

PROBLEMS AND PROSPECTS OF MODIFICATION OF POLYMERIC  
MATERIALS WITH THE AIM OF LOWERING THEIR FLAMMABILITY

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ABSTRACT

The main problem concerning the modification of polymeric materials in order to reduce their combustibility is preservation or improvement of main characteristics reflecting the nature of the original material by a simultaneous imparting the material new qualities typical of fire-safe materials. The solution of the problem is impossible without creating experimental and mathematical models of processes taking place in polymeric composites when flame and thermal sources act on them. At the same time there appeared a tendency of transformation from volume modification to surface and pseudosurface modification of polymeric composites. Under a pseudosurface modification reactionable additives being phosphorylated, epoxy resins or polyvinyl alcohol migrate at processing into more heated surface layers of polymeric matrixes, in our case polyolefine ones forming cross-linked structures and a more dense fire-proof surface layer compared to a polymeric matrix. And under surface modification when hardened epoxy polymers, epoxy polymer-base organoplastics and fibre-glass plastics which include phosphorusvanadium containing flame-retardant systems are subject to weak thermal shocks, the flammability of composites decreases two times. The application of intumescent coating after thermal treatment of the surface greatly increases the effectiveness and reliability of flame-protection. By using a complex of methods which includes methods of studying chemical structure of surfaces, physical and chemical processes in the interphase layers have been investigated.

Key words: flame-retardant systems, modification, thermal shock surface treatment, flame-protected intumescent coating, X-ray photo-

electron spectroscopy.

## INTRODUCTION

In most cases to make constructions fire-proof is to change the main properties of polymeric materials that are present in appropriate constructions. At the same time it is necessary for the designer to preserve and improve the service characteristics of materials together with their adaptability to environmental changes and to applied ultimate loads, e.g. to fire sources. The solution of this problem is hampered by an insufficient development of the designing of polymeric composites with a layer combustibility as well as by the development of experimental and mathematical models of processes, taking place in polymeric composites under the influence of high temperature flows. It is also difficult to solve this problem because the research methods especially physical and chemical interphase phenomena and control of fire-proof polymeric composites are developed insufficiently. The above factors make it difficult to predict either optimal polymeric composites with a lower combustibility or fire-proof constructions. The preservation of service properties of composites is possible under pseudosurface or surface modification. Therefore, in this paper great attention is paid to the application of modification methods.

## EXPERIMENTAL

Polymeric materials and flame retardant systems. Modified polymers are low density polyethylene (LDP), secondary LDP epoxy resins ED-20, EDT-10 hardened polyethylenepolyamine or trietanolaminotitanate. Flame-retardant systems are: phosphorusvanadium containing substances obtained from red phosphorus (8 m.p.) and barium or calcium metavanadates (1 m.p.) epoxy resins or polyvinyl alcohol phosphorylated by derivatives of methylphosphonic acid (phosphorus content 6-8%); polyammonium phosphate with carbamide oligomer. Modified materials are: reinforced plastics based on glass fabric and epoxy resins with hardeners at 70 mass % of a filler, organoplastics based on cotton strips, containing phosphorylated fibers and on the epoxy polymers up to 30 mass % of a filler, polycapramide and polypropylene fabrics. Methods of modification : modification of epoxy resins, glass fabric and organic fiber and reinforced-plastics based on them was carried out by distribution in some volume, while introducing phosphorusvanadium containing flame-retardant system. Later on the surface of the

materials obtained was heated by infrared radiation up to 700K in a cyclic regime 10 times for 30 sec till the formation of pyrolyzed layers on the surface. After that the surface of the material so treated was covered with an intumescent coating based on an epoxy resin, containing carbamide oligomer and polyammonium phosphate. Polyethylene and secondary polyethylene modification was performed by using phosphorylated epoxy resins and polyvinyl alcohol with the introduction of FRS up to 15%. Particle size of FRS did not exceed 5  $\mu$ m. The surface layers modification of polycaproamide and polypropylene fabric has been carried out by means of treatment with 15% solution of phosphorus-chlorine containing dimethacrylate with the subsequent action of low temperature plasma on the samples. In this case oligomer polymerization and immobilization of a film formed on the material surface take place.

Research methods. The study was conducted using a complex of methods, which involved photoelectron X-rays spectroscopy, infrared and ultraviolet spectroscopy, wide- and small-angle radiography, electron microscopy, methods of determining thermal characteristics and material combustibility indices, the fire resistance limits of constructions, containing the materials tested.

## RESULTS AND DISCUSSIONS

Under pseudosurface modification of the secondary polyethylene by reactionable phosphorus containing FRS with 75-95% polymer in the composition and 5-25% FRS, partial interaction of FRS with polymeric matrix has been determined on the basis of wide-angle radiography and infrared spectroscopy data. The results of photoelectron X-ray spectroscopy indicate the tendency to a gradient distribution of FRS through the thickness of a polyethylene sample.

Number of cuts <sup>a)</sup>	1	2	3	4	5
Phosphorus content	3,1	2,9	2,6	2,4	2,4
%, in cuts with $10^{-4}$ m thickness in film samples with $2 \cdot 10^{-3}$ m thickness					

a) cut No 1 from the film surface

Concentration increase of cross-linked polymers formed from FRS in the surface layers grows in case of polyethylene modified by phosphorylated epoxy resin. When the content of reactionable FRS in the

polyolefin compositions increases their flammability, combustibility, breaking elongation and flow behavior index decrease. In the area with FRS from 5 to 20 mass % there occurs the increase of breaking strength of polymeric material obtained by extrusion, castable pressing and pressing (Fig.1).

