

THERMAL AND SURFACE ANALYTICAL STUDY OF FLAME RETARDED POLYOLEFINS

I. Interaction of additives and structure formation

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Abstract

Pentaerythritol may react with tetraethoxy-silane and ammonium-polyphosphate in flame retarded polyolefins and an interfacial layer can be formed around the ammonium-polyphosphate particles. It is advantageous to study such systems using methods of thermal and surface analysis together.

Keywords: interfacial layer, phosphorous flame retardants, polypropylene, silicone additive, TOF-SIMS

Introduction

The research and development of new engineering materials belong to the most actual and important fields of material science. One can see the continuous competition between the traditional inorganic engineering materials and the polymers. Although the polymeric materials (including the composites), due to their economic versatile applicability, are promising, there is a certain area where inorganic materials have an inevitable advantage: this is the production of flame resistant structures. The importance of the flame proofing character of materials is growing continuously with the more and more severe safety requirements. The increase of the application of polymers will not stop, so the development of safe and environmental flame retarded polymers is of great importance. The problem is sharpened in case of polyolefins, which are the most widely used and nearly the less flame resistant materials.

The question may occur: what is the relationship between the flame retardancy and the thermal analysis? In fact the degradation caused by flame and the mechanism of important flame retardants are in close connection with thermal processes and consequently methods of thermal analysis are currently used and developed for characterisation of flame retardant (FR) systems [1-3].

One of the strongly developing group of flame retardants are the intumescent additives, that form a protective barrier char layer at the surface.

Generally used components of the intumescent systems are ammonium-polyphosphate (APP), pentaerythritol (PER) and melamine (applied as spumific agent)

[4, 5]. The stability and activity of such system should be improved therefore we proposed to introduce zinc-borate and silicone compounds in our recent works [1, 4, 6]. Intumescent FR systems containing zinc-borate and silicon compounds were studied recently by French and Russian research group respectively [7-9].

The advantages and limitations of thermal analysis at this area are as follows:

- The development of new intumescent FR formulations are based generally on the results of thermal analysis, as the reduced mass loss (that means the increased char formation) and the endothermic reactions (that cool the systems) can be studied this way.

- TG is a powerful method not only to evaluate the residue char, but also to measure the thermo-oxidative resistance of the char and to study the mechanism of action of spumific agents [2, 10].

- Cone calorimeter is the most widely used method for determining the heat released by the material in case of fire [11].

- A new equipment was developed by Lyon *et al.* [12] for micro scale analysis that is designed for separate study of the solid phase and gas phase processes.

These thermal analytical methods promote the conscious choice of new FR additives, but in some cases does not allow to predict the efficiency of certain additives. The reason for it is the lack of information about the

- interaction between the components,
- the rate of charring and
- the changes of surface composition.

All of the three mentioned parameter may play determining role in the FR process [1, 13].

The scale of the thermal analytical methods used in this field is expected to extend in order to follow the charring process directly, and to determine all the interactions in a multicomponent system. On the other hand the study of surfaces and interfaces must not be neglected either.

From our practice and the literature we realised that the use of certain methods of thermal analysis is the most powerful, but still not an entirely satisfactory way for elaborating new FR formulations and understanding their mechanism.

In our concept the thermal analysis and surface analysis of model systems should be used together for achieving a good modification:

- The effects of synergistic additives that reduce the weight loss or decompose endothermically is studied using the conventional thermal analytical methods.

- The charring is followed using a modified TG method.

- Model reactions between the additive components is carried out in a computer controlled reactor-calorimeter.

- The structure and mechanism of some additives is planned to be clarified using the advanced surface analytical methods TOF-SIMS and XPS.

Some results of this project is presented in this paper.

Experimental

Materials

The polyolefin grades used in this study were products of Tisza Chemical Works (Hungary): ethylene-propylene copolymer (Tipplen K793); density: 0.9 g cm^{-3} ; melt index: 4 g min^{-1} (21.6 N, 230°C); PP homopolymer (Tipplen H 348F) density: 0.9 g cm^{-3} ; melt index: 12 g min^{-1} (21.6 N, 230°C).

Organoboron siloxane elastomer were prepared using OH end group containing siloxane oligomer and boric acid according the method described in literature [14]. Tetra-ethoxy-silane (TES) was also added to promote the coupling with other components.

