

THERMOPHYSICAL INVESTIGATION OF EPOXYPOLYMERIC COMPOSITIONS AND CARBON FOAMFORMED

V.I.Kodolov, K.I.Larionov, S.G.Shuklin, A.M.Lipanov

Abstract

The formation of an effective fire retardant coating which contains three layers as well as results of the thermophysical investigation of this coating and the foamcoke (carbon foam) formed from it are discussed. The three layer coating contains a) glass reinforced plastics or organoplastics modified by the phosphorus vanadium containing fire retardant system, b) the layer of these plastics partly pyrolyzed and also c) the epoxy resin layer with a crosslinking agent which contains carbonization agent, carbonization catalyst and gasificator. The following facts of the investigation are established:

1. The thermal conductivity of the first layer (the glass- and organoplastics layer which has been modified by the phosphorus-vanadium containing fire retardant system) increases 2-3 times slower than the heat capacity when the temperature increases. The consequence of this process is the decreasing of temperature conductivity.
2. The temperature conductivity of the second layer formed after six heat shocks decreases to a greater extent compared to the temperature conductivity of the first layer, but a packed density and heat capacity increase.
3. The third layer (or an outer layer relative to the heat source) is transformed to the foamcoke or carbon foam under the action of a flame source. Pores of the carbon foam are occupied by ammonia and water vapours, and the inner surface of pores contains carbon substances and polyphosphates with polyanmonium phosphates. The temperature conductivity of this layer is small, and its adhesion to the pyrolyzed layer (the second layer) is the greatest because chemical bonds between layers are formed.
4. The three layer fire resistant coating when heated by the heat flow with a power more than 30 kW/m^2 gets intumescent and can be stable to heat flows during the fire for an hour and longer without a stratification.

The degree of intumescence of the outer (third) layer is determined by the composition of this layer, and also by the composition and defectness of the second layer.

Introduction

The possibilities of the creation of a carbonized layer formed by repeated heat shocks on the surface of epoxy-polymer-based glass- or organoplastics after the modification of them by phosphorus vanadium containing fire retardant systems (P,V-FRS) are considered in [1]. However any transformation of a material or product surface with the formation of a carbonized layer is accompanied the appearance of some defects such as microcracks and micropores. Therefore to increase the resistance of the layer to outer effects it's necessary to use an active coating which decreases the

defectness of a surface layer and forms a intumescent coke (carbon foam) under the action of flame sources. In this case the three layer intumescent coating is formed which consists of a modified layer, a carbonized layer and an intumescent layer.

Objects and methods of investigation

Objects of investigation. Epoxypolymer-based glass- and organoplastics whose outer surface was modified by P,V-FRS, as well as epoxypolymers containing polyammonium phosphate with a particle linear size equaled to $5 \cdot 10^{-5} \text{m}$ were investigated.

A three layer fire resistant coating is formed when a partly pyrolyzed surface (the pyrolysis is carried out at six repeated heat shocks with the power of $46\text{-}50 \text{ kW/m}^2$ during 30 s) is covered with an epoxypolymer-based composition containing polyammonium phosphate. Three organoplastics and four glassplastics with a three layer intumescent coating are studied:

1. The organoplastic is the epoxypolymer filled with 30 mass % ribbon modified by the FRS. The epoxypolymer contains epoxy resin and polyethylenepolyamine in the ratio of 10:1, and also 4 % P,V-FRS (the ratio of P/V = 4/1). The crosslinked material is subject to heat shocks with the power of $46\text{-}48 \text{ kW/m}^2$. After that the pyrolyzed surface is covered with the composition which contains 30 % of polyammonium phosphate (PAP), 10% phenol rubber mixture, 30% of melamine formaldehyde resin in the solution of benzene and methylacetate in the ratio of 1:1 (30%). After drying an intumescent coating is obtained on the organoplastic surface.
2. The organoplastic differs from the previous one by the content of an intumescent layer composition which is the mixture of a phenol rubber composition (80%) and PAP (20%).
3. The organoplastic differs from the first one by the quantity of a viscose fabric (50%).
4. The glassplastic is the epoxypolymer filled with glass fabric (70%) which contains epoxy resin and polyethylenepolyamine in the ratio of 10:1, and also 4% mass P,V-FRS (the ratio of P/V = 4/1). The crosslinked material is exposed to heat shocks with the power of $48\text{-}50 \text{ kW/m}^2$. Then its surface is covered with the composition containing 78% of epoxy resin and polyethylenepolyamine mixture in the ratio of 10:1,5, 13% of PAP, 1,4% of carbamideformaldehyde resin and CCl_4 as the solvent (7,6%). After drying an intumescent coating is obtained.
5. The glassplastic is analogous to the fourth one but differs from the above by the power of heat shocks and by the content of an intumescent composition. The power of heat shocks equals $46\text{-}48 \text{ kW/m}^2$. The intumescent layer is obtained from the following composition: 30% of PAP, 10% of phenol rubber mixture, 30% of melamine formaldehyde resin, 30% of the solvent.
6. The glassplastic differs from the fifth one by the type of glass fabric.
7. The glassplastic differs from the above plastic by the power of heat shocks which is equaled to $48\text{-}50 \text{ kW/m}^2$.

