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GEORGE OLAH PhD SCHOOL**

Development of flame retarded polyolefine systems containing nanoparticles

Theses of Ph.D. Dissertation

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2009

## INTRODUCTION

The strict European regulations, proposed in the past few years directed the attention not only to the costs and competitiveness aspects but also to the environmental and safety aspects. As a consequence of this progress the range of the industrial fields where the plastic products should meet a complex set of requirements is enlarging rapidly. The basic mechanical, acoustic and recyclability requirements should be combined with high performance of flame retardancy. The world market for polymers will continue to grow in the next decades according to its favorable cost/benefit ratio. The polyolefines have a leading position among the polymers as they can be easily processed by various technologies. Polypropylene (PP) is one of the fastest growing polymers in the world. A recent market research report forecasts the consumption of PP to reach 52 million tons by the end of 2010. The polyolefines that are most widely used are the least expensive but tend to be the most flammable. Flammability, which generally refers to the propensity of a substance to ignite easily and burn rapidly with a flame, is one indicator of fire hazard. The usage of flame retardants (FR) in plastics, according to general context, improves their performance in case of fire significantly.

Therefore, the demand for efficient flame retardants is increasing in multiple areas such as building and construction, transport, electric and electronic engineering (E&E), furniture, etc.

The FR materials must be compliant with the new market and legislative environmental requirements. Thus some of the efficient halogen-based FR additives have been banned due to potential risks related to their decomposition products. The progressive shift away from halogenated FR, has led to a new interest in mineral fillers and intumescent fire retardants. Nanotechnology will also play a key role in improving fire-retardant performance and reducing production costs.

The advantages and the potentials of usage of the nanostructured additives as efficient and environmental friendly additives in flame retardancy of polymers have been widely studied. But nowadays, it is clear that the nanoadditives such as clays or carbon nanotubes can only perform FR effect in a certain flammability properties. As one can notice in other areas of material science, in case of flame retardancy of polymers the composite materials approach might be the solution. The fact that the FR mechanism of nanoadditives is completely unknown or partly unknown makes the development of multicomponent systems more difficult. In order to improve the efficiency of FR systems it is necessary to know the basic FR mechanism of nanoadditives.

As the number of FR additives and so that the possible FR combination increased with the usage of nanoadditives a need appears for a characterization technique which is able to model the fire scenario and analyze fast both the condense and gas phase with low sample need.

After the review and systematization of the relevant literature, in the course of the experimental part our overall aim was to investigate the **real potentials of nanoadditives** (such as montmorillonite, sepiolite and carbon nanotubes) **in flame retardancy** of polymers and to **develop halogen-free flame retardant additive systems**, which may be able to substitute halogenated additives and improve the performance of composites. In order to develop multi-component systems first of all the **basic FR mechanisms of nanoadditives** were investigated. This was planned by preparing polymer composites of unmodified nanofillers followed by determination of their fire resistance in function of morphology, chemical composition and concentration of nanoadditives. The results and the FR mechanism were discussed in point of view of the chemical, structural and thermo physical of nanoadditives. During the investigation of mechanisms a need appeared for **development of a new characterization system and methodology** for help to better understanding the role of nanofillers in flame retardancy. During the development of coupled system emphasis

was placed on ability of modeling the fire circumstances on a small sample and on-line monitoring the chemical changes in the condense- and gas phase as well. In order to increase the flame retardant efficiency of the additive systems we intended to recognise synergistic effects by **combining nanoadditives together and with traditional FR additives**. Our work also aimed to define the role of nanoadditives in these multi-component systems. The further increase of flame retardant efficiency was planned to perform by combining nanoadditives with various **polymers having flame retardant activity** and with the goal of reduction the non-polymeric material ratio in the composites. It was also aimed to achieve higher reduction in non-polymeric material ratio by forming **multilayer systems** where the outer layers consist of the previously developed flame retarded composites.

