CLUSTER P-V CONTAINING SYSTEMS FOR THE DECREASING OF POLYMERIC MATERIAL COMBUSTION

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ABSTRACT

Cluster systems are microcrystals of vanadiumoxided compounds such as Barium, Calcium or Sodium Metavanadates or Sodium Vanadium Bronze which are distributed into dimethyl- or diethylphosphites or microcrystals of vanadium oxides, for instance, vanadium oxide (+3), distributed into the methylphosphonic acid melted. During the interaction of vanadium compounds with the correspondent phosphororganic substances biue viscous liquids are formed. These liquids have paramagnetic properties. According to the UV and IR spectroscopic investigations as well as the results of EPR spectra the substances obtained consist of the nucleus containing 6 to 12 of vanadium atoms and the shell including ligands which are molecules of phosphites or methylphosphonic acid. Here every atom of vanadium interacts with four of phosphorus containing molecules. Sizes of the particles in these systems donot exceed 200 nm. Introduction of cluster systems (0,1 - 0,3 % vanadium) into epoxy compositions before the introduction of curing agent - polyethylenepolyamine 6 -8 % leads to the acceleration of composition crosslinking and to the combustion decreasing: 1) Oxygen Index grows to 35; 2)mass losses during combustion decrease to

1-2 %; 3) combustion time does not exceed 1 s; 4) the intumescence of material sample is being observed during the burner action as well as the foam coke formation.

INTRODUCTION

For the decreasing of polymeric materials combustion the investigation of the surface layer carbonization is interesting. Earlier the phosphorus containing catalysts of the carbonization as fire retardants were investigated. The activity of these catalysts is increasing when the sizes of their particles are decreasing to cluster sizes. In this paper the results obtained by the investigation of cluster P-V containing fire retardant systems as carbonization catalysts are discussed.

OBJECTS AND INVESTIGATION METHODS

Specimens for the investigation and their preparation. Phosphorus-vanadium containing fire retardant systems (FRS) were prepared by the mixing of vanadium oxide systems (vanadium oxides, vanadium bronzes and Ba or Ca metavanadates) with phosphorus compounds such as acidic phosphites and red phosphorus. In these systems the ratio of phosphorus to vanadium was equaled to 4. In the case of red phosphorus application the mixtures obtained are warmed up to 70 degrees. For the investigation of electron paramagnetic resonance spectra the specimens of coloured complexes obtained are dissolved in liquid ligands (phosphites). Here the drop dissolution occurs with the cluster formation.

The mixtures of the fine powders (the sizes of powders are less than 10^{-6} m), obtained by the interaction of red phosphorus and Ba or Ca metavanadates at a ratio of phosphorus and vanadium equaled to 4, were dispersed using ultrasonic disperger in solutions: polycarbonates - in chloroform, and polyamide PA-54 - in alcohol. From these solutions the films with the P-V systems content of 4-5% and with the thickness not more than $7*10^{-6}$ m are obtained. The films were prepared on the ceramic substrates by the evaporating of solvent during the heating and vacuum treatment. The thick polymeric specimens (up to $5*10^{-3}$ m) were pyrolized in a quartz tube fur-nace at 1073 K for 300 s in the inert atmosphere.

Investigation methods. The thermogravimetric investigations were carried out using thermobalance with the rate of 5 and 20 K/min (sizes of samples: up to $5*10^{-5}$ kg, at-mosphere: air or nitrogen).

The x-ray photoelectron spectra of the specimens were obtained using the magnetic x-ray electron spectrometer (MXE) as well as spectrometer ES 2401 with AlK_α(MXE) and MgK_α(ES 2401) radiation. The calibration of the compound electron spectra was made according to the elements which did not change their surrounding during the thermolysis, or according to the elements of the mask applied as a nonametric layer on the surface being investigated. The relative content of the elements in the specimens under investigation was calculated using sensitivity factors. The specimens prepared for the photoelectron spectroscopy were placed on a specially made conducting substrate (copper or glass carbon).

