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Publisher *Taylor & Francis*

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## International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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G. E. Zaikov<sup>a</sup>; A. Ya. Polishchuk<sup>a</sup>; M. I. Artsiz<sup>a</sup>

<sup>a</sup> Institute of Biochemical Physics, Russian Academy of Sciences, Moscow, Russia

**To cite this Article** Zaikov, G. E. , Polishchuk, A. Ya. and Artsiz, M. I.(1996) 'Recent Advances in Flame Retardancy of Polymeric Materials Materials, Applications, Research and Industrial Development Markets', International Journal of Polymeric Materials, 33: 1, 127 – 131

**To link to this Article:** DOI: 10.1080/00914039608028615

**URL:** <http://dx.doi.org/10.1080/00914039608028615>

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# Recent Advances in Flame Retardancy of Polymeric Materials

## Materials, Applications, Research and Industrial Development Markets

G. E. ZAIKOV, A. Ya. POLISHCHUK and M. I. ARTSIZ

*Institute of Biochemical Physics, Russian Academy of Sciences, 4, Kosygin Street, Moscow 117334, Russia*

*(Received August 10, 1995)*

The Sixth Annual Conference on Flame Retardancy was held in Ramada Plaza Hotel in Stamford, Connecticut, USA on May 23–25, 1995. As before it was organised and sponsored by Business Communications Company. Scientists from 9 countries (USA, Canada, Germany, Holland, Russia, UK, India, China and Israel) contributed in the Conference. The meeting was aimed to:

- create a forum for introducing new technological achievements and development in the field of flame retardancy (FR);
- review the current state of science and technology in FR;
- review the applications and markets for FR products;
- present recent developments in local and global standardisation and in testing technology;
- discuss toxicity and environmental issues;
- provide a unique opportunity for newcomers to FR research technology and marketing to become acquainted with the FR field in all its aspects, and
- discuss halogen-based and non-halogen-based flame retardant chemicals, synergism, intumescence, FR mechanisms, modelling, flame parameters, inherently FR polymers and polymer blends.

Thirty plenary lectures were presented at the Conference which also included 2 Poster Sessions and the Exhibition of industrial chemical additives for polymers reducing flammability of materials. Several leading US companies demonstrated their production in the Exhibition.

The work in the Conference was organised in 7 Sessions. The meeting was opened with remarks of Professor Menachem Lewin (Polymer Research Institute at Brooklyn Polytechnic University, New York, USA) who emphasised the present interest of science and practice of the aforesaid problems.

The first session considered new directions in FR technology and the FR industry.

There were 6 main lectures which presented the development of fundamental research in fields of the flammability of polymeric materials and flame retardancy, and new ways of the creation of environmentally friendly additives for polymers.

The first lecture of Professor J. R. Ebdon (Lancaster University, UK) reviewed work in the area of chemical modification of polymers and its effect on flame retardance. He considered modifications of various, relatively simple, polymers with phosphorous-, boron-, silicon- and tin-containing groups, as well as very recent work on modifications with transition metal chelates. Influences of some of these modifications upon smoke emissions was also described.

Professor G. E. Zaikov (Institute of Biochemical Physics of the Russian Academy of Sciences) reported new aspects of ecologically-safe polymer flame retardant compositions. The speaker and his colleague Dr. S. M. Lomakin proposed two different types of ecologically-safe flame retardants:

- high temperature polymer-organic carbonisators, and
- silica-inorganic-flame retardant compositions - gaseous phase inhibitors of polymer combustion.

The research was aimed to find a way to increase the tendency of plastics to char when they are burned. Silica (metal)-inorganic compositions had been found to be one of the most interesting modern flame retardant compositions. The idea of gaseous phase inhibition based on the presence of HCl can be produced only at temperatures above 400–500°C. This research might be one of the first step to improve different properties of a polymer by the way of “polymeric synergy.”

The surface treatment of polymers for flame retardation was a topic of the lecture of Professor Ch. A. Wilkie (Marquette University, Milwaukee, WI, USA). The speaker, mainly, focused upon the grafting of a surface coating of methacrylic acid onto acrylonitrile-butadiene-styrene terpolymer, ABS. This method produced a system that offered very good thermal protection to the ABS phase because char formation occurred at the surface and this retained the ABS substrate. Other polymeric systems and other char-forming monomers were also highlighted.

In the lecture “Char and Flame Retardancy” Professor Menachem Lewin over-viewed the pyrolytic high temperature chars obtained from a variety of polymers without the presence of additives, as well as the combustion chars obtained in the presence of flame-retardant additives. There were discussed the mechanical, physical and structural properties of chars, and the methods for their assessment and possible means for their improvement.

