Development of new type of fire retarded polypropylene systems

Theses of Ph.D. Dissertation

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1. Introduction, aims

In the last decade the application area of those plastics and fibers expanded mainly, which possess special, new properties distinguishing them from the general products. In most of these application areas – automotive industry, electronical industry, building industry, protective clothing- the reduced flammability or entire flame retardance is a basic requirement.

Due to their favourable price, advantageous physical and chemical properties and simple, versatile processing the polyolefines are increasingly preferred among the different types of polymers.

The development of flame retarded types became also an important issue because countries the polyolefines can be applied only in flame retarded form in the most industrialized due to the increased attention to safety regulations.

The research of the flame retardancy in Hungary began in the 1970's. Methods were developed for the industrial control of the flammability of the polymers at the Polymer Research Institute. At the Budapest University of Technology Judit Simon and her co-workers published numerous articles on halogene-, phosporus- and nitrogen-containing flame retardant additives and on the processes taking place during the burning examined by thermoanalytical and atomic absorption methods.

However, most of the relevant periodic and patent literature is in connection with the recent results of the international research. After their review and evaluation, our aim was, in the course of the experimental work, to develop a stable and halogen-free flame retardant additive system, which may be able to substitute expensive technical plastics and can be produced by a simple technology. This was planned by the modification of the ammonium polyphosphate based intumescent systems and by eliminating their disadvantageous properties (stability-, processing problems).

After the basic characterization of the components, their hydro-thermal stability was intended to increase by applying surface modification techniques. During the experiments we wished to confine the moisture adsorption of the ammonium polyphosphate during the storage and the reaction between the components of the intumescent additive system leading to development of water, because without this, the flame-retarded system cannot result in a product with appropriate quality.

The chemically or physically modified additives respectively were qualified by surface analytical methods, the effect on the hydrolitical and thermal stability was characterized by thermal analytical and conductometric measurements.

After the characterization and amelioration of hydrothermal stability of the modified additives, we planned to develop polyolefin based flame retarded systems. During the development emphasis was placed on the study of the effect of shear stress during the mixture preparation on the structure of the flame retardant additives.

In order to increase the flame retardant efficiency of the additive systems with appropriate hydrothermal stability we intended to limit the mass transport on the surface of the burning polymer by the combination of the flame retardant additives and other synergistic intermediates. With the help of the novel modifications we also wished to contribute to the better understanding of the mode of action of flame retardant additive systems.

We also aimed to increase the flame retardant effect by using the possibilities hiding in the mode of action of nanocomposites, so the combination of the additive systems developed by us and the clay minerals. The investigation of the mechanism of the combined flame retardant nanocomposite system made up an important part of our plans.

2. New scientific results

1. It was established that the hydrolytic stability of ammonium polyphosphate (APP) flame retarded additive can be improved significantly by surface treatment with suitable surfactant (glycerol monostearate). Consequently, the flame retardant components are hindered from migrating to the surface during utilization. Decrease of the water sensibility was determined by thermogravimetric methods. The formation of the chemically bonded protective layer was checked with the XPS method.
2. Melamine protective layer on the surface of ammonium polyphosphate was formed using a physical coating process. The aim of this modification was to produce a material of similarly excellent hydrolitical stability like melamine polyphosphate (MPP) having. The comparison of XPS data of the surface-treated ammonium polyphosphate to those of melamine polyphosphate showed that the spectra of coated APP is almost identical to MPP. The XPS results were also used for calculating the thickness of melamine layer, that was 1,45 nm. The improved hydrolitical stability was confirmed by conductivity measurements.
3. In order to achieve further improvement in hydro-thermal stability silicon elastomer was used. The coating of APP with elastomer was found to be effective in delaying the esterification reaction of APP and polyol (that causes difficulties during processing because of the evolved water). The formation of polyorganosiloxane protective layer on the surface of APP particles was proven by TOF-SIMS and SEM-EDX methods in polypropylene matrix.
4. Organic siloxane polymers showed synergistic effect with ammonium polyphosphate/polyol system in fire-retardancy performance. The synthesized polyboroxo siloxanes act in a complex way: the additive

promotes the accumulation of fire retardant components on the surface in case of fire, forms a barrier layer and increases the melt viscosity of polymer to avoid dripping. Due to the applied additives other properties (hydrolitic stability, elongation at break, impact resistance) were also improved. The presence of boric atom has an important role in the efficiency of polyboroxo siloxanes: it increases the residue of the polysiloxane during burning and forms a coherent glassy/ceramic layer on the polymer surface. Using XPS method it was proven that the transformation of polyboroxo siloxane to inorganic (ceramic) layer is not complete at the temperature of fire. This is an advantageous behaviour, which preserves the deformable, durable character of the protecting layer on the surface.

5. Combination of two mechanism for barrier layer formation, the use of nanoparticles (montmorillonite) and organic polymer precursors (polyboroxo siloxanes), is a new way for improving the performance of flame retarded polymers. Forming an interfacial layer around nanoparticles and their combination with the intumescent fire retardant system had a beneficial effect on the fire performance. The system showed good fire resistance even at ignition in vertical position. We composed a schematic model to describe the behaviour of such system. According to this concept polyboroxo siloxane coated nanoparticles accumulate on the surface in the case of fire and act as a skeleton in the transformation of the precursor to the barrier layer. Polyboroxo siloxane, in turn, may act as glue keeping the particles together. The assumed mechanism was proved using WAXS, μ-TA, XPS and thermal analitical methods.
6. Phosphorilation of the polyol additive of the intumescent fire retradant system inhibited its esterification reaction with ammonium polyphosphate, which was established by conductivity measurements. Decreasing the part of phosphor pentoxide and using nanoparticles respectively improved the

hydrolitical stability. Combination of phosphorylated polyol and nanoparticles affects the fire retardant performance significantly. The additives accumulates on the polymer surface and hinder the degradation of the polymer matrix in a very early stage of fire. Our concept was confirmed by TG and XPS methods.

Applications

The new knowledges described in the Theses initiated industrial research programmes, the results of which were realised in new products cooperating with local (Pemü Rt., Ajka Alumínium Rt. Ikarusbus Rt.) and international (Clariant Co., Furukawa Electric Co., CREPIM, Brunel University) institutions. . The utilization of the results took place in the frame of a program of the European Union. The recipes and technologies of various bus units, train seats, flame retarded noise insulating sheets, and fibre reinforced composites has been elaborated.

3. List of publications

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