Spectra of electron paramagnetic resonance (EPR spectra), UV and IR spectra, and also diffractograms were obtained by the Standard methods.

Tests on the flammability of materials modified by the cluster containing fire retar-dant systems are carried out according to National Standards.

RESULTS AND DISCUSSION

During the interaction of phosphorus containing compounds(phosphites or red phosphorus) with vanadium containing compounds (vanadium oxide systems) the coloured substances are formed. In accordance with data of investigations these substances are olygomeric complexes or clusters consisting from a nucleous (6-10 vanadium atoms) and a shell in which there are 20 - 40 phosphorus atoms included in corresponding number of ligands. The quantity of vanadium atoms in the nucleous was established by the investigation of EPR spectra structure obtained when we investigated the dilute solutions of above substances (solvent: the corresponding ligand) [1]. Besides according to IR and UV spectra and also diffractograms two types of interactions between phosphites and vanadium oxide systems occur. In the dependence on types of interaction between ligands and vanadium oxide systems the compounds are obtained with blue or green colour. In the first case the coordination reaction is explained by the interaction of P=O...V, and in the second case - by the interaction of POC - groups with vanadium atoms.

Using IR spectroscopy, x-ray photoelectron spectroscopy and diffractometry the interaction of red phosphorus and Ba or CA metavanadates was established. As a result of this interaction the Barium or Calcium Olygovanadylphosphates are formed [2]. In these cluster systems the redox pair is created: vanadium is reduced, and phosphorus is oxidized. In this case the activity of P-V containing fire retardant systems in polymers having active functional groups grows.

During the investigation of polymeric materials based on epoxy resins, polycarbonates and polyamides in which the correspondent additives are used the changes in UV and IR spectra, diffractograms, x-ray photoelectron spectra and also microphotographs of splits (electron microscopy) are found. For example, in the modified polyamides the changes in surrounding of phosphorus and vanadium (additives or fire retardant systems) and also of nitrogen and oxygen (polymer) are determined.

When the temperature action on specimen increases, the line of C1s corresponding to Carbon of graphite is appeared in x-ray photoelectron spectra [3-5]. In the dependence on the chemical composition and structure of additive and polymer the degree of transformation of polymer into the above Carbon changes. Here the carbonization process can be caused by the secondary polymeric structure formation [5]. If P-V containing cluster system which can be used as fire retardant system (FRS) has the laminated structure the formation of secondary structure of chemisorbed and orientated polymer is possible. The appearance of this structure in polyamide leads to the main crystallinity change. When the above FRS is introduced into polycarbonate the maxima appear in its diffractogram. These maxima are preserved in the diffractograms of pyrolysis residues and also coke residues obtained under the fire action. At the same time the main peaks of diffractograms, corresponding to the polymer crystallinity, vanish after the fire or heat action on the polymer. This fact can testify to the preservation of active centre promoting the heterogeneous catalysis of carbonization.

On the basis of the combustion theory and experimental data of carbonization during the combustion we proposed [5] the criteria of unstable combustion for the carbonizing polymers:

$$80 < S_c (\%) < 100,$$

where S_c - the carbonizing surface of polymer in accont to overall surface expressed in % or fractions which is calculated with using the following equation -

$$S_c (\%) = c(\%)\ n\ q_{cm}\ q_{am} ,$$

in turn, c(%) - active element content (in %); n - number of functional groups interacting with active centres of FRS; q_{cm} - amount of macromolecules chemisorbed layers taking into account on the FRS layer; q_{am} - amount of active macromolecules forming phase zone in polymer taking into account on FRS layer.

According to this proposition if the size of active particles, which promotes the carbonization in the material surface layers, is less the efficiency of FRS containing these particles is more.