An experimental approach to non-halogen flame-retardant ABS was proposed in the lecture of Professor E.D. Weil (Polymer Research Institute at Brooklyn Polytechnic University). Because ABS has been difficult to flame retard to without the use of halogens, the speaker and his colleagues approached this problem by a multiple additive strategy. They used experimental design and regression analysis as a guide to finding cooperative (“synergistic”) additive system. Combining different types of phosphorous compounds and different types of char-forming additives also appeared to be a useful methodology.

Compatible intumescent and flame-retardant fibre combinations are able to form char by similar and interactive physicochemical mechanisms. The char-bonded flame

and heat barriers in these fibre reactive systems were discussed in the lecture of Professor A. R. Horrocks (Bolton Institute, UK). The original flexible fibrous assembly transformed to a char-reinforced, resilient barrier having superior mechanical properties with respect to conventional intumescent char. These textile composite structures did enable extremely high level of flame and heat resistance to be achieved.

The recent advances in FR polymers and systems were the topic of the Session II. The lecture of Cure Kinetics and Thermal Degradation of Cyanate Ester Resins was given by Dr. J. Rodriguez-Arnold (technical Center of the Federal Aviation Administration, Atlantic City International Airport, USA). He reported the results of investigations of the cure and pyrolysis kinetics of a difunctional and trifunctional cyanate ester resins by differential scanning calorimetry and dynamic mechanical analysis. The thermal stability of the phenolic triazine was found to be comparable to high temperature polymers such as poly(benzobis-oxazole) termoset polyimides with regard to the overall activation energy for pyrolysis and peak decomposition temperature.

Dr. Ahamad A. Y. Khan (the University of Tennessee at Knoxville, USA) gave the lecture entitled "Melt Blowing of Novel Flame Retardant Polymer." He presented poly(ethylene-chlorotrifluoroethylene) resin which is novel to the area of non-wovens and had unique characteristics compared to conventional thermoplastic resins used in melt blowing.

Dr. B. B. Serkov ("Antip-Ltd" Company, Moscow, Russia) described the recent status of the flame retardancy in Russia. He summarised the general directions currently developed in Russia for the creation of fire-retardant polymer materials with minimal environment impact. The speaker informed about the peculiarities of the Fire Regulation System in Russia and considered new specific approaches to flame retardance for composite plastics, polymer glasses, foams, textiles and elastomeric materials.

Three lecture were presented in the Session III, Non-Halogenated FR Polymer Technology. Dr. Larry L. Musselman (Polymer Additives Group, Ridgeville, CT, USA) reported new results on mechanisms and performance of molybdenum and zinc containing flame and smoke suppressants for PVC and other polymers. Dr. R. D. Pike (College of William and Mary, Williamsburg, VA, USA) discussed low-valent metal complexes as reductive coupling agents for smoke suppression in vinyl chloride polymers. The speaker, mainly, focused upon the coupling effect of low oxidation state complexes on model compounds and PVC at elevated temperatures. Dr. D. F. Agunloye (Albright and Wilson Ltd., West Midlands, UK) proposed the principles which had led to the development of improved intumescent flame-retardant systems for polyolefins, especially for polypropylene and its copolymers. Examples of the areas of real and potential applications were also given.

The Session IV considered important trends in halogenated FR polymer technology. The use of chlorine/bromine synergism to flame retard polymers was a topic of the lecture of Dr. R. L. Markezich (Occidental Chemical Corporation Technology Center, Grand Island, NY, USA). A synergistic effect using a combination of chlorine and bromine flame retardants allowed the flame retardant levels to be lowered, resulting in improved physical properties and lower cost formulations. This result was shown for all combinations of chlorinated flame retardant with several different brominated flame retardants.

Professor V. Dave talked about processing, characterisation and degradation studies of flame-retarded Nylon 66. This polymer was blended with poly(pentabromobenzyl acrylate) and antimony oxide as flame retardant and synergist, respectively. The materials were compounded in different proportions on a co-rotating twin screw extruder and were later injection molded. The degradation studies were conducted by pyrolysis-chemical ionization-mass spectrometry. The results indicated that the mechanism of flame-retardancy occurs both in the gas phase and in the condensed phase.

Phosphorus-bromine flame retardant synergy had been earlier reported for polycarbonate/PET blends. Dr. J. Green (FMC Corporation, Princeton, NJ, USA) convincingly demonstrated this effects also for polycarbonate/ABS blends. When both phosphorus and bromine are in the same molecule the synergy is further enhanced. There were studied processability and thermal and mechanical properties of products with the various polycarbonate/ABS ratio from 1/1 to 8/1.

With the increase in antimony oxide pricing, there is considerable interest in finding suitable alternatives. Dr. C. J. Nalepa (Albermale Corporation, Baton Rouge, LA, USA) reported studies of alternate synergists for bioaromatics in FR-HIPS using small scale tests such as TGA and UL 94. The successful search of either partial or complete substitutes for antimony oxide was reported in the lecture of Dr. K. K. Shen (US Borax, Inc., Valencia, CA) entitled "Recent advances on the Use of Borates as Fire Retardants." the speaker reviewed the recent advances on the use of zinc borates and boric oxide as fire retardants in both the halogen-containing and halogen-free polymers.

