

NEW CONCEPTS IN POLYMER SCIENCE

Fire Resistant and Thermally Stable Materials Derived from Chlorinated Polyethylene

A.A. Donskoi, M.A. Shashkina
and G.E. Zaikov

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“Noises of moments drown
the music of eternity”

Rabindranat Tagor (1861 – 1941)
the famous Indian writer

“Not finished is much
worse than undone”

Alexander V. Suvorov (1730 – 1800),
the famous Russian military leader,
the founder of the Russian military arts

Preface

Science in the USSR lost many of its priorities owing to the secrecy cultivated in this country during the rule of Joseph Stalin from 1924 till 1953. After his death in 1953, the situation did not change till the 1990s. In particular, Electron Spin Resonance had been formulated already by Zavoiskii in 1939 and demonstrated in 1944, but publications of these works were not permitted until the late 50's, when this effect was re-discovered in the USA. A discovery by O.I. Leipunskii had the same fate: he had calculated theoretically the method of producing diamonds from carbon under high pressure and temperature.

It was very difficult to publish anything possessing dual output in practice, i.e. suitable for both military and civil purposes. As a result, we lost many priorities in constructing atomic power plants and exploration of space.

If anybody wanted to publish something during the era of socialism, permission (publication certificate) had to be granted by a committee. Two last phrases of this certificate read as follows: "The article presents no fundamental discoveries and is of no interest for application in practice. The article can be freely published", i.e. if an article possessed any scientific or practical interest, it could not be printed in the free press (even in Russian).

Now times have changed (or more or less changed) and many things, from positions of publication, have become publishable. That is why the authors decided to fill in some blanks and to publish some data on development of polymeric materials for aviation. We suggest this information could be suitable for students, postgraduates, engineers and scientists working in the field of material science and engineering and especially for those who deal with creation of new polymeric materials for aviation, ship building and automobile construction or manufacture.

The authors will be very grateful for any suggestions and advice on the theme on the present monograph, which will be taken into account in future work and publications.

A.A. Donskoi, M.A. Shashkina, G.E. Zaikov

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Introduction

The problem of creating materials with reduced combustibility based on a variety of organic polymers widely applied in various fields of industry and national economy, as well as of using polymeric materials for protection of separate devices or whole compartments from fire or overheating, is discussed in the book.

Fire is a great helpmate: controlled fire is our helper in everyday life, but if it is out of control – it becomes a great disaster.

Fire exerts its effect by combustion, the process which is rather complicated and manifold. In simplified form, combustion can be represented as fast oxidation of various substances with evolution of a large amount of heat and light irradiation. To reduce consequences of fire in a required direction, the laws of the combustion process must be studied, and appropriate transformations in material must be investigated. Many works are devoted to these problems, in which the factors causing inflammation, behavior of separate substances in the zone of flame influence with all accompanying displays are studied. However, every particular case of protection from fire demands an individual approach to material selection and on frequent occasions, the creation of new more effective ones in the given particular conditions of their application. Ignorance of the properties of applied materials may lead to an undesirable result. By way of illustration let us present the case of using fireproof silicate bricks in constructing a common Russian stove for house heating. The result was poor – the stove burnt firewood, but did not heat up the apartment.

There are materials in nature sustaining combustion and fire shield, i.e. avoiding flame spreading over the surface. However, these materials are capable of heating up under the effect of high temperature, which is an obligatory companion of fire, and become the source of inflammation for other materials themselves.

By far the majority of polymeric materials are combustible. At the same time, many polymers with reduced combustibility and materials based on them were developed. However, combustibility degree of these materials or ability to protect from fire or high temperature can be indicated only in particular case of combustion. Widespread requirements can be imposed upon materials in the fire zone, such as non-sustaining of combustion, non-release of toxic or combustible products, non-admission of flame spreading over the surface or inside the article and, at times, non-transmission of heat through them.

Discussed in the book are the results of the development of physicochemical bases for creating organic polymeric materials with

reduced combustibility, capable of protecting devices and compartments covered by a material layer from influence of high temperature.

Chlorinated polyolefins as organic polymers with reduced combustibility are presented in this book.

1. Combustion of polymeric materials and methods to reduce it. The mechanism of fire and heat shield covers

Fire injuries in the second half of the twentieth century demanded development of noncombustible and low combustible polymeric materials. Analysis of a large amount of theoretical data on reducing combustibility of polymers gives us an opportunity to establish a better understanding of the fundamental aspects of this phenomenon.