Methods of investigation. The three layer fire resistant coating and separate layers were investigated by a complex number of methods including the determination of a heat layer thickness, thermophysical characteristics, changes of the surface and interface layers chemical structure during the pyrolysis as well as the determination of combustibility of tested materials.

The heat layer thickness δ determined by the temperature distribution throughout the sample thickness is the distance from the combustion surface to the layer whose temperature is $T = T_s / e$, where T_s - the surface temperature.

The temperature distribution throughout the sample thickness is determined by thermocouples placed inside the sample. The thermoelectromotive force is registered by the lightray oscillograph. The heat source is directed the sample during 30 s with a simultaneous registration of a temperature distribution through the sample thickness. After the heat action the heat source is taken away from the sample surface and after the sample cooling the heat action is repeated again.

The fire resistance limit (FRL) investigation is carried out in the following manner.

The tested sample is fastened in the holder together with the heater. The holder with the sample is placed in the test camera and then the sample is subject to heat radiation. The radiation source is the furnace. The tested camera can move to and from the furnace. So it becomes possible to regulate the degree of radiation. The sample heating temperature is determined by means of the thermocouple on the reverse side of the sample for an hour.

Standard calorimeters are used for the investigation of the material thermophysical properties. Tested samples are cut out from plates of the material obtained by means of pasting. The properties of materials subject to different rate of destruction were studied using a step pyrolysis method. The pyrolysis proceeds in a quartz tube furnace. Two temperature intervals for the pyrolysis are known: the first interval is before the destruction process (643K), the second interval - before the carbonization process (823K).

The changes of surface and interface layers chemical structure during the pyrolysis and combustion are investigated using X-ray photoelectron spectroscopy with K_{α} -radiation of Mg anode.

Results and Discussion

The action of heat shocks on the surface of modified plastics with the subsequent covering of the pyrolyzed surface with the epoxy polymer intumescent composition changes the thermophysical characteristics and conditions of carbonization under the action of fire sources .

The heating layer thickness when the intumescent layer is used in the coating is less than the thickness of modified plastics or plastics with a pyrolyzed layer during the heating (Fig. 1)

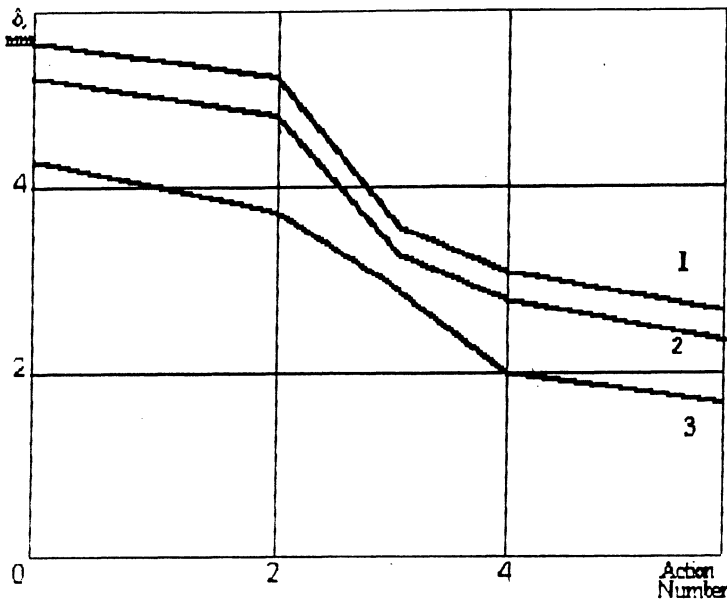


Fig. 1. The dependence of heating layer thickness on the number of heat actions.
 1 - the pyrolyzed layer of glassplastic surface;
 2 - the intumescent layer,
 3 - the three layer intumescent coating.

It is seen from Fig. 1 that the introduction of an intumescent layer leads to the synergism when pyrolyzed and intumescent layers are used together. It's interesting to note that between the 4-th and the 6-th heat actions the values δ for the pyrolyzed layer change less than for the intumescent layer. This fact is explained by the completing of the surface carbonization process, while processes of foam carbon formation proceed further.