Dr. J. Reyes (Ameribrom, New York, USA) presented FR-1808, a novel flame retardant for environmentally friendly applications. This compound is based on aromatic bromine. The speaker described the characteristics of FR-1808 and its effect on the thermal and physical behaviour of styrenic copolymers, polypropylene and engineering thermoplastics or alloys. The last lecture of the session presented by Dr. Robert Grey (Great Lakes Chemical Corporation, West Lafayette, IN, USA) was of specific interest due to the consideration of the influence of flame-retardant structure on the UV stabilisation of polypropylene.

The Session V ("Important Applications, Trends and In-Use Parameters") was started with the keynote lecture of the Director of Polymer Research Institute at Brooklyn Polytechnic University (NY, USA), Professor Eli M. Pearce who reviewed the fundamental aspects of the design of FR materials for FR interiors. This review was then extended by examples given by Dr. R. E. Lyon (Federal Aviation Administration Technical Center) in his lecture "Thermal Stability and Fire-Resistance of Polymeric Materials"). There was particularly reported the use of transient pyrolysis kinetics to explore the relationship between polymer thermal stability and the fire-resistance between polymer thermal stability and the fire-resistance of aircraft cabin materials in a post-crash fuel fire.

The use of polypropylene (olefins) fibres has grown considerably in the last 5–10 years. Polypropylene is finding uses in ever increasing areas of textiles: automotive, marine, aircraft, home furnishing, industrial, and apparel. Many of these applications require the textile article to meet various flame retardancy specifications. Topical FR treatment of polypropylene fibre and fabrics with organo-phosphates was described

by Dr. F. B. Savel III (eastern Color and Chemical Co., Providence, RI, USA). This application of organo-phosphates allowed the use of polypropylene in areas in many years previously restricted due to polypropylene's inherent flammability. Dr. Leonard Davis (Ciba-Geigy Corporation, Ardsley, NY, USA) had presented the recent developments in UV stabilisation of polypropylene fibre containing melt processible halogenated flame retardants.

Other communications of Session V related to the concrete applications of flame retardants. They were lectures of Dr. P. J. Briggs from Warrington Fire Research Centre, UK ("Fire Behaviour of Floor-Coverings: Comparative Studies of Room/Corridor Scenarios and Small-Scale Test Methods") and Dr. Napela ("Recycling of Flame-Retarded Styrenics").

Session VI on Testing and Standards consisted of 3 presentations. The first lecture was given by Dr. P. K. S. Wu (Factory Mutual Research Corporation, Norwood, MA, USA) and entitled "The Evaluation of Flame-Retardant Materials by the FMRC Technique." The speaker and his colleagues developed a technique, based on a model to streamline the testing. This technique involved the use of an upward fire spread model and the flammability apparatus of FMRC. The technique was applied to various polymers and composites, and the results were consistent with the earlier Fire Propagation Index (FPI) evaluation. The method provided a more comprehensive description of the fire propagation than that from the FPI value.

The majority of fire fatalities are a result of inhalation of smoke, rather than the simple effect of burns. This idea was emphasised in the lecture of Dr. M. M. Hirschler (Safety Engineering Laboratories, Rocky River, OH, USA). The speaker offered and analysis of issues involved and the approaches taken (and suggested) for assessment of smoke toxicity with the context of overall fire safety. Dr. H. Forsten (Du Pont, Wilmington, DE, USA) gave then more examples of methods for testing fire toxicity.

The final session directly related to the environmental issues and toxicity. The most interesting lectures were given by Dr. D. Lenoir from the GSF Research Centre at Oberschleissheim, Germany ("Evaluation of the Ecotoxicological Potential in Incineration of Halogenated Flame Retardants of Duroplastic Materials") and Dr. G. L. Nelson from Florida Institute of Technology at Melbourne, USA ("Carbon Monoxide and Fire Toxicity"). Dr. Lenoir reported the results of studies and tests of the ecotoxicological behaviour of the pyrolysates of several new halogenfree materials developed by Siemens AG, and Dr. Nelson summarised comprehensive studies on CO toxicity to humans in both fire and nonfire incidents.

The Conference was of very high level and showed that either fundamental research on polymer flammability or practical applications of novel flame retardants successfully develop. However the number of participants (100 last time) reduce from year to year. We explain this fact by relatively high registration fee which does not allow many scientists and students from universities to contribute in conferences. Presently, the list of participants mainly includes scientists from research centres of industrial companies for whom registration fee does not matter.

The next BCC Conference on Flame Retardance is scheduled on May, 1996.