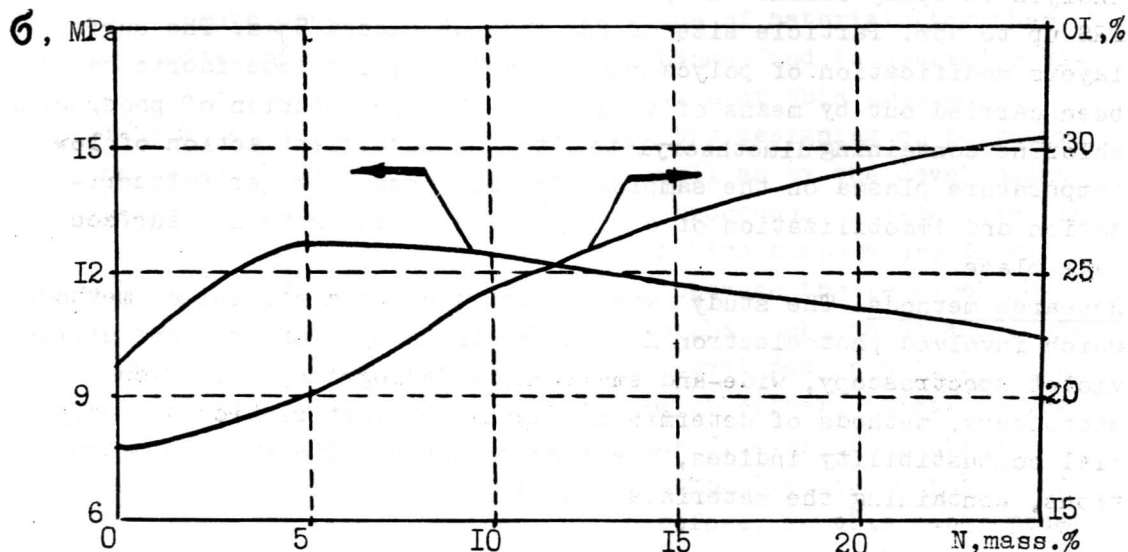


Fig.1 Dependence of destructive tensile stress ( $\sigma$ ) and oxygen index (OI%) upon FRS content (OI, %).

The proposed method of polymeric materials modification with partly joined or unjoined reactionable polymeric type additives allows a wide-scale regulation of polymeric composite properties at the expense of variation of reactionability of an additive and its compatibility with a polymer matrix, and at the expense of changing technological modes of composition processing as well.

In 1,2 the methods of modification of epoxy resins and the materials based on them using phosphorus-vanadium containing systems with a subsequent treatment of a material surface by weak thermal shocks have been discussed. To increase fire-proof of materials and constructions made of them as well as to improve service characteristics it is proposed to cover the material surface after thermal treatment with intumescent coating as a protective layer. Of a special interest

is the changing of thermophysical parameters ( $C_p$ ,  $\lambda$ ) and the density of the layers formed, as well as the changing of chemical structure of external and internal surfaces under the action of high temperature sources on the materials. The formation of "heat shield" decreases thermal conductivity ( $\lambda$ ) with a simultaneous increase of heat capacity ( $C_p$ ) (Fig.2). At the same time the surface carbonization and the formation of fragments in a surface layer  $[-PO_4]_n$  take place. When heat flow acts on an intumescent coating "heatprotective layer" is formed. This results in a considerable thermal conductivity decrease ( $\lambda$ ) with a further increase of porosity (closed pores) and a heat capacity growth ( $C_p$ ) in the area of intensive foaming. In the range of 573K carbonization of internal surface perhaps on the boundary of gas bubble and its polymeric wall has been noticed.

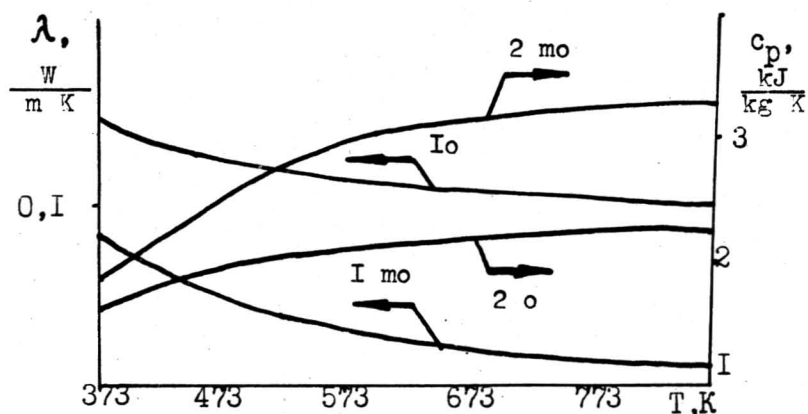


Fig.2. Change of  $\lambda$  (1) and  $C_p$ (2) pyrolysis residue (1073K) with temperature  
 O - organoplastic  
 MO - modified organoplastic

Thus, structurization of foamcoke is accounted for the processes which take place in the interphase of polyammonium phosphate and polymeric matrix. Under the influence of plasma and a subsequent surface modification at the expense of plasma polymerization on the material surface of the reactionable phosphorus containing oligomers, flame-protected fabrics have been obtained. These fabrics practically are not subject to flame propagation.

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