Here it should be noted the used principle of FRS efficiency estimation when the relative parameter of combustion as well as relative content of active element promoting to the combustion decreasing effect are taken into account. Therefore the following equation is proposed:

$$P = (c_0/c_i)*(k_0/k_i),$$

where c_0 - content of active element taken as a standard (corresponding to 5,9% for epoxy resin), c_i - content of active element in polymeric material taken into account on phosphorus, k_0 - combustion parameter taken as a standard (if the mass losses are taken as a combustion parameter, $k_0 \sim 10\%$), k_i - combustion parameter corresponding to material investigated (for example, Δm_i - mass losses during the combustion).

Besides relative values ($\Delta P/P$) are proposed. For additive effect of FRS ($\Delta P/P$) = 0, and P = = 1. The increasing of ($\Delta P/P$) more than zero, and $P > 1$ corresponds to the synergism of P-V containing cluster system. If ($\Delta P/P$) < 0, and $P < 1$ one can say about the presence of antagonism region in which the polymer and additives are found.

As an example of the efficiency estimation of P-V containing cluster systems for epoxy resins can be represented. In this case we used systems containing the following pairs of substances:

P_r - $Ba(VO_3)_2$, P_r - $Na_{0,33}V_2O_5$, Diethylphosphite (DEP)- $Na_{0,33}V_2O_5$, DEP- $VOSO_4$

In accordance with the activity of above FRS these pairs of substances can be disposed in the following order:

P_r - $Ba(VO_3)_2$ >> P_r - $Na_{0,33}V_2O_5$ > DEP - $Na_{0,33}V_2O_5$ >> DEP - $VOSO_4$

(1) (2) (3) (4)

This range defines the linear relation in the coordinates ΔP/P - P with the determination of the synergism and antagonism regions (Figure). P and ΔP/P for the above pair of FRS have the following values:

Numbers of FRS	(1)	(2)	(3)	(4)
P	5,45	2,7	0,8	0,47
ΔP/P	4,45	1,74	-0,2	-0,53

Thus P-V containing cluster systems are the carbonization catalysts and effective FRS simultaneously. At the same time these systems promote the change of main material structure with the improvement of its physico-mechanical characteristics or of its stability to the environment action. For instance, the introduction of 4-5% of P-V containing FRS into the glass reinforced plasics based on the Kapron leads to the growth of the breaking stress in bending in 1.4 times at the considerable decreasing of combustion.

CONCLUSION

1. The effective P-V containing fire retardant systems of cluster type which considerably decrease the polymeric material flammability are proposed. Great efficiency is possible when the interaction between the active centres of cluster systems and the functional groups of polymeric materials occurs.
2. The pattern of interactions between macromolecules of polymeric materials containing functional groups and P-V containing cluster systems is determined under the high thermal stream action.
3. The system of material fire resistance estimation as well as the system of fire retardants efficiency estimation in terms of active element relative concentration and of its application effect are proposed.

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FIGURE

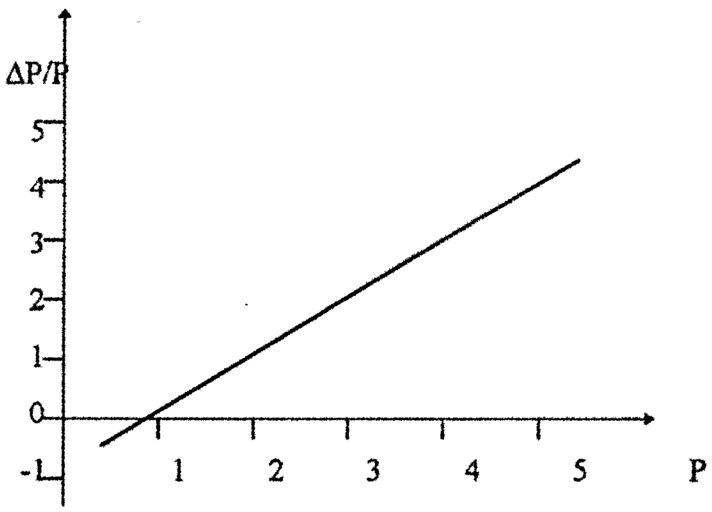

Figure. Changes of P-V containing cluster FRS activity in the dependence on thier compositions for the decreasing of epoxy resin flammability