PERSPECTIVES IN FIRE RETARDANCY OF POLYMER MATERIALS

INTRODUCTION

In the last 10 years, a rapid progress in the field of flame retardancy of polymers occurred. On the market appeared new additives, new application systems leading to an ever increasing diversity of products for which flame retardancy is a dominant requirement and in new standards and testing methods and instruments. The developments were accompanied by a pronounced effort to gain a better understanding of the underlying principles and mechanisms governing flammability and flame retardancy and to develop new mechanistic approaches for the emerging new flame retardancy systems [1].

A flame retardant should inhibit or even suppress the combustion process. Depending on their nature, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, e.g. during heating, decomposition, ignition or flame spread. The various ways in which a flame retardant can act are described in the following. They do not occur singly but should be considered as complex process in which many individual stages occur simultaneously with one dominating (e.g., using hydroxides in addition to an endothermic reaction, dilution of the ignitable gas mixture, due to the formation of inert gases, may also occur).

There are several ways in which the combustion process can be retarded by physical action:

a) *By formation of a protective layer*. The additives can form under an external heat flux a shield with a low thermal conductivity which can reduce the heat transfer from the heat source to the material. It then reduces the degradation rate of the polymer and decreases the “fuel flow” (pyrolysis gases issued from the degradation of the material) able to feed the flame. It is the principle of the intumescence phenomenon [2]. Phosphorus additives may act in similar manner. Their pyrolysis leads to pyro- or polyphosphoric species thermally stable which form a protective vitreous barrier. The same mechanism can be observed using boric acid based additives, inorganic borates or low melting glasses.

b) *By cooling*. The degradation reactions of the additive can play a part in the energy balance of combustion. The additive can degrade endothermally which cools the substrate to a temperature below that requires for sustaining the combustion process. Aluminium trihydroxide (ATH) acts under this principle and its efficiency depends on the amount incorporated in the polymer.

c) *By dilution*. The incorporation of inert substances (e.g. fillers such as talc or chalk) and additives which evolve inert gases on decomposition dilutes the fuel in the solid and gaseous phases so that the lower ignition limit of the gas mixture is not exceeded.

The most significant chemical reactions interfering with the combustion process take place in the condensed and gas phases:

a) *Reaction in condensed phase*. Here two types of reaction can take place. Firstly, breakdown of the polymer can be accelerated by the flame retardant causing pronounced flow of the polymer and, hence, its withdrawal from the sphere of influence of the flame which breaks away. Secondly, the flame retardant can cause a layer of carbon (charring), a ceramic-like structure and/or a glass to be formed on the polymer surface.

b) *Reaction in gas phase*. The radical mechanism of the combustion process which takes place in the gas phase is interrupted by the flame retardant or their degradation products. The exothermic processes which occur in the flame, are thus stopped, the system cools down, the supply of flammable gases is reduced and eventually completely suppressed. In particular, metallic oxides can act as flame inhibitors. The active radicals $HO\bullet$ are adsorbed on the surface of oxide particles. A part of collision energy is transferred to the oxides and it is formed less reactive radicals $HOO^\bullet$ than the initial radicals $HO^\bullet$. An other example, the "hot" radicals $HO^\bullet$ and $H^\bullet$ can react in gas phase with other radicals, such as halogenated radicals $X^\bullet$ issued from the degradation of the flame retardant, to create less energetic radicals [1].

It is to notice that fire retardant additive systems may be used alone or in association with other system (sometimes using low amounts of the last system) in polymeric materials to obtain a synergistic effect, i.e. the protective effect is higher that this assumed from addition of the separate effects of each system [1].

