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Research Article

Layers of Active Coal with Grafted Porous Macromolecular Cyclic Ethanolamines on the Surface of PVC Materials

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Abstract

Materials from a transparent PVC film with a layer of active carbon with grafted macromolecular cyclic ethanolamines that are sewn to one side of the film were synthesized. Tthe electron conductivities of materials were measured. Using the X-ray diffraction method, it has been shown that grafting of macromolecules affects the internal structure of coal particles. The surface of the layer is formed by external pores with walls of cyclic amine nets, to which internal pores with the same walls adjoin by the holes of the cycles. The transition zone is formed by pores with walls from sections of cyclic amines and carbon structures on the surface of coal particles. Pores from coal adjoin to them. The structure of the transition zone is luminescent. Sorption of solvents of different nature was studied, the effect of the layer composition on its sorption capacity was revealed. It is established that the structural elements of the transition zone bind solvents to host-guest complexes.

Keywords: PVC, layer, active coal, grafting, cyclic ethanolamines, electronic conductivity, luminescence, sorption, complexes

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Introduction

The development of the synthesis of electron-conductive luminescing layers sewn to the covers on the basis of active coal, the particles of which are combined with macromolecules grafted to their surface with cyclic ligand groups, is promising in terms of creating new multifunctional materials. In [1] the possibility of synthesis of a layer from active coal with grafted macromolecular cyclic ethanolamines (Layer 1) was shown. For this, coal with OH groups located

$$R_3C\text{-}OH + Cl\text{-}CR_3 + (CH_2CH_2OH)_3N \rightarrow R_3C\text{-}O\text{-}CR_3 + (CH_2CH_2OH)_3NHCl,$$

Where, $Cl\text{-}CR_3$ is the PVC group, $(CH_2CH_2OH)_3N$ is the triethanolamine.

Then under the action of ethanolamine with the reactionthey were converted into macromolecular cyclic ethanolamines with a porous structure.

$$2\ R_3C\text{-}Cl + 3NH_2CH_2CH_2OH \rightarrow (R_3C)_2NCH_2CH_2\text{-}OH + 2(NH_3CH_2CH_2OH)Cl$$

The layers are sorbents, with three types of interconnected pores. The surface forms external pores with walls of cyclic amine nets, to which internal pores with the same walls adjoin the holes of the cycles. The transition zone is formed by pores with walls from sections of cyclic amines and carbon structures on the surface of coal particles. Pores from coal adjoin these pores. Groups of coal with conjugated structures, linked through ether groups by radicals including hydroxy and amino groups, are structural analogues of a number of organic luminophores [2]. According to [3], the structural elements of pore walls from cyclic amines bind a part of the sorbed organic molecules to host-guest complexes. It is possible that such complexes are formed in the walls of the pores of the transition zone. Particles of coal, combined with cyclic ethanolamines, are at distances at which electrons can move in the layer.

The purpose of this work is to synthesize materials from a transparent PVC film with Layer 1 with different coal content on one side of the film, establish the structure of materials and measure the effective thickness of the layer, trace the effect of grafting on carbon structures, measure the volumetric electronic conductivity of the layers, measure the sorption capacity of the layer with different contents coal in the absorption of vapors and liquid benzene and hexane, as well as to investigate the nature of the interaction of molecules of organic solvents in the pores of the layer using the luminescence spectra. It could be expected that the receipt of this information will reveal the features of Layer 1.

Experimental

Materials

Transparent PVC film (grade PR-M180/09-09/9406, production of China) PVC resin (SG -7, manufactured in China), crushed active coal (BAU, production Russia),

Reagents

Tetrahydrofuran, benzyl alcohol, triethanolamine, decane, hexane, benzene, toluene, 1,4-dioxane, dimethylsulfoxide (qualifications pure or chemical pure).

The methods of chemical analysis such as luminescence spectroscopy, X-ray diffraction, microphotography, resistