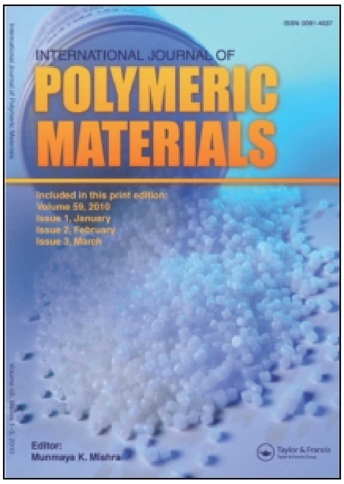

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Cluster Systems as Carbonization Promoters and Fire Retardants of Polymeric Materials

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Cluster systems obtained by fractional dissolution of ultradispersed powders of metal salts (sodium, barium, calcium metavanadates) in active media such as dialkylphosphites are used as fire retardants of polymeric materials which contain functional groups. The control of the coordination reaction proceeding is carried out according to the color change (till painting stability). When cluster phosphorus-vanadium containing systems are introduced into olygomeric or polymeric compositions, the interaction of functional groups of polymeric component with the active centers of fire retardants of cluster type occurs. As a result of such interaction the considerable increase of fire-resistant properties of the obtained polymeric materials is observed. The materials fire resistance is increased due to the stimulated carbonization proceeding in the surface layers. The scheme of stimulated carbonization process is suggested. This process consists in the dehydropolycondesation of aromatic hydrocarbons and is carried out in active media, containing metal ions or ultra dispersed metal powders. The result is the formation of carbon-metal containing nanostructures, having the defects due to the conditions of their extraction from the medium.

Keywords: Fire retardants; polymers; clusters; carbonization; metal salts

INTRODUCTION

The efficiency of phosphorus-vanadium containing fire retardant systems for the flammability decreasing of a wide class of polymeric

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materials containing functional groups which can interact with active centers of fire retardant systems, has been shown [1–4]. Besides, it has been determined [5–7] that the presence of metal salts, the derivatives of alkyl(aryl) phosphonic acids or a polyphosphoric acid stimulates the formation of carbon containing particles from aromatic hydrocarbons. In this case the structures similar to carbon "embryos" of fibers are obtained.

It is of interest to form cluster systems by fractional dissolution of sodium, barium and calcium metavanadates in dialkylphosphites and to use them as fire retardants in epoxypolymers. The investigation of carbonization in surface layers of materials and stimulated carbonization of aromatic compounds with the extraction of carbon-metal containing nanostructures can be also perspective.

EXPERIMENTAL

The Investigation Objects

The interaction products of diethyl- or dimethyl phosphites with sodium, calcium and barium metavanadates proceeds at molar ratio of the components from 4 : 1 to 8 : 1. During the interaction process the mass painting occurs. After the stable painting is established the solution is separated from the precipitate, and the excess phosphite is removed in vacuum. The obtained viscous and glassy substances of blue and green color are introduced into the composition which contain epoxy olygomers before the introduction of cross-linking agent – polyethylene polyamine (otherwise it is impossible to regulate the process of hardening).

The obtaining of carbon-metal containing cluster systems is carried out by consequent-parallel processes of dehydropolycondesation and coordination from antracene, phenanthrene or naphthaline in active medium which contain ultra dispersed powder of cuprous chloride and copper, or polyphosphoric acid and copper. After keeping the reaction mixture in a snugly closed vessel in the range of temperatures 573–723 K to obtain unchangeable black painting, the mass is treated by acids and dissolvent for the removing of salts and organic substances which have not reacted or reacted only partly. The extracted particles in alcohol (acetone) are treated in ultrasonic field for the separation of adhered particles.

The Investigation Methods

The obtained substances (phosphorus-vanadium containing and carbon-metal containing cluster substances) are investigated by means of EPR spectroscopy, IR- and UV-spectroscopy, X-ray photoelectron spectroscopy and diffractometry. IR spectra are investigated in the range $700-4000\,\mathrm{cm}^{-1}$, and UV spectra – in the range from 200 to 400 nm. Diffractograms are obtained using CuK_α radiation. X-ray photoelectron spectra are obtained by X-ray photoelectron magnetic spectrometer during the excitation by Al K_α radiation in vacuum 10^{-6} torr.

RESULTS AND DISCUSSION

In the majority of cases after the precipitate separation and its removing from the solution obtained during the interaction of metavanadates of the above metals with dialkylphosphites, oil-like or glassy substances of blue ($NaVO_3$) or blue-green color ($Ba(VO_3)_2$, $Ca(VO_3)_2$) are formed.

During the studying of solutions of such substances a super thin structure of EPR spectra is investigated in corresponding phosphites by EPR spectroscopy. When interpreting the structure it can be supposed [8] that the substances formed contain from 6 to 11 atoms of vanadium. According to IR spectra and X-ray photoelectron spectra it is determined that the bonds between phosphites molecules and vanadium-oxide systems are formed (four ligands, formed from phosphites molecules, fall at one vanadium atom).

By analogy with [2] during stepped heating (in accordance with temperature changes during thermogravimetric investigations of the compositions) the change of energies of corresponding atoms (C1s, N1s, P2p) in X-ray photoelectron spectra (after the dispersion of obtained cluster system inside the compositions in ultrasonic field) is noted.

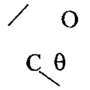
In accordance with the results of X-ray photoelectron spectroscopic investigations it can be concluded that the increase of temperature up to 873 K leads to the carbonization of epoxy polymers in surface layer and to the increase of phosphorus oxidation degree (PO_4 fragment in polyphosphoric acid E_b P2p = 134.7 eV).

During the action of fire source on hardened compositions the intumescence effect is observed. This effect can be explained by the interaction of polyethylenepolyamine and clusters (the competition of phosphorus-ester and amines groups during the coordination on vanadium atoms). At high temperatures the evolution of ammonia with the formation of carbon layer proceeds. The oxygen index for cross-linked epoxy polymers, which contain phosphorus-vanadium cluster system, changes from 28 to 40 depending on the cluster system used.

The carbonization process, when bound aromatic rings or multinuclear aromatic fragments are present in the material with Lewis acids, can be investigated on model systems containing aromatic hydrocarbons and media which have ultra dispersed metal powders and polyphosphoric acid or metal salts and metals in their composition. It is known [7] that aromatic polymers are obtained from benzene and other aromatic hydrocarbons during the dehydropolycondesation in the presence of Lewis acids. In our case, active media based on cuprous chloride with copper ultra dispersed powders or on polyphosphoric acid with the same powder are used. After heating for 24 hours at 573–723 K stable black painting of reactive mass is obtained. The reactive mass is treated by acids (hydrochloric and nitric), the residue is washed till pH decrease and treated by organic dissolvents (benzene and its derivatives, acetone and alcohol). The obtained particles of black color endure high temperatures. According to the diffractograms the main reflex occurs in the range of interplane distances 0,34 nm. The interaction of π-electrons of aromatic hydrocarbons with ions of 3d elements leads to the decreasing of C—H bond energy and to further removing of proton towards complex anion $[Cu_2Cl_4]^{2-}$. This interaction is found by means of quantum-chemical calculating experiment (the first stage of dehydropolycondesation). The aromatic polymer obtained by dehydropolycondesation in the surroundings of complex anions, transforms into spiral in accordance with quantum-chemical calculations and between the spires dehydropolycondesation and coordination processes continue. The result of such quantum-chemical experiment is a carbonic nanotube containing metal atoms and ions.

However, it is necessary to note that X-ray photoelectron spectra are characterized by the presence of carbon, oxygen (Figs. 1a, b), and of carbon, oxygen and phosphorus (Figs. 2a, b, c).

Evidently, the treatment of reactive mass by nitric acid leads to partial oxidation of carbon-metal containing systems, and nanostructures contain up to 20% of oxidized groups having carbonyl (286,5 eV) and scheme



O - groups (288 eV).

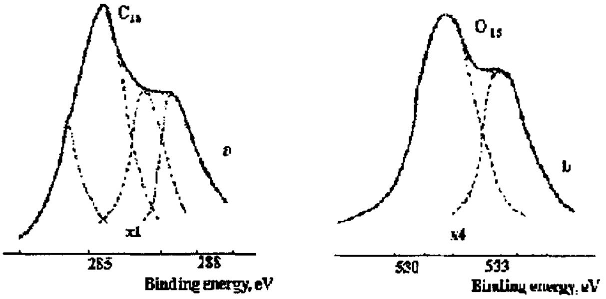


FIGURE 1 X-ray photoelectron spectra of nanostructures obtained from aromatic hydrocarbons in the presence of polyphosphoric acid and copper powder mixture.

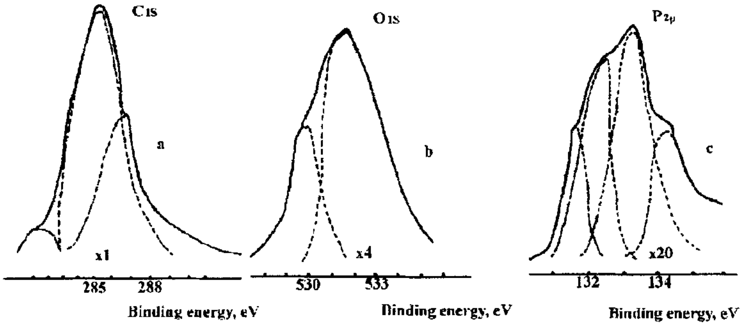


FIGURE 2 X-ray photoelectron spectra of nanostructures obtained from aromatic hydrocarbons in the presence of cuprous chloride and copper powder mixture.

Independently from the used medium in the spectra of products obtained there are peaks of low intensity typical for C-Cu (283,5 eV) bonds. The intensity of corresponding peak in the surroundings of particles obtained in the medium where phosphoric acid is used is lower in 3 times comparing with the analogous peak in the spectrum of particles obtained in the melt of cuprous chloride. This fact can be explained due to binding of copper by phosphate ions.

Besides, there are two maxima responsible for PO_4 and PO_3 (PO_2) groups in P2p spectrum. Although, according to the spectra, the content of these groups is not great, it can be supposed that after the treatment by acids and dissolvents on the ends of tube nanostructures phosphorus oxide groups connected with a carbon frame and metal ions are left. UV spectra of the particles obtained have the maxima in the range of wavelengths of 320 and 380 nm. The action of a naked flame on the products mentioned leads to their heating that is observed for fire resistant carbon coatings.

CONCLUSION

Thus, joined dehydropolycondesation and coordination with widely investigated dehydration processes occur during the action of high temperatures and fire on polymeric materials containing cluster fire retardant. This fact can explain the action mechanism of cluster fire retardant on the decrease of polymeric materials flammability.

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