This paper reviews recent approaches for making flame retarded polymers. The mechanisms of action of flame retardant are first described and commented. Synergistic aspects are also considered. New strategies are then examined. The first considered strategy is to substitute classical polyols (char forming agent) by char forming polymers (polyamides, thermoplastic polyurethanes, polycarbonate …) in intumescent systems. The advantage of this concept is to obtain flame-retarded (FR) polymers blends with improved mechanical properties in comparison with polymers loaded with classical formulations and to avoid the problems of water solubility of the polyols and of their migration. Polymer clay nanocomposites exhibit a combination of unique properties, such as increased heat distortion temperature, reduced permeability, improved mechanical properties [3] and also, as pointed out by Gilman et al., reduced flammability [4]-[7]. To achieve these properties, mica-type layered silicates, such as montmorillonite (MMT), are generally dispersed at the nanoscale level in the polymer to yield the so-called "nanocomposite". The second strategy is thus to combine the "nanocomposite" approach with intumescent systems in order to investigate potential synergistic effects. Finally, the third strategy is to use surface treatment (cold plasma treatment) to make FR polymer. This approach has the advantage to not modify the intrinsic properties of the materials [8]. The potentiality is examined and discussed.

CREPIM CREPIM

I THE MOST IMPORTANT FLAME RETARDANTS AND THEIR MODE OF ACTION

The market of the flame retardant (FR) is international and is mainly constituted by ATH, $Mg(OH)_2$, phosphorus-containing compounds including organic phosphates, halogenated compounds, antimony trioxide and nitrogenated compounds which act in gas and/or condensed phase.

Flame retardants acting through gas phase mechanism

The most effective commercial fire retardants are halogen containing compounds often used in combination with metallic compounds. The widely accepted mechanism of fire retardancy of these systems is based on chemical reactions which occur mainly in gas phase [1] although some studies have shown that condensed phase reactions with the polymeric matrix may also be involved [9-13].

Due to the release of halogenated acid during decomposition, halogen containing compounds interrupt the chain reaction of combustion by replacing the highly reactive $OH^\bullet$ and $H^\bullet$ radicals by the less reactive halogen $X^\bullet$. Flame inhibition studies have shown that the effectiveness decreases in the order : HI>HBr>HCl>HF [14-15]. Brominated and chlorinated organic compounds are generally used because iodides are thermally unstable at processing temperature and effectiveness of fluorides is too low. The choice depends on the type of polymer for example in relation with the behaviour of the halogenated fire retardant in processing conditions (stability, melting, distribution, etc…) and/or effect on properties and long-term stability of the resulting material. In particular, it is advisable to use an additive which supplies the halide to the flame in the same range of temperature at which the polymer decomposes to combustible volatile products. Thus, fuel and inhibitor would reach the gas phase together according to the “right place at the right time” principle [16].

Several metallic compounds which when used alone do not impart significant fire retardant properties to polymers, can strongly enhance the effectiveness of halogenated compounds [13-14]. These mixtures evolve on heating metal halides which are well-known flame inhibitors with greater effectiveness than hydrogen halides. The metal halides give metal oxides in the flame, with elimination of hydrogen halide. The most widely used synergistic agent is the antimony trioxide.

Flame retardant-polymer interaction in the condensed phase

As a rule there is in the condensed phase a chemical interaction between the flame retardant agent, which is usually added in substantial amounts, and the polymer. This interaction occurs at temperatures lower than those of the pyrolytic decomposition [19].

CREPIM

Dehydration

The varying efficiency of phosphorus compounds in different polymers has been related to their susceptibility to dehydration and char formation. Cellulosics are adequately flame retarded with ca 2% of P, whereas 5-15% are needed for polyolefins. The interaction of P derivatives with the polymers not containing hydroxyls is slow and has to be preceded by an oxidation. It has been suggested that 50-99% of the P derivatives are being lost by evolution, possibly of P_2O_5 or other oxides formed from the pyrolysis of the P derivatives [20]. This may be one of the reasons for the low yield.