Commercial samples of ammonium polyphosphate (APP; Hostaflam 422, Hoechst), pentaerythritol D/S (PER; Degussa), and melamine (ME; Reanal, Hungary) were used as supplied. Their ratio in the intumescent flame retardant (IFR) system was APP:PER:ME=1: 0.2: 0.2.

Test methods

The mixing of components was carried out using Brabender Plasti-Corder PL2000 (mixing chamber 350) with rotor speed 50 rpm. The compounds were then injection moulded at 230°C .

TG measurements were performed using Setaram Labsys TG equipment, sample mass: 48.8 mg, heating rate: $20^\circ \text{C min}^{-1}$, atmosphere: N_2 . Model reactions were carried out using a computer-controlled reactor constructed in our laboratory in order to develop controlled organic chemical reactions and measure their heat effects in line. The hardware and software description of this computer-assisted reactor calorimeter system is elsewhere [15].

The AFM images of the broken surface of injection molded samples were prepared using a NanoScope III (Digital Instruments), scan size 11–5 μm .

The parameters of TOF-SIMS measurements: detection of negative secondary ions, Cs+8.0 keV primary ion, neutralization: low energy electron gun pulsed. Imaging: acquisition: Ga+25 keV primary ion, ion dosage: $2.E+11 \text{ ions cm}^{-2}$, image parameters: $200 \times 200 \mu\text{m}$ raster size, 120 min acquisition time, 10–160 m/z mass range.

Results and discussion

TG measurements

Mixtures of flame retardant components (APP-PER and PER-TES in N_2 , without polymer) were analysed as model systems and compared to the theoretical values. (The theoretical values were calculated from the TG results of individual components without considering any interaction.)

The results in Figs 1 and 2 show that the amount of residue increased, especially in case of PER-TES additive pair, probably due to some interaction of the components. Further experiments needed in order to clarify the type of interaction.

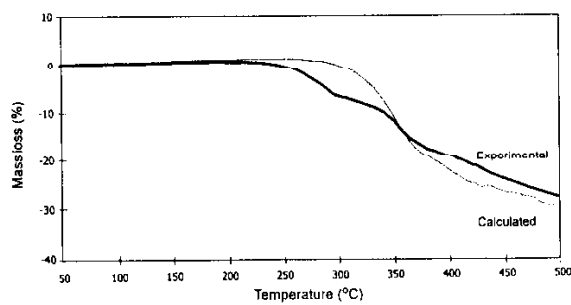


Fig. 1 Mass loss curve of mixture of ammonium polyphosphate and pentaerythritol (heating rate: $20^{\circ}\text{C min}^{-1}$, atmosphere: N_2)

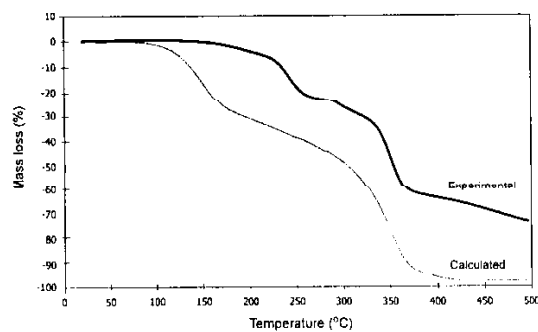


Fig. 2 Mass loss curve of mixture of pentaerythritol and tetraethoxy silane (heating rate: $20^{\circ}\text{C min}^{-1}$, atmosphere: N_2)

Charring test

The character of residue is important, because char formation is known to contribute to the improvement of flame resistance, therefore we constructed a simple test system (Fig. 3) to follow the charring process if it occurs.

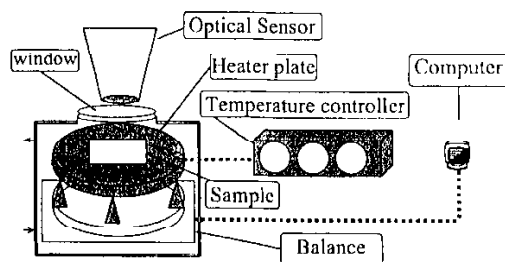


Fig. 3 Method to follow the charring process

Using this method the change of colour (which is attributed in the studied systems mainly to charring) and the mass loss can be followed under isothermal an-isothermal circumstances.

The optical sensor was a video camera when FR additive components were studied (meantime it has been replaced with Datacolor Microflash 200d colour measuring sensor).