Combustion of a polymeric material is quite complicated and involves transformations proceeding both in the flame and in the material. To understand the combustion mechanism, combustion conditions and transformations proceeding in the material must be studied in conjunction with one another. The mechanism of polymeric material combustion depends upon the component composition, conditions of flame and combustion occurrence and the processes proceeding in the polymer, as well as the influence of polymeric material and products of its degradation on combustion. Proper fire shielding requires studying kinetics of thermal and mass transfer during combustion, clearing up the role of three components of the thermal flux affecting the material surface at heat transmission from flame to combusting surface, studying a change in optical characteristics of flame and polymeric material surface, and rheological characteristics of the products obtained during temperature treatment of polymer in the condensed or gas phase. Most important among the latter are properties of polymeric melts and degradation products, which in combination with the gas formation theory allows understanding of porous coke shielding layers [1].

For this purpose the mechanism of chemical reactions in the pre-flame zone and in the flame should be studied, as well as formation of products in the boiling layer, which lead to formation of cross-links and curing. A great influence on polymeric material combustion is exerted by heat-physical characteristics, and foam formation of the coke layer in accordance with all mechanisms of heat transfer. Therewith, of importance is determination of critical conditions for flame extinguishing, when heat passing through the coke layer is insufficient for gasification of the next batch of the polymer. Moreover, the kinetics and mechanism of chain reactions in the flame and pre-flame zone, and the role of inhibitors on various stages of combustion, including radical and ionic processes of active center formation, in which carbon black particles are formed, should be understood.

Traditional technical literature indicates the following main ways of reducing inflammation degree of polymeric materials:

1. Application of various hydrates, salts and compounds, which release inert substances during thermal degradation and decrease flame temperature diluting the gas phase by incombustible products, in their composition.
2. Filling a polymeric matrix by inert substances to increase the induction period of inflammation and ignition energy by diluting combustible products in the condensed phase [1].
3. The use of various organic and inorganic combustion inhibitors, fire shielding materials, which operate in the condensed phase and change the rate of thermal degradation.
4. The use of gas-phase combustion inhibitors, for example, ones containing halides of compounds, leads to a change in the reaction mechanism in the flame and pre-flame zones.

However, it should be noted that usually the effect of combustion inhibitors is a complicated process and includes several mechanisms. Thus, on the other hand, inhibitors operating in the condensed phase shift the equilibrium of combustible substances by decreasing the amount of volatile degradation products. On the other hand, inhibitors provide conditions in which a coke layer with low thermal conductivity is formed on the combustion border. This happens due to a change in rheological properties of the material during high-temperature pyrolysis and gas formation during degradation. Hence, the effect of combustion inhibitor in the condensed phase influences directly the processes proceeding in the gas phase.

Gas-phase inhibitors reduce extent of gasification and polymer degradation product combustion. Therewith, heat release in flame decreases and radiation losses of heat increase due to increasing the amount of carbon black formed [2].

At the present time, reduction of combustibility of polymers and materials is a topical problem that requires a cardinal solution. However, the empirical approach to development of new low combustible materials still dominates. Fundamental investigations of combustion of polymers may serve development of a unified combustion theory for polymeric materials [1].

Combustion of a polymer represents a process proceeding with time. Therewith, the following five main stages can be outlined: ignition, flame spreading, combustion, smoke formation and material extinguishing. Consequently, five zones are separated in space: the heating zone on the polymeric material surface, conversion in the condensed phase, pre-flame zone, reaction products (gas phase) and oxidation zone. This process is readily illustrated by the elementary scheme, described in ref. [3] and shown in Figure 1.

Analysis of the scheme presented suggests preliminary methods for reducing combustibility of a polymeric material. Increase of

gasification heat, reduction of the heat flux to the polymeric material surface by decreasing combustion heat or flame temperature by diluting the gas phase with incombustible gasification products or thermal degradation of polymeric composite components are the most efficient. Smoke and carbon black formation are usually associated with incomplete burning off, but therewith heat release reduces.

The main ways of combustibility reduction can be formulated as follows:

1. Fuel isolation; reduction of fuel concentration in the flame zone.
2. Oxidant concentration decrease.
3. Solid propellant cooling.
4. Oxidant cooling.
5. Inhibition of homogeneous reaction.
6. Inhibition of heterogeneous reactions.
7. Flame blowoff by high rate approach flux.

Problems of decreasing combustibility can be solved by various methods: changing polymers, synthesizing new ones with decreased combustibility or incombustible, modifying chemically the existing ones, or creating composite materials based on previously existing or newly developed polymers. However, these problems can be solved only if the essence of combustion is understood, in particular, the combustion of polymeric materials.

By combustion of usual polymeric materials is meant an exothermal process, based on oxidation-reduction reactions with participation of air oxygen with luminosity (flame) occurrence. Combustion of polymeric materials includes many stages, among which the main ones are warming thoroughly and gasification of surface layers of the material. As a result of thermal influence on the polymeric material reactions of the aggregate state change, degradation accompanied by formation of gaseous low-molecular products, capable of combusting and sustaining combustion and exothermal reactions in the gas phase proceed.