Intumescence

Flame retarding polymers by intumescence is essentially a special case of a condensed phase mechanism. Intumescent systems interrupt the self-sustained combustion of the polymer at its earliest stage, i.e. the thermal degradation with evolution of the gaseous fuels. The intumescence process result from a combination of charring and foaming of the surface of the burning. The resulting foamed cellular charred layer which density decreases with temperature [21] protects the underlying material from the action of the heat flux or of the flame. Intumescent formulations contain three active additives : an acid source (precursor for catalytic acidic species), a carbonific (or polyhydric) compounds and a spumific (blowing) agent (Table 1).

Table 1 : Examples of components of intumescent coatings [2].

Inorganic acid source *Acids* Phosphoric Sulfuric Boric *Ammonium salts* Phosphates, polyphosphates Sulfates Halides *Phosphates of amine or amide* Products of reaction of urea or Guanidyl urea with phosphoric acids Melamine phosphate Product of reaction of ammonia with P_2O_5 *Organophosphorus compounds* Tricresyl phosphate Alkyl phosphates Haloalkyl phosphates	Polyhydric compounds STARCH Dextrin Sorbitol Pentaerythritol, monomer, dimer, trimer Phenol-formaldehyde resins Methylol melamine Amines/amides UREA Urea-formaldehyde resins Dicyandiamide Melamine Polyamides Others Charring polymers (TPU, …)

CREPIM

Physical effects

Flame retardancy due to physical effects usually requires relatively large amounts of additives: 50-65% in the case of aluminium trihydrate (ATH) and magnesium hydroxide ($MgOH_2$). The activity of these additives consists : (a) dilution of the polymer in the condensed phase; (b) decreasing the amount of available fuel; (c) increasing the amount of thermal energy needed to raise the temperature of the composition to the pyrolysis level, due to the high heat capacity of the fillers; (d) enthalpy of decomposition - emission of water vapour; (e) dilution of gaseous phase by water vapour - decrease of amount of fuel and oxygen in the flame; (f) possible endothermic interactions between the water and decomposition products in the flame; (g) decrease of feedback energy to the pyrolysing polymer; (h) insulative effect of the oxides remaining in the char; (i) charring of the materials [22].

Nanocomposites

The pioneering work of Gilman et al. has pointed out the way to organo-modified montmorillonite clay which contributes to a substantial improvement in fire performance in polymeric matrices such as polystyrene and polyamides [4]-[7]. Peak of RHR (Rate of Heat Release) is decreased by from 50 up to 70% in a cone calorimeter experiment. It is assumed that the accumulation of clay at the surface plays the role of protective barrier as a main mechanism of protection but that the clay may also modify the degradation pathway of the polymer.