The following conclusion could be drawn from the results in Table 1: The charring process in case of APP-PER is quite quick in both studied ratios. The difference between the calculated and measured values of mass loss determined with this isothermal method is much more pronounced than in case of TG results, probably due to less chance for PER to sublime at low temperature, before a reaction with APP may occur. No change of colour could be detected in case of PER+TES mixture, so the residue is not char. The mass loss in accordance with TG result suggest a reaction between PER and TES.

Model reactions

A computer controlled reactor was developed for studying the reactions that may occur between the additive components. The reactor is similar to a Mettler reaction calorimeter, but it is mainly designed for using as a model of industrial computer controlled reactors. We found it appropriate for optimizing the run of reactions in order to complete them in situ in a compounding extruder.

At first we repeated the already published reaction between APP and PER according to the results of Camino *et al* [16] and then the PER and TES were studied. An amount of 1 mol PER and 1 mol TES reacted in the computer controlled system, which consisted of a 500 cm³ flask and reflux condenser. The mixture boiled at 140°C for 90 min. After removal of ethanol white insoluble (polymer) powder was yielded, that was analysed. The -OC₂H₅ conversion factor was 75.4%.

The model experiments in the reactor calorimeter suggest the occurrence of coupling reaction between the additive components at the circumstances of reactive compounding. On the other hand, no direct reaction could be found between APP-TES.

The comparison of the calorimetric results obtained by the reactor with DSC data will be discussed in a subsequent part of this series of papers.

The product of PER-TES reaction was analysed by FTIR. Comparing the FTIR spectra of the product (Fig. 4) to the spectra of PER (Fig. 5) the shift of the peak corresponding to the C-OH bond from 3328.4 cm⁻¹ (PER) to 3421.3 cm⁻¹ (product) reflects the decrease of -OH/H associations due to the reaction of OH groups of PER.

Based on these results one can conclude that the reaction takes place according the equation in Fig. 6.

Due to this reaction with TES, chemically bounded interlayer of silicone compounds may form around the APP particles using organoboron siloxane elastomer as described earlier [1].

Table 1 Results of charring test of flame retardant additive components

Material	Components in mass%	$f_{\text{discoloration at } 300^{\circ}\text{C/s}}$			Relative mass loss/%		Comments
		yellow	brown	black	measured	calculated	
PER (white powder)	100	no	no	no	95.3		sublimating evaporates
TES (liquid)	100	no	no	no	100		
APP (white powder)	100	no	no	no	1.2		
PER+APP (white mixture)	17+83	18	20	26	62.0	82.6	foaming
PER+APP (white mixture)	20+80	15	18	23	13.3	20.8	foaming
PER+TES (white mixture)	50+50	no	no	no	63.1	99.6	

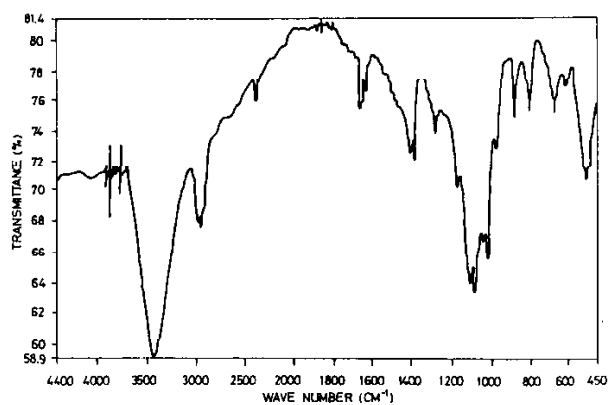


Fig. 4 FTIR spectra of the product of pentaerythritol and tetraethoxy silane reaction

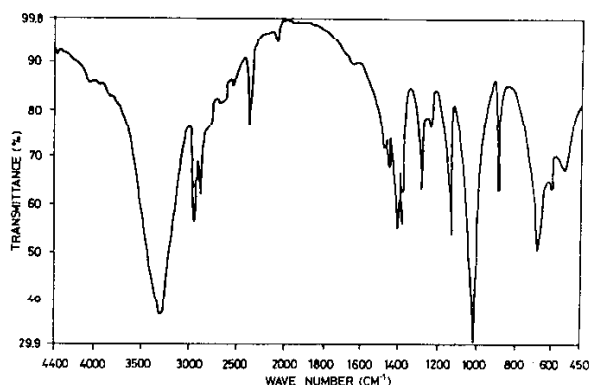


Fig. 5 FTIR spectra of pentaerythritol

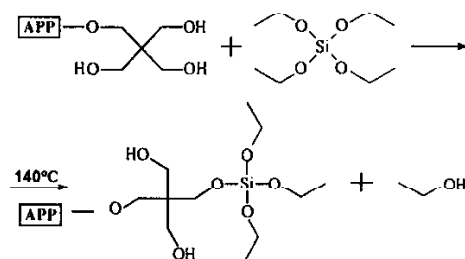


Fig. 6 Scheme of bonding of tetraethoxy silane to flame retardant particles

The structure formed this way has been determined with the surface analysis of samples broken under liquid N₂.

