friendly Flame Retardant PVC Compounds
1886222	Pivsa-Art, Sommai/ Pathumthani, THAILAND	Improvement of Thermal Stability of PVC Plastisol Dip Molding Products

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PMAD Program at ANTEC 2014, Continued

TUESDAY PM (April 29, 2014) - PMAD SESSION		
SESSION TITLE : FUNCTIONAL FILLERS/ADDITIVES FOR POLYMERS		
CONTROL ID	Author/ Affiliation	PAPER TITLES
1886202	Rul, Alicia/ Nanocyl	Importance of Processing And Converting Conditions on the Use Of Carbon Nanotubes In Thermoplastic Applications
1886395	Yang, Yuzhen/ SABIC	Sb ₂ O ₃ Free FR PBT Product Development
1865735	Levchik, Sergei/ ICL-IP, America	Polypropylene Block Copolymers Flame Retarded With The Blends of Poly(Pentabromobenzyl Acrylate) And Magnesium Hydroxide
1870926	Kim, Neung Hyun/SAMYANG Corp	Hollow glass microsphere polymer composites for uniform pearlescent appearance in Injection molded products and their mechanical and rheological properties
1871043	Forcum, Anne/ HENKEL	Effects of Surface Treatment on Hard to Bond Plastics
1888603 (INVITED)	Steve E Amos/3M	Thermal Conductivity Improvements For Plastics Through The Use of Engineered Boron Nitride
1886831	Baris Yalcin/3M	Recent Advances in Glass Bubble Polymer Compounds

WEDNESDAY AM (April 30, 2014) - PMAD TUTORIAL SESSION		
Additives and Modifiers for Plastics Moderator: Thoi Ho (Flint Hills Resources)		
Time	Author/ Affiliation	PAPER TITLES
8:00 – 8:45	Ron Becker / Addivant	The chemistry of polymer stabilization
8:45 – 9:30	Rick King /BASF	UV Stabilization: An Overview of Chemistry, Effects & Selected Applications
9:30 – 10:00	Madhusudan Chari / 3M	Benefits and use of (fluoro)polymer processing additives
10:00 – 11:00	Saied Kochesfahani / Imerys	Functions of Minerals in Plastics

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