Layered Silicate Nanocomposites Based on Polyvinylchloride Plasticate and Carbamide-Containing Organoclay: Synthesis, Structure, and Properties

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Abstract—Novel layered silicate nanocomposites based on PVC plasticate and carbamide-containing organ-oclay are developed and studied. The results obtained provide the possibility of creating cable PVC composi-tions combining fire resistance with enhanced physicomechanical characteristics and reduced emission of toxic fumes upon burning.

Keywords: layered silicates, polyvinylchloride, montmorillonite, organoclay, urea, polymer nanocomposites.

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INTRODUCTION

At the present time, the development of reliable methods for the preparation of high-technology nano-structured polymer-layered silicate composites is one of the principal directions in the technology of poly-mer materials. Besides enhanced mechanical strength characteristics, such materials have a number of other special properties even at low filling degrees (up to 5%).

Interest in polymer-layered silicate nanocompos-ites is not only attributable to the possibility of their application in various fields but also due to the devel-opment of new basic concepts in chemistry and related sciences. This is associated with the fact that the prop-erties of nanocomposites differ significantly from the bulk properties of phases of which they are composed and are determined by the properties of filler nanopar-ticles, by the structures they form, and by interfacial interaction at the boundary between the polymer matrix and the filler. The character of interaction at the interfacial boundary may be adjusted both by means of introduction of various surface functional groups and by reduction in filler particle size. Layered silicates are capable of ion exchange with organic cat-ions and of spontaneous dispersal with formation of highly anisometric particles with nanoscale thickness.

Several dozen kinds of polymer nanocomposites based on polymers and layered silicates, many of which possess enhanced performance characteristics, have been obtained by different groups of researchers over the last 10—15 years [1]. The possibility of using virtually all kinds of polymerization and polyconden-sation polymers as a matrix was demonstrated [2—4].

In spite of the extensiveness of the studies con-ducted so far, layered silicate nanocomposites based on polyvinylchloride have been mentioned very sel-dom [5].

The aim of our work consisted in development and investigation of novel composite materials based on a polyvinylchloride plasticate and an organomodified montmorillonite.

EXPERIMENTAL

The following starting components were used: (1) montmorillonite (MMT) prepared from natural clay of the Gerpegezh deposit (Russia, Kabardino-Balkarian Republic) according to the procedure [6] where the cation exchange capacity was equal to 95 mg-eq/100 g of clay; (2) chemically pure grade car-bamide; and (3) PVC plasticate of I40-13A grade of standard formulation 8/2 prepared according to GOST 5960—72.

Procedure for Organomodification of Montmorillonite

In a 2 L four-necked flask equipped with a stirrer, a reflux condenser, a separation funnel, and a thermom-eter, 50 g of montmorillonite and 1 L of distilled water were charged. The calculated amount of carbamide aqueous solution was poured into the separation fun-nel. The stirrer was switched on and the temperature inside the reaction medium was raised to 70°C. After the temperature had reached the predetermined value, the carbamide solution was added by drops. Addition by drops was continued for 3 h followed by stirring for 30 min. Then the temperature was reduced to room
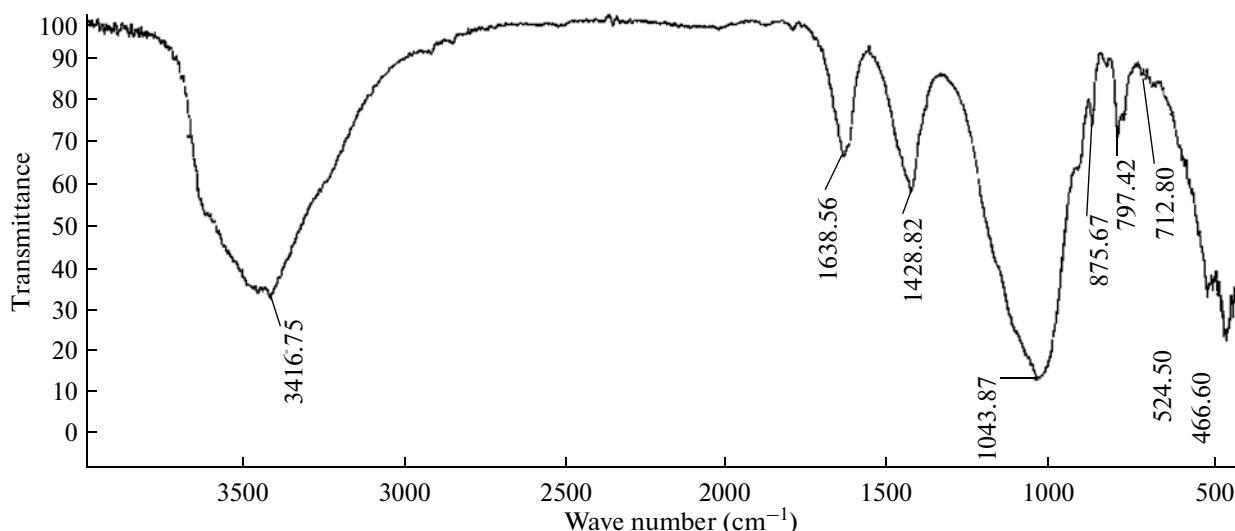
Fig. 1. IR spectrum of montmorillonite.