Heat released as the result of oxidation-reduction (redox) reactions is transmitted to the surface of the unburnt layer by radiation, convection and thermal conductivity [4].

Turning to the combustion elementary model, shown in Figure 1, one can suggest that polymers forming a network structure, capable of transformation into the coke-like state under the effect of high temperature, are the most combustion proof.

Besides the polymer, the fire shield role can be played by combustion inhibitors participating in the material composition.

Traditionally, the effect of combustion inhibitors is subdivided into two large groups: those working in gas and condensed phases [5]. Combustion inhibitors in the condensed phase intensify carbonization,

reduce release of volatile degradation products, and hinder reaching the lowest concentration limit of combustion. Gas-phase combustion inhibitors decelerate chain oxidation reactions in flame.

Analysis of data from literature indicates the most efficient combustion inhibitors are compounds of phosphorus and halogens. In polymers, phosphorus compounds decrease ignition rate of the material, and are capable of glowing termination after flame extinguishing, by which they prevent repeated ignition [1].

Materials with reduced combustibility are widely applied as fire- and thermal proof covers for devices and articles. The same principles and approaches, as in creation of materials with reduced combustibility, are used in development of materials of the latter design. However, it is not always advantageous to get an incombustible material as the fire- and thermal proof cover, which is able to form a network structure transforming into the coke-like state during thermal interaction.

In the case of short-term high-temperature influence, degradable polymeric materials transforming into the gas phase up to the end of high temperature influence and, consequently, are not a source of thermal influence, are more advantageous. Remaining on the shielding surface in the form of an overheated material layer, coking polymers are themselves a source of heat.

Combustion of a material occurs under definite conditions: necessary ones among them are high temperature, presence of oxidizer (oxygen, for example) and combustible material – the products of combusting material gasification, because not a polymer itself but products of its gasification combust. Concentrations of combustible gases and oxidizer, the rate of its delivery, pressure and other parameters influence the combustion stability. Violation of any of these conditions may cause termination of combustion or fire focus localization [4].

Creation of fire and heat shielding materials is associated with some features of operation of these materials. An effective fire and heat shielding material is one providing a high temperature gradient in the combustion zone. The material is designed for violating heat transfer from the surrounding to the material surface and from it to the shielded one. The usual conditions of heat transfer provide for transferring heat from higher heated (hot) bodies to less heated (cold) ones by means of thermal conductivity or convection. In the fire conditions, the main type of heat transfer from flame or incandescent surface to the shielding material surface is radiation. Radiant flux impinging on the material surfaces is reflected, absorbed and passes through it, and the incident heat flux is divided into three components: reflected, absorbed and penetrated fluxes [6 – 8].

Radiant thermal flux penetrating though the cover is transferred into the condensed phase and supplied to the surface of the shielded object. Absorbed thermal flux accumulates in the material and is

transferred by thermal conductivity to underlying layers, and is also spent transforming into other types of energy: electric, chemical, etc. [9, 10].

The level and spectral characteristics of the radiant flux, absorption properties of the material, reflective ability of its surface in relation to the emission spectrum of incident flux influence the amount of energy absorbed by the polymeric material.

Reflected flux heats up the surrounding and all the bodies absorbing heat by radiation and convection in the gas phase, transferred mostly by radiation. The reflective ability depends on the angle of incidence, the state of the reflecting surface, wavelength of the incident flux, and refractive index of the medium. Fluxes possessing wavelength much shorter than material roughness size scatter. Fluxes with wavelength much greater than this size permeate freely [9].

Transmission and absorption factors depend on chemical composition and structure of the substance. If the absorption factor of the material is low, the radiant flux transmits throughout the material thickness, and heating is decelerated. However, if the absorption factor is high, radiant energy is absorbed near the surface and a thin layer of material is heated up rapidly up to the critical temperature of its decomposition.

It is important to increase the reflective ability of the material in the context of object shielding. However, polymers and other organic substances used in composite materials possess low reflection factors [9]. Reflective ability of the material can be increased by both surface modification and introduction of fillers into the composite material capable of reflecting radiant energy in the infrared part of the radiation flux spectrum. Various metal oxides can be used as such fillers.

Depth of heated up layer and time of its heating up to the critical temperature are defined by the nature of the polymeric material, its thermal physical properties and the amount of supplied heat [10]. The depth of heated up layer increases and time of its heating reduces as the thermal flux supplying the material surface increases, and thermal inertness decreases.

Porous or cellular polymeric materials possessing a low thermal inertness therefore display higher heat-insulating characteristics. However, compared with monolith analogues, there is a danger of more rapid ignition flame spreading by the surface of such materials.

Polymeric fire and heat shield materials are composites. They possess in their composition a great number of components of various end uses (fillers, plasticizers, combustion decelerators, crosslinking agents, etc.).