The adhesion strength between pyrolyzed and intumescent layers increases compared to the strength of a pair of modified and intumescent layers. The changes of the intumescent layer of the composition influence the adhesion strength less than the material surface preparation. The action of heat shocks on the glassplastics compared to organoplastics is more effective (Table 1).

The influence of the pyrolyzed layer changes the character of temperature dependence on heat capacity of the three layer coating (fig.2). The initial heat capacity of a formed residue of the pyrolysis increases with increasing the pyrolysis temperature. The character of the temperature dependence of heat capacity for the three layer coating on glassplastics is not practically changed (fig.2). The increase in heat capacity of the pyrolyzed residue at 823K corresponds to the formation of carbonizing solid residues with the phosphorous fragments which are, likely to be, in a

Table 1. The comparative data of adhesion strength characteristics for pair of surfaces of plastics and intumescent layers.

№№	Sample	Adhesion strength, N/m	Heat conductivity, kJ/m ² s	Heat capacity, kJ/kg*K	Pacted density, kg/m ³
1	Organoplastic as described in 1.	802	0,18	1,22	2,20
2	Organoplastic as described in 2.	811	0,16	1,22	2,19
3	Organoplastic as described in 3.	800	0,14	1,25	2,20
4	Glassplastic as described in 4.	689	0,22	1,28	2,09
5	Glassplastic as described in 5.	694	0,21	1,19	2,02
6	Glassplastic as described in 6.	682	0,20	1,26	2,10
7	Glassplastic as described in 7	674	0,21	1,29	2,09

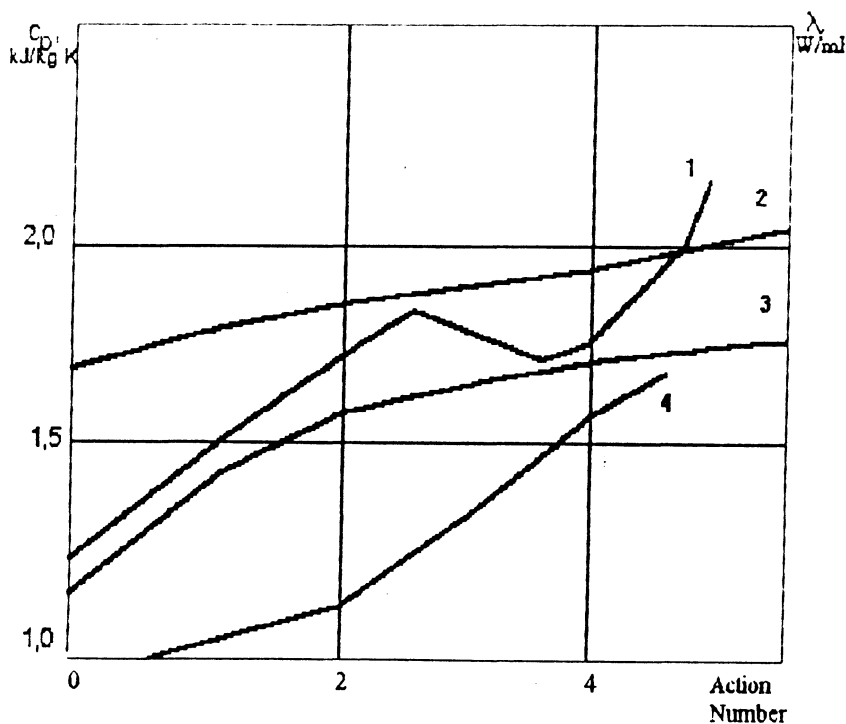


Fig. 2. The temperature dependence of heat conductivity (1,3) and heat capacity (2,4) of three layer fire resistant intumescent material after pyrolysis.

Pyrolysis temperatures: 1,3 - 723K; 2,4 - 643K

chemisorbtional state on the inner surface of pores or bubbles in the pyrolyzed material. In this case the desorption of ammonia and water vapors proceeds in pores or bubbles at 473-573K. It's known [2] that the decomposition of ammonium phosphates proceeds at this temperature interval. The increase in carbonization processes on the inner walls of pores and then the increase in the pores surface heat conductivity are possible. As a result the temperature dependence of the heat conductivity of surface of pyrolyzed residues at 643 and 823K changes proportionally to changes of heat capacity of the same residues (fig.2).

The X-ray photoelectron spectra of surfaces of pyrolyzed residues and their spits confirm the data of thermophysical investigations (Table 2).