Pre-ceramic additives

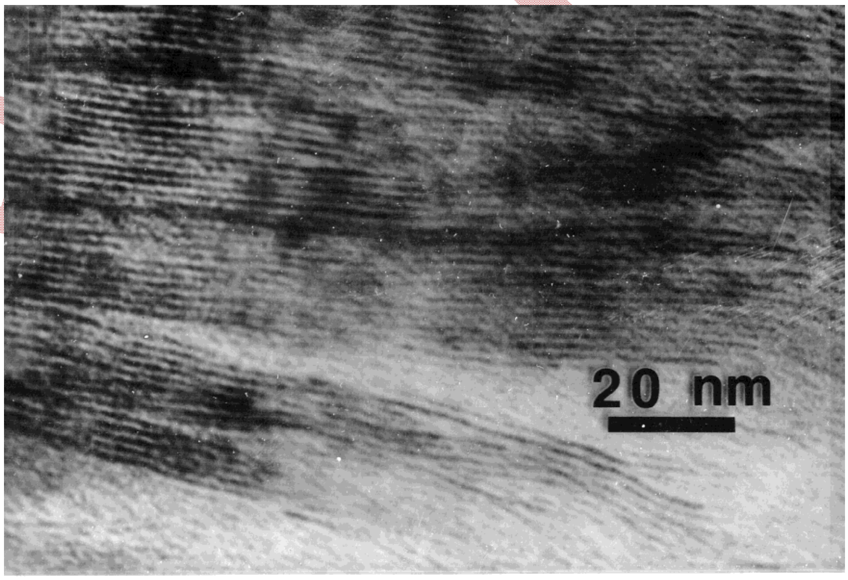
A new generation approach of nanocomposites is the development of nanostructured chemical feedstocks based on polyhedral oligomeric silsesquioxanes (or POSS). The nanoscopic size of POSS enables POSS segments to effectively reinforce polymer chains-segments and control chain motion at the molecular level through maximizing the surface area and chemical interactions of the nanoreinforcement with the polymer [27]. Lichtenhan et al. [28] have shown the efficiency of using POSS in commodity and engineering polymers. As an example, peak of heat release rate (external heat flux = 35 kW/m^2) of polyether block amides polymer (PEBAX) is decreased by 77% when using POSS compared to virgin polymer. The suggested mechanism is char formation at the surface of the material which can act as an insulative barrier. The organic groups on POSS cages undergo homolytic Si-C bond cleavage at ~300-350°C in air. This process is immediately followed by fusion of POSS-cages to form a thermally insulating and oxidatively stable silicon-oxycarbide “blackglass” surface char (“Si-O-C ceramified char”).

II POLYMER/CLAY HYBRID NANOCOMPOSITE AS INGREDIENT FOR INTUMESCENCE

It is well known that the use of nanocomposite in polymers improves their mechanical properties. The basic idea here is to combine char forming polymer nanocomposite in intumescent formulations to improve both FR performance and mechanical properties of the polymer [29]. The concept is evaluated with the combination of Ammonium PolyPhosphate (APP)/PA-6 as intumescent system in an EVA (EVA24 ; EVA containing 24 wt.-% vinyl acetate).

When burning the EVA24-APP/PA-6 and EVA24-APP/PA-6-nano (PA-6nano: PA-6 clay hybrid exhibiting an exfoliated structure) formulations, it is observed the formation of an intumescent char which smothers the flame. In terms of LOI (Limiting Oxygen Index), a synergistic effect is observed in both EVA24-APP/PA-6 and EVA24-APP/PA-6-nano formulations. This effect is observed at APP/PA-6 mass ratios equalling 3. One can observe that the use of PA-6-nano improves the values (from 32 vol.-% without exfoliated clay to 37 vol.-% with clay at APP/PA-6 = 3 (wt/wt)). V-0 rating is achieved for 13.5 ≤APP≤ 34 wt.% without clay and for 10 ≤APP≤ 34 wt.% with clay (the total loadings in APP/PA-6 and APP/PA-6-nano remain equalling 40 wt.-%). This result shows that the use of PA-6-nano in the formulation allows V-0 rating to be achieved at relatively low loading in APP (10 wt.-% in comparison with 13.5 wt.-%). It is a real advantage because it permits to decrease the amount of APP in the formulation which can lead sometimes to a blooming effect and to its migration throughout the polymer. It also permits the preservation of mechanical properties.

Figure 1 : polyamide 6 nanocomposite



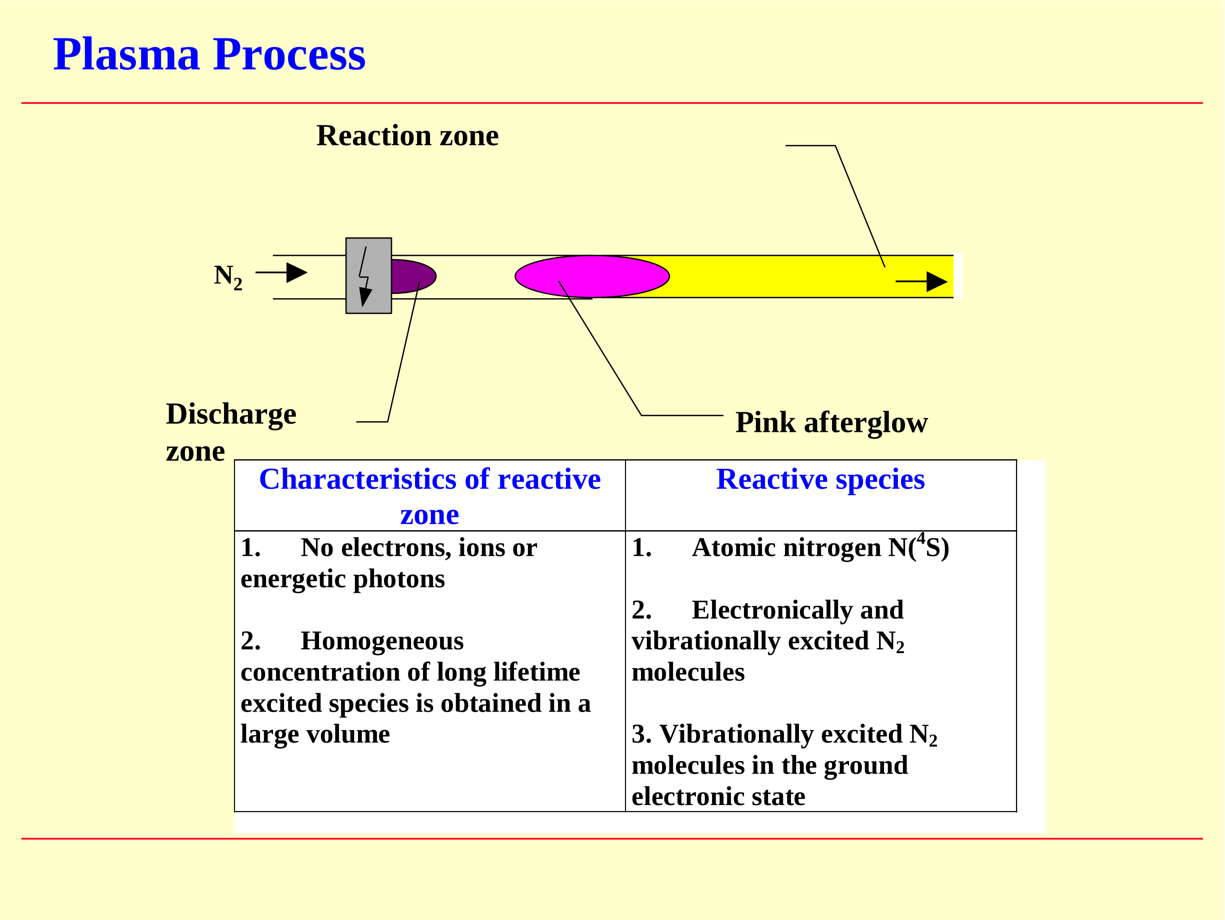
The RHR values of the intumescent EVA-based polymers are strongly reduced in comparison with the virgin EVA-24. It also is confirmed that the use of PA-6-nano improves the FR performance: RHR peak = 320 kW/m² with PA-6 and RHR peak = 240 kW/m² with PA-6-nano. Visually a char layer is formed and intumescences after the ignition of the material. The height of the intumescent shield is about 1.5 cm.

Nevertheless after combustion, the intumescent residue of the formulation containing PA-6nano seems to be less fragile than this one without PA-6nano.

III PLASMA TREATMENT FOR FLAME RETARDANCY

Another route for making polymer with low flammability is to modify its surface laying down a thin film on the polymer using plasma assisted polymerisation techniques [8]. Cold remote nitrogen plasma (CRNP) assisted polymerization of organosilicone compounds is an interesting preparation technique of thin polysiloxane based films. These polymers are known to have good thermal stability and flame retardancy properties of interest. CRNP process is used to deposit thin films on a PA-6 and PA-6nano substrate by reaction with 1.1.3.3-tetramethyldisiloxane monomer. LOI of PA-6 and PA-6nano treated by CRNP jump from 21 and 23 vol-% to 25 and 46 vol.-% respectively. These good results are confirmed by cone calorimeter experiment. Peaks of RHR compared to virgin PA-6 are decreased by 30% and by 60% for PA-6 and PA-6nano treated by CNRP. This approach appears as very interesting because only one treatment of a polysiloxane coating of about 10 µm thick on polymer allows to get low flammability, but also, film deposition or hindering of additives diffusion out of the host matrix, and it can be expected that the mechanical properties of the polymer are not significantly modified.

Figure 1: plasma process overview



Plasma Process

Characteristics of reactive zone	Reactive species
1. No electrons, ions or energetic photons 2. Homogeneous concentration of long lifetime excited species is obtained in a large volume	1. Atomic nitrogen N(^{4}S) 2. Electronically and vibrationally excited N_2 molecules 3. Vibrationally excited N_2 molecules in the ground electronic state

CONCLUSION AND OUTLOOK

This paper has reviewed different ways to achieve flame retardancy of polymeric materials via several concepts. The approach of char forming polymers as additives (blend technology) in an intumescent formulation is a promising way for intumescence because it allows materials to combine acceptable mechanical properties and fire retardancy. "Nanocomposite approach" provides low flammability and enhances mechanical properties but it is not able to pass tests such as V-0 rating at UL-94 test required for many industrial sectors. However, the combination "intumescence via the blending approach and nanocomposite" enhances both flame retardancy and mechanical properties, and allows to pass many specifications (as an example, design of EVA-based materials for flame retarded low voltage cable and wire). It seems to be one of the most promising ways for designing new efficient intumescent materials. Finally, plasma is technique emerging in the field of flame retardancy. It provides pretty new perspectives to design flame retarded polymer without alteration of its structure and of its intrinsic properties (mechanical properties). As a bonus, the surface aspect of polymer may be enhanced.