temperature, and the product was filtered off, repeatedly washed with distilled water, and dried in a vacuum cabinet at 70°C for 48 h.

Preparation of Nanocomposites

In an R600/HC2500 two-speed mixer manufactured by Diosna, where the mixer design provides intense turbulent mixing with high homogenization of the composition and blowing with hot air, the following components were mixed: PVC plasticate of I40-13A grade of formulation 8/2 prepared according to GOST 5960−72 and organoclay in a ratio of 85−95 : 5−15 wt %, respectively. After intense stirring of PVC plasticate with organoclay in the hot mixer at the temperature of 110−120°C resulting in a free-flowing, highly homogenized mixture, the composition was cooled down to the temperature of 40°C and supplied to a twin-screw extruder. The temperature in the extruder zones was as follows: 150°C (I), 145°C (II), and 125°C (III). The screw rotation speed was 48 rpm.

Samples for testing were pressed from granules at the temperature of 160−170°C under pressure of 120 kgf/cm² for 3 min.

Physicomechanical tests of the nanocomposites were conducted according to the following procedures: GOST 11262−80 (tensile test); GOST 21207−81 (combustibility); GOST 15088−83 (Vicat softening temperature); GOST 24621−91 (Shore hardness); GOST 19109−84 (Izod impact strength); GOST 14236−81 (modulus of elasticity, ultimate tensile strength, and elongation at rupture); GOST 28157−89 (fire resistance).

RESULTS AND DISCUSSION

It is known from the literature that, when preparing polymer-layered silicate nanocomposites based on natural montmorillonite clays and organic polymers, difficulties arise owing to their incompatibility [7]. This problem is eliminated by modifying montmorillonite with various surfactants. To this end, we used carbamide (urea).

An intercalated hybrid based on clay and urea was obtained for the first time in human history in the process of production of early Chinese porcelain [8]. At the present time, urea is not used as a clay organomodifier for the subsequent preparation of layered silicate polymer nanocomposites in spite of the fact that it is more available and cheaper than alkyl ammonium salts which are conventionally used for these purposes. In this respect, it is of scientific and practical interest to study the process of organomodification of clay with urea and the possibility of application of the prepared organoclay for the preparation of nanocomposites based on polyvinylchloride.

The IR spectra of natural and carbamide-modified montmorillonite are shown in Figs. 1 and 2.

Interpretation of the montmorillonite spectrum shows that the main bands appearing in the spectrum refer to valence bonds between silicon and oxygen and between hydrogen and oxygen in montmorillonite (see Fig. 1). The strong wide band at 1040 cm⁻¹ corresponds to valence vibrations of Si−O−Si tetrahedra of the silicon−oxygen framework, while bands at 467 and 524 cm⁻¹ correspond to deformation vibrations of Me−O bonds. The band in the region of 797 cm⁻¹ corresponds to Si−O−Si vibrations of rings formed by SiO₄ tetrahedra. The absorption bands in the regions of 712 and 1429 cm⁻¹ are due to an admixture of calcite. The intense broad band in the range of 3100−3500 cm⁻¹ and the band at 1638 cm⁻¹ refer to OH
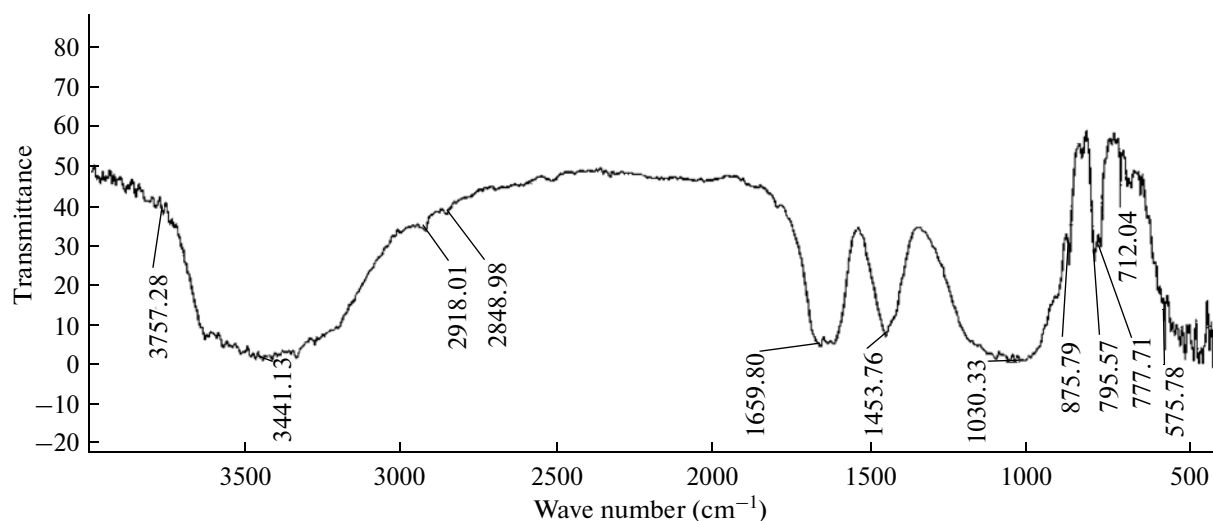
Fig. 2. IR spectrum of carbamide-modified MMT.

valence and deformation vibrations of free and bound water.

As one can see, in the spectrum of modified montmorillonite (see Fig. 2) in addition to the bands intrinsic to the plain mineral, the band due to valence vibrations of amino groups in the region of 3757 cm^{-1} arises, while the band in the region of 3400 cm^{-1} widens significantly, which indicates that this group forms hydrogen bonds with oxygen atoms of the silicate group of clay. The bands at 777 and 1660 cm^{-1} corresponding to valence and deformation vibrations of carbonyl group in urea also arise. Significant broadening and shift of band at 1043 to 1030 cm^{-1} is apparently due to formation of relatively strong coordination bonds between urea and Si−O$^-$ and Si−OH active functional centers of basal surfaces of montmorillonite.

To prove the fact of organomodification of MMT with carbamide, we conducted an X-ray diffraction study (Fig. 3) and scanning of the surface of the obtained samples using an atomic-force microscope (Fig. 4).

The diffraction pattern of MMT (see Fig. 3, curve *1*) has a characteristic peak in the region of 2θ = 7.53° (d = 1.1 nm) corresponding to Bragg periodicity in arrangement of heterogeneous regions and related to the distance between the basal surfaces of clay. Incorporation of carbamide between the layers of nanosilicate (see Fig. 3, curve *2*) results in hydrophobization (organomodification) of the montmorillonite basal surfaces and in a shift of the peak into the low-angle region of $2q$ = 4.9° (d = 1.8 nm).

The results of scanning of the modified MMT surface (Figs. 4 and 5) also indicate the existence of interaction between carbamide and Si−O$^-$ and Si−OH active functional centers of basal surfaces of montmorillonite.
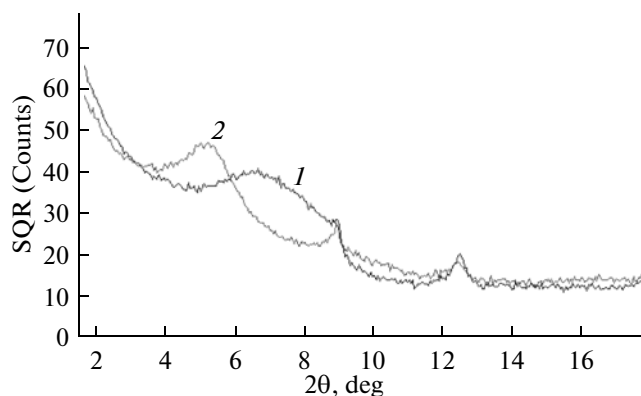

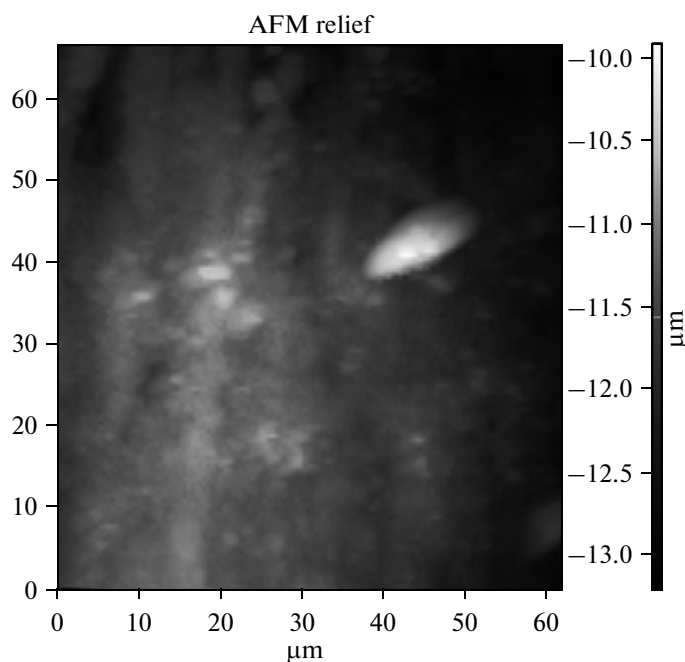**Fig. 3.** Diffraction pattern of (*1*) starting and (*2*) modified MMT.

Fig. 4. Picture of relief of montmorillonite surface.
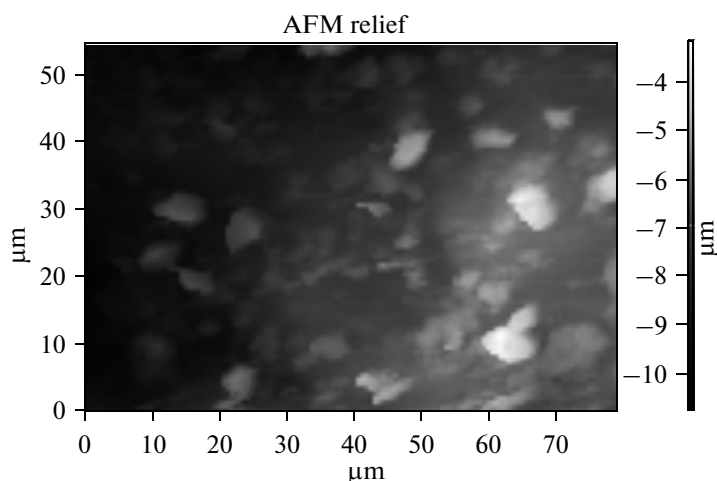
AFM relief

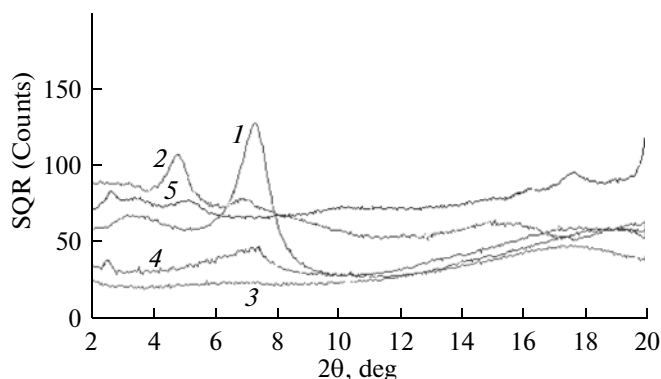**Fig. 5.** Picture of relief of carbamide-modified montmorillonite surface.

Fig. 6. Diffraction patterns: (*1*) montmorillonite; (*2*) organomodified montmorillonite; (*3*) PVC plasticate; (*4*) PVC plasticate + 3% organoclay; (*5*) PVC plasticate + 7% organoclay.

Figure 6 shows the diffraction patterns of montmorillonite, organoclay, and polyvinylchloride nanocomposite.

When the content of organoclay in PVC plasticate is 3 wt % (see Fig. 6, curve *4*), the structure of the nanocomposite is exfoliated, which is confirmed by the absence of the organoclay peak in the diffraction pattern of the composite. As the amount of the layered silicate nanofiller increases to 7 wt % (see Fig. 6, curve *5*), an appearance of a small peak in the region of 2.4° ($d = 3.5$ nm) is observed, giving evidence of transition to a mixed structure containing both exfoliated and intercalated silicate plates.

The table summarizes the results of the study of the influence of the developed organoclay on the physico-mechanical properties of PVC plasticate.

It is seen from the table that the modulus of elasticity of the nanocomposites surpasses that of the starting plasticate by 20−50%, while the tensile strength and relative elongation remain virtually on the level of the starting polymer.

As the content of organoclay increases, an increase in the flow behavior index of the melt of PVC plasticate takes place. This is indirect proof of change in the supramolecular structures in a polymer melt as a result of introduction of organomodified montmorillonite. In other words, it seems that nanoparticles of organo-

Physicomechanical characteristics of layered silicate nanocomposites based on PVC plasticate

| Characteristic name	I 40-13A PVC plasticate	PVC + 3% OC	PVC + 5% OC	PVC + 7% OC
Flow behavior index of melt, g/10 min	0.55	1.5	2.1	2.36
Tensile strength at rupture, MPa	20.0	23.5	22.6	19.0
Ultimate elongation, %	276	273	269	267
Specific volume electrical resistance, [Ω cm]	3.4×10^{14}	2.5×10^{15}	2×10^{15}	1.5×10^{15}
Hardness at 20°C, kgf/cm^2	22	24	24	25
Modulus of elasticity, MPa	75.5	92.3	99.7	115.3
Flammability (time to extinguish, s)	4.5	1.4	1.2	0.9
Vicat heat resistance, °C	90	110	118	127
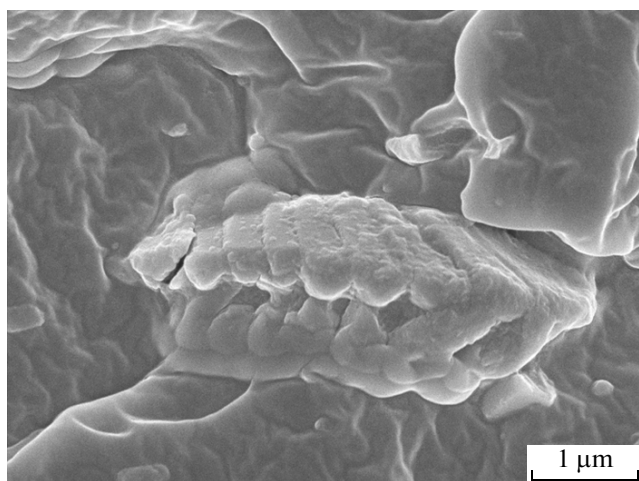
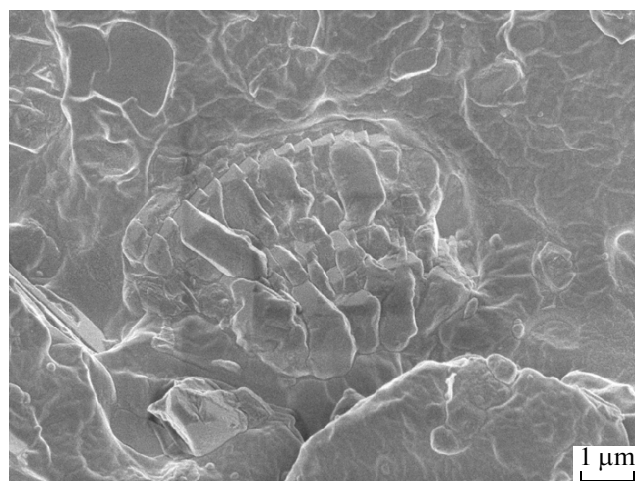**Fig. 7.** Electron microphotograph of PVC plasticate.

Fig. 8. Electron microphotograph of nanocomposite PVC plasticate (5% organoclay).

clay act as nucleation centers in this case. The presence of supramolecular structures in the polymer melt was confirmed upon investigation of starting and modified polyvinylchloride plasticate by raster electron microscopy (Figs. 7 and 8). Note that new supramolecular formations arise in the melt along with retention of existing supramolecular structures upon introducing the developed organoclay. It is assumed that the main reason for their appearance is the orientation because the flowing is closely associated with this process, which initiates nucleation upon crystallization of polymers [9]. An amazing improvement in volume resistance of plasticized PVC upon addition of organoclay is also observed. The layered nature of montmorillonite probably serves as a hindrance for the trajectory of current leakage through the composition. A decrease in electrical conductivity and increase in dielectric strength is also observed upon appearance of crystalline regions in polymers [10]. In our case, the appearance of a relaxation region of dipole losses due to movement of polymer chains inside crystalline formations is possible.

As a result of the performed studies, it was possible to establish that the optimal structurizing of nanocomposite polyvinylchloride resulting in enhancement of properties is achieved at a nanofiller content of 3−5%.

Investigation of combustibility of PVC plasticate and modified compositions thereof showed that fire resistance increases when carbamide is used as an organomodifier for MMT.

Currently, two mechanisms of decrease in combustibility are proposed to explain the influence of layered silicates on the process of combustion of polymers. One of them is associated with formation of a carbonized layer affecting the mass and heat transfer between the combustion zone and polymer material. The other variant takes into account catalytic activity of aluminosilicates in the process of polymer thermal destruc-

tion, which makes it possible to shift the process in the direction of decreased thermal effect and thereby decreases the maximum rate of heat release [11]. One may assume that, in the considered case, a fraction of polyvinylchloride macromolecules located inside the silicate nanolayers is transformed, owing to low close contact with catalytically active silicate surfaces and oxygen atoms, into a condensed coke-ceramic residue which is much more thermally stable than conventional carbon coke. In this case, in spite of effective coke formation, the maximum level of smoke formation upon burning of PVC nanocomposites is not higher than that of conventional PVC, and its amount is virtually the same in all the cases. The results obtained lead to a conclusion about the key role of coke formation of nanocomposites in the mechanism of inhibition of their burning.
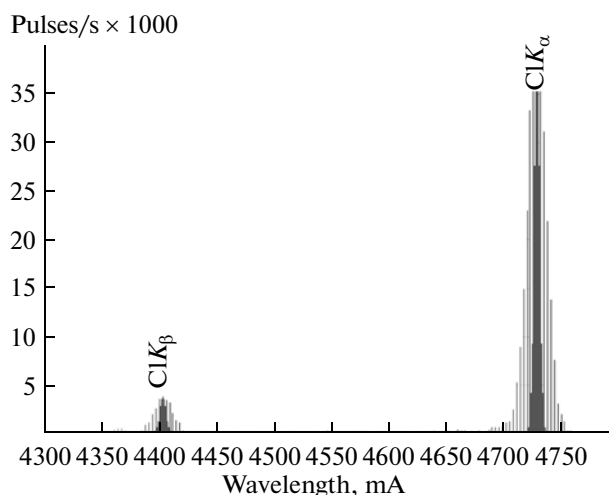

Fig. 10. X-ray fluorogram of coke residue from PVC plasticate modified by 5% organoclay for chlorine content.
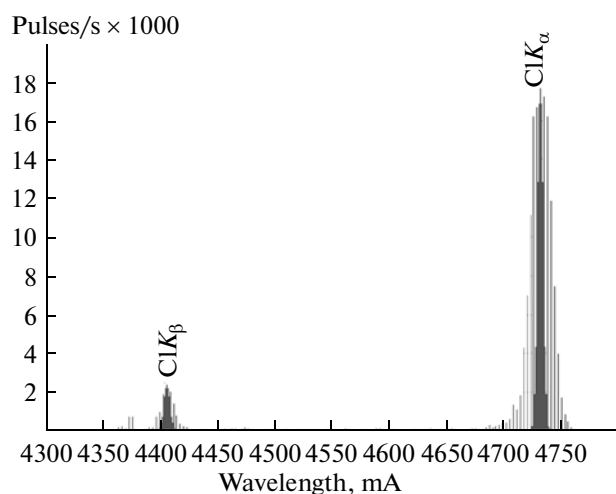
Pulses/s × 1000

Fig. 9. X-ray fluorogram of coke residue from PVC plasticate for chlorine content.

It is important to note that in this case carbamide-containing organoclay, which is an ecologically friendly product resulting in no pollution of the environment upon thermal action and under operating conditions, functions as a flame retardant.

Figures 9 and 10 show X-ray fluorograms of coke residue from starting PVC plasticate and one modified by 5 wt % of the developed organoclay.

Elemental analysis of the coke residue for chlorine content showed that the coke residue from compositions with organoclay (see Fig. 10) contains two times more chlorine than starting plasticate, which is indicated by a decrease in evolution of hydrogen chloride upon burning.

Therefore, the developed carbamide-containing organoclays are functional nanofillers for PVC plasticate, which are capable of producing effects resulting in an enhancement in the physicomechanical and processing properties, and a decrease in flammability. The results obtained open the possibility for the development of PVC compositions combining in themselves fire resistance with enhanced physicomechanical characteristics and simultaneously being low smoke and emitting a negligible amount of hydrogen chloride upon burning, which is nowadays of immediate interest and in demand both from the cable manufacturing industry and from the field of production of polymer composite materials.

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