## 2. MATERIALS AND METHODS

The composites were prepared in polypropylene (PP) matrix with various melt flow index. Ethylene vinyl acetate (28% va. content) was also used for model experiments. Composites containing nanoadditives were prepared by using three types of additives. Two types of clays with different morphology: montmorillonite (MMT, Microtec<sup>®</sup>) with layered structure and sepiolite (SEP, Pangel S9<sup>®</sup>) with needle like structure. Two types of carbon nanotubes were applied for composites preparation: multi-walled (MWCNT, Nanocyl-3100<sup>®</sup>) and double-walled (DWCNT, Nanocyl-2100<sup>®</sup>).

Maleic acid anhydride grafted PP (PPgMA, Licomont AR504<sup>®</sup>) was used in same quantity as the filler in order to improve the compatibility between the polymer matrix and nanofillers. Organically modified montmorillonite (OMMT, Bentone SD-1<sup>®</sup>) and sepiolite OSEP, Pangel B40<sup>®</sup>) were also applied as clay additives. The carbon nanotubes were used in untreated forms.

The effect of nanoadditives was investigated in combination with traditional flame retardants such as intumescent system (ammonium-polyphosphate (APP, Exolit 422<sup>®</sup>) and pentaerythritol (PER, Montedison Spa.)) and magnesium hydroxide (MH, Magnifin<sup>®</sup> H5MV). The nanoadditives were combined with polymers (polyboroxosiloxane and epoxy resin) which have flame retardant effect. The polyboroxosiloxane based composites were prepared using hydroxyl terminated polydimethylsiloxane (PDMS, {HO-[Si(CH<sub>3</sub>)<sub>2</sub>O]<sub>n</sub>-H}), Silicone OEL CT-601M<sup>®</sup>) crosslinked with boric acid and tetraethoxysilane in presence of catalytic agent (dibutyl-tin-dilaurate, Szilorka K-1<sup>®</sup>). The epoxy resins were prepared by using epoxy component (AH16, Eporezit AH-16<sup>®</sup>) cured either with commercially available reactive amine (T58, Eporezit T-58<sup>®</sup>) or with laboratory synthesized phosphorus-containing reactive amine (TEDAP).

The composites were prepared in Brabender PL2000 internal mixer (mixing head W 50 type). Before melt processing the powder of PPgMA and nanoadditives was premixed (weight ratio: 1:1), then the mixture was added to the molten PP. The specimens for tests were formed by compression molding in Collin P200 press.

The thermal stability of the materials was characterized by thermogravimeter (TG). The structure analyses were carried out using X-ray diffractometer (XRD), transmission electron spectrometer (TEM) and scanning electron spectrometer (SEM).

The chemical composition of the condense phase was determined by X-ray photoelectron spectroscopy, Raman and ATR-FTIR spectroscopy. The chemical changes in gas phase were monitored by EGA technique. A rheological method for char characterization was carried out in TA Instruments AR2000 type rheometer in oscillation method. The fire resistance of the composites and references was characterized by Mass Loss Calorimeter, UL-94 tests and Limiting Oxygen Index measurements.

## THESES - SUMMARY

The most important conclusions and the new scientific achievements of this PhD thesis are the following:

1. New mechanistic approaches have been established regarding to flame retardancy of polymers. The flame retardancy performance of nanoadditives of various morphology (layer and needle like) and of various chemical composition was compared. The effect of the morphology and chemical composition on the fire behavior was determined. We established by flammability tests and calorimetric analysis that the different nanoadditives affect the fire behaviors (burning rate, dripping, time to ignition, peak- and total heat release rate) in various ways. The advantageous effects of nanoadditives on the flame retardancy of composites were deduced from the following three basic FR mechanisms: i. chemical-catalytic effect, ii. structural-mechanical effects, iii. thermophysical effect.
  - We proved by modified clay model systems that the variable-valence metal content of the clays is a critical factor in thermal stability of polymer/clay composites. For instance, through its catalytic effect the iron content of clays accelerate the formation of gaseous degradation products decreasing the time to ignition (TTI) of the composites. We confirmed that the influence of clays on TTI is more complicated than it was earlier published in literature. We proposed that the catalytic and thermophysical effects of clays should be also taken into consideration along the bubble-nucleating effect.
  - We proved by Raman and FTIR-ATR spectroscopic condense phase studies that the catalytic features of clays affect not only the first period of burning but also the later stage processes. We point out that in presence of clay the carbonization of composites is accelerated as well as the formation of carbonaceous barrier surface layer.
  - Based on computer simulation of the laser pyrolysis of PP/CNT and PP/clay we showed that the condense phase during the burning is a dynamically changing system. In case of PP/CNT a lower surface temperature and a faster thermal equalization were calculated than in PP/clay composite. According to calculations, we determined that the surface of PP/clay act as an insulating layer. This statement was confirmed also by laboratory experiments. We proved by thermogravimetric analysis that the thermophysical properties of nanoadditives have a significant influence on the thermal stability of composites.
  - Based on varied temperature rheology measurements we established that the nanoadditives have a remarkable reinforcing effect on the carbonaceous barrier surface layer. We found that this effect depends on the morphology and the thermal stability of the nanoadditive. The needle like particles such as carbon nanotube and sepiolite increase the strength of residue more than the montmorillonite with layer structure. From SEM analysis we concluded that in case of needle like particles a network structure is formed on the surface during the burning. These networks decrease the heat release more efficiently than the barrier layer containing layered nanoadditives.
2. A new analytical system and characterization methodology have been developed, which is suitable for the simulation of the rapid thermal degradation caused by fires. The results suggest that the method is applicable for monitoring the chemical changes in condense and in gas phases.
  - Applying the recently developed LPyr-FTIR evolved gas analyzer system we proved that the iron content of clays affects mainly the dynamics of formation of the gaseous degradation products: at the beginning an intensive and than a gradually slowing down of gas formation was detected.
  - Concerning the thermal degradation mechanism of polymers a better understanding was given by LPyr-Raman analysis through connecting the condense phase processes with

changes in gas phase. The observed reduction in formation rate of gaseous degradation products is the consequence of the detected catalytic effect of nanoadditives resulting in an activated carbonization in the condense phase.

- A new degradation step of poly(ethylene-vinyl acetate) has been determined by LPyr-Raman and LPyr-FTIR studies. We detected the scission of the chain in the neighborhood of acetate group and formation of acetate-esters derivatives of short carbon chain as a first degradation step, before the cleavage of acetate group.
3. New flame retarded composites have been developed by combining nanostructured additives and traditional FR additives. We established that the combination of nanoadditives with each other or with traditional flame retardants is an efficient way to improve the FR performance of the composites.
    - We found that the fibrous SEP and layered MMT clay nanofillers act synergistically. It was proved that the morphology, the catalytic and barrier layer reinforcing effects of the nanofillers play an important role in flame retardancy. The heat conductivity of the fillers has no significant effect on the fire properties comparing the sepiolite and carbon nanotube containing systems.
    - We found that the flame retardancy of PP composites can be improved advantageously by combining nanoclays as synergistic additive with magnesium-hydroxide. The FR effect of these nanofillers depends on the total amount of additives.
  4. The thermal stability and the flammability of PP have been improved by blending with flame retarded epoxy resin (PEP). Concerning the thermal stability of organomodified clays it was stated that the clays with thermoset interlayer are thermally more stable than the clays modified with the widely used quaternary ammonium salts. We found that the FR efficiency of the phosphorylated epoxy resin (PEP) in polyolefine matrix can be further improved by using as nanofiller interlayer. Based on SEM and thermoanalytical analyses the favorable effect of nanofillers in these systems can be explained by better dispersion and the activation effect of the clay on the carbonization process.
  5. A new phosphorus- and halogen and phosphorus free flame retardant system has been developed. This environmental friendly additive system contains polyboroxsiloxane (BSil), melamine-borate and sepiolite. It was determined that at the burning temperature the BSil forms glassy-/ceramic like protective layer. It was stated that the melamine-borate plays role in both forming a foamed structure by its decomposition and helps to form the ceramic layer due its boron content. The sepiolite dispersed in polysiloxane elastomer matrix increase the strength of the foam structure. The flame retardant performance of the FR system was originated to the efficient gas barrier properties and to the heat and mechanical resistance of the protective layer.
  6. The recently developed PP/PEP and PP/BSil polymer based FR composites were applied as outer layer in multilayer systems prepared by co-extrusion technology. It was established that the heat release rate during the fire significantly reduced by forming few hundreds micron thickness outer layer. According to vertical burning test this multilayer systems provide self extinguish rate that meets the most strict flammability standards. Applying epoxy resin or polyboroxosiloxan elastomer the hydrophilicity of the PP surface can be controlled.

### **Exploitation perspectives of results**

The unrealistic expectations for nanocomposites were clarified by results and findings published in this thesis. On the other hand by recognizing the synergistic effects of nanoadditives bring the application of nanofillers in new polymeric systems into the reality. The combined FR additive systems, providing both application and economic benefits,

initiated further research and development programs. In cooperation with PEMÜ Plastic Processing Co. Ltd. new products have been developed for automotive application.

The recently developed characterization technique provides essential information about the so called "dark flame" zone and thereby helps to investigate the mechanism of flame retardants. The spreading of this technique might give an impulse to research of the flame retardancy of polymer.

The results of PhD dissertation were utilized in the NANOFIRE (Environmentally friendly multifunctional fire retardant polymer hybrids and nanocomposites, Project no.505637) European Union project. In the frame of this international project new polymer hybrids and nanocomposites have been developed in collaboration with Italian, French and German firms and academic institute.

#### List of publications related to the thesis

- I. A. Szabo, **B. Marosfoi**, P. Anna, G. Marosi, Complex Micro-analysis Assisted Design of Fire Retardant Nanocomposites- Contribution to the Nano-mechanism, Fire Retardancy of Polymers, New Strategies and Mechanisms, (ed. K. Kandola and R. Hull), The Royal Society of Chemistry, **6**, 74-91 (2008). (*IF: 0*)
- II. **B. B. Marosfoi**, G. Marosi, A. Szabo, B. Vajna and A. Szep, Laser pyrolysis micro-spectroscopy for modelling fire-induced degradation of ethylene-vinyl acetate systems, *Polym. Degrad. Stabil.*, **92** (12), 2231-2238 (2007). (*IF: 2,1, I: 1*)
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### Oral presentations

1. **B.B. Marosfoi**, B. Bodzay, T. Igricz, G. Marosi, Polymer degradation studies using laser pyrolysis-FTIR microanalysis 5<sup>th</sup> International Conference on Polymer Modification, Degradation and Stabilization, 8<sup>th</sup>-11<sup>th</sup> September 2008, Liege, Belgium
2. B. Bodzay, **B.B. Marosfoi**, T. Igricz, K. Bocz, G. Marosi, Polymer Degradation Studies Using Laser Pyrolysis-FT-IR Microanalysis, 18<sup>th</sup> International Symposium on Analytical and Applied Pyrolysis, 18<sup>th</sup> -23<sup>th</sup> May 2008, Costa Teguisse - Lanzarote, Spain
3. Gy. Marosi, **B. Marosfoi**, Zs. Nagy, Gy. Bertalan, A. Toth, Stability features of advanced composites, 3<sup>rd</sup> China-Europe Symposium on Processing and Properties of Reinforced Polymers, 11<sup>th</sup>-15<sup>th</sup> June 2007, Budapest, Hungary
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9. **B. Marosfői**, E. Zimonyi, Gy. Marosi, Use of Various Surface Modified Nanoparticles as Flame Retardant Synergists, 10<sup>th</sup> European Meeting on Fire Retardant Polymers, 7<sup>th</sup>-9<sup>th</sup> September 2005, Berlin, Germany
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