Table 2. Changes of binding energy C1s, N1s and P2p in samples of intumescent layer at 533-573K

Sample	E_b , eV	Atoms and groups	At. %	E_b , eV	Atoms and groups	At. %	E_b , eV	Atoms and groups	At. %
Pyrolyzed surface, 533K	285,0	-CH-	30,9	400,7	-NH ₂ -	3,2	134,6	(PO-)	3,2
	286,5	-C(O)- (CNC)	15,1	402,1	-N ⁺ H-	5,1			
	288,8	-C(O)O-	10,1						
Surface of spit, 533K	285,0	-CH-	38,1	401,3	-NH-	2,2	134,7	(PO-)	2,5
	286,5	-C(O)- (CNC)	24,6	402,1	-N ⁺ H-	2,6			
	288,0	-C(O)O-	11,7						
	290,0	-C(O)O	3,9						
Pyrolyzed surface, 533K	285,0	-CH-	47,1	400,5	-NH ₂ -	3,1	134,4	(PO-)	3,0
	286,5	-C(O)- (CNC)	22,1	402,4	-N ⁺ H-	2,6			
	288,0	-C(O)O-	4,3						
Surface of spit, 533K	283,7	=C=	7,2	401,7	-NH-	4,0	134,5	(PO-)	8,1
	285,0	-CH-	24,1	403,4					
	286,5	-C(O)- (CNC)	18,7		-N ⁺ - 	3,2			
	288,0	-C(O)O-	7,8						
	289,2	-C(O)O ⁻	2,4						

There are no ionic carboxy groups and ammonium ions in the surface layers of pyrolysis residues (from the data of XRPES), however amine groups of the initial composition are present. With the increasing of temperature from 533 to 573K the ratio of phosphate fragments in the surface and inner (surface of spits) layers of phosphorus residues changes from 3,68 to 0,62. On the surface of spit there are approximately 1,6 times more polyphosphate groups and 20% more nitrogen containing groups than in the

surface of the pyrolyzed residue at 573K. In this case nitrogen containing groups are ammonium ions. At the same time at this temperature 7,2% of the carbon substance is discovered on the surface of spit. This fact is accounted for by the carbonization. The increasing of temperature should lead the increasing of the carbonization rate. In its turn this process is accompanied by the increasing of surface heat conductivity. The changes of heat capacity and heat conductivity of the surface as a result of processes in the intumescent coating increase the stability of the material at high temperatures and under the action of fire sources.

The fire resistance limit (FRL) is determined for glassplastics and for organoplastics with the three layer coating (fig. 3).

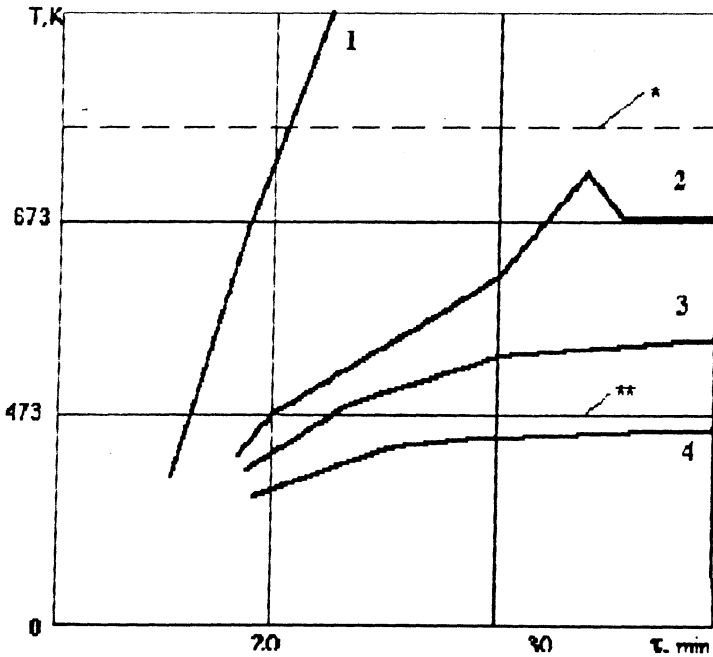


Fig.3. Comparing fire resistance limits of glassplastics on metallic plate and without it.

- 1 - nonmodified glassplastic;
- 2 - intumescent layer on metallic plate;
- 3 - intumescent, pyrolyzed and modified layers of glassplastic on metallic plate;
- 4 - three layer coating without metallic plate;
- * - Fire Resistant Limit for metals;
- ** - Fire Resistant Limit for polymeric materials.

In this case the temperature of a heat radiation source equals 1223K and on the reverse side of samples the temperature for glassplastics does not achieve 453K during 1 hour.

Thus the application of the three layer resistant intumescent coating for organo- and glassplastics is effective.

References

1. K.I.Larionov et al. Physics of combustion and explosion, 1990, № 6, p.20.
2. V.A.Baranova et al. Phosphorous containing flame retardants. M.: NIITECHIM, 1978.