AFM measurements

The comparison AFM images in Fig. 7 taken from the surface of broken samples suggest a significant difference in the interfacial structure. The round shape surface of particles in the silicone containing samples (Fig. 7b) in contrast to the sharp edges of the reference sample (Fig. 7a) is a consequence of the reactions at the surface of APP resulting in the encapsulation of its particles.

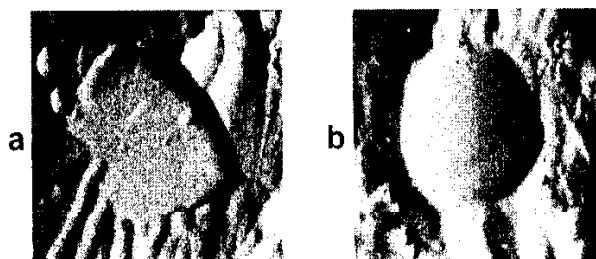


Fig. 7 Atomic Force Microscopic image of ammonium polyphosphate particle: a) without modifier (the image represents 5×5 μm area of the surface), b) with silicone modifier (the image represents 11×11 μm area of the surface)

Nucleating effect of APP was reported in our earlier paper, which was found to be reduced due to interaction with PER [1]. The AFM images seem to confirm these results: fibrils of transcrystallization of polypropylene are attached on the surface of unmodified APP, such effect, however, is not visible in case of surface modified particle.

TOF-SIMS measurements

The TOF-SIMS measurements were applied for determining the arrangement of silicone compounds in the IFR containing PP. The samples were broken under liquid nitrogen and chemical map of the characteristic ions on the formed surface was determined. The TOF-SIMS spectrum of the broken surface of PP, flame retarded with silicone additives containing APP-PER-ME system, reflects the presence of all the flame retardant components and the concentration of silicone additive on the surface is enough for TOF-SIMS imaging [17].

The image prepared on the base of SiO_x ions proves the existence of a silicone interlayer around the APP particles:

The image in Fig. 8a shows the distribution of hydrocarbon molecules at the surface. The white areas are rich in hydrocarbon, while the lack of hydrocarbon at the dark areas is due to the presence of APP particles. The size and shape of them is in accordance with SEM images published earlier [4].

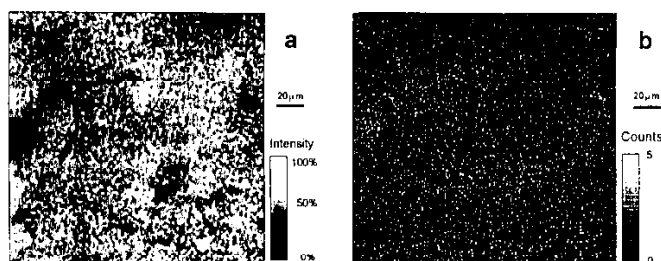


Fig. 8 TOF-SIMS image of broken surface of flame retarded polypropylene: a) C_xH_y image, b) SiO_x image

If we compare it now to the SiO_x surface image, where the white areas show the place of silicone additive, it is clear, that SiO_x concentrates to the areas, where the APP particles were detected.

The results of our measurements suggest a structure, where a layer of PER covers the solid APP particles and it is bonded to a silicone elastomer layer through TES.

The effect of this structure on the mechanism of intumescent flame retardant systems is the subject of the second part of this paper.

Conclusions

The study of flame retardant polymer systems is an important field, where the application of thermal analysis is essential and increases rapidly. Several new methods have been developed recently and are expected to develop in the close future.

Modification of intumescent flame retardant containing polyolefin systems using silicone additives has been carried out and studied in model experiments. The application of methods of thermal analysis together with surface analysis proved to be efficient, for the development of the composition of flame retardant system and for conscious formation the structure:

TG measurements and charring test indicate the components that may interact with each other. The appropriate circumstances for interaction between the flame retardant additives can be elaborated using a computer controlled model-reactor. Physical and chemical mapping can be carried out using AFM and TOF-SIMS methods

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