CREPIM

REFERENCES

1. Lewin, M., 1998. *In: Fire Retardancy of Polymers : The Use of Intumescence*, Le Bras, M., Camino, G., Bourbigot, S. & Delobel, R. (Editors), The Royal Chemical Society (Publisher), Cambridge, pp. 3-34.
2. Vandersall, H.R., *J. of Fire Flammability*, 1971, 2, 97.
3. Alexandre, M.; Dubois, P. *Mat. Sci. Eng. R.*, 2000, 28(1-2), 1-63.
4. Gilman, J. W.; Kashiwagi, T.; Lichtenhan, J. D. *SAMPE J.*, 1997, 33, 40-46.
5. Gilman, J. W. *App. Clay Sci.*, 1999, 15(1-2), 31-49.
6. Gilman J.W.; Kashiwagi T.; Giannelis E.P.; Manias E.; Lomakin S.; Lichtenhan J.D.; Jones P. 1998. *In: Fire Retardancy of Polymers – The Use of Intumescence* ; Le Bras M.; Camino G.; Bourbigot S.; Delobel, The Royal Society of Chemistry: Cambridge, 223-235.
7. Gilman, J.W.; Jakson, C.L.; Morgan, A.B.; Harris, R.H.; Manias, E.; Giannelis, E.P.; Wuthenow, M.; Hilton, D.; Philips, S.H. Chem. Mater. 2000, 12, 1866-1873.
8. Jama C., Quédé A., Le Bras M., Delobel R., Goudmand P., Dessaux O., Bourbigot S., Gilman J.W. and Kashiwagi T., *ACS Symposium Series N° 797*, 2001, Chapter 16, pp. 200-213.
9. Lewin, M;, 1998. *In: Proceedings of Recent Advances in Flame Retardancy of Polymeric Materials*, Volume 9, Lewin, M. (Editor), BCC inc.(Publisher), Norwalk (CT, USA).
10. Green, J., 1998. *In: Proceedings of Recent Advances in Flame Retardancy of Polymeric Materials*, Volume 7, Lewin, M. (Editor), BCC inc.(Publisher), Norwalk (CT, USA).
11. Pal G. et McSkasy H., 1991. In : « Studies in Polymer Science 6 - Plastics, their Behaviour in Fires », Elsevier Sci. Pub. Co, New-York (USA), pp. 304-332
12. Hindersinn, R.R. and Witschard, G., 1978. *In: Flame Retardancy of Polymeric Materials*, Kuryla, W.C. and Papa, A.J. (Editors), Dekker, M. (Publisher), New-York, Vol. 4, Chapter 1.
13. Camino, G. and Costa, L., *Polym. Deg. & Stab.*, 1988, 20, 271.
14. Coulees, C.F. and Hirschler, M.M., 1981. *In: The Combustion of Organic Polymers*, Clarendon Press (Publisher), Oxford.
15. Schwarz, R.J., Kuryla, W.C. and Papa, A.J., 1973. *In: Flame Retardancy of Polymeric Materials*, Kuryla, W.C. and Papa, A.J. (Editors), Decker, M. (Publisher), New-York, Vol. 2, Chapter 2.
16. Rhys, J.A., 1969. *Chem. Ind.* (London), 187.
17. *In: Developments in Polymer Degradation-7*, 1987. Camino, G. and Grassie, N. (Editors), Applied Science (Publisher), London, Chapter 7.
18. *In: Flame Retardant Polymeric Materials*, 1982. Lewin, M., Atlas, S.M. and Pearce, E.M., Plenum Press (Publisher), Vol. 3.
19. Weil, E.D., Hansen, R.H. and Patel, N., 1990. *In: Fire and Polymers I* (Chap. 8), Nelson, G.L. (Editor), ACS Symp. Series 425, Washington DC, 97.
20. Brauman, S. K., *J. of Fire Retardant Chemistry*, 1977 4. 18.
21. Bourbigot, S. and Leroy, J.M., 1998. *In: Fire Retardancy of Polymers : The Use of Intumescence*, Le Bras, M., Camino, G., Bourbigot, S. & Delobel, R. (Editors), The Royal Chemical Society (Publisher), Cambridge, pp. 129-139.
22. Hornsby, P. R., *Fire and Mater.*, 1994 18, 269.
23. Hornsby, P. R. and Watson, C. L., *Polym. Deg. & Stab.*, 1990, 30, 73.
24. Molesky, F., 1990. *In: Recent Advances in Flame Retardancy of Polymeric Materials*, Vol. 1, Lewin, M. and Kirshenbaum, G. (Editors), BCC inc.(Publisher), Norwalk, p.92.
25. Levesque, J., 1990. *In: Recent Advances in Flame Retardancy of Polymeric Materials*, Lewin, M.and Kirshenbaum, G. (Editors), BCC (Publisher), Vol. 1, p.102.
26. Kalisky, O., Mureinik, R. J., Weismann A. and Reznik, E., 1993. *In: Recent Advances in Flame Retardancy of Polymeric Materials*, Vol. 4, Lewin, M. and Kirshenbaum, G. (Editors), BCC inc. (Publisher), Norwalk, p.140.
27. Lichtenhan, J.D., Haddad, T.S., Schwab, J.J., Carr, M.J., Chaffee, K.P., and Mather, P.T., 1998. *Polymer Preparation (ACS - Division of Polymer Chemistry)* 39(1), 489.
28. Lichtenhan, J.D.; Gilman J.W. *US Patent 6,362,279* (2002) assigned to US Air Force.
29. Bourbigot S., Le Bras M., Dabrowski F., Gilman J.W. and Kashiwagi T., *Fire & Mater.,* 2000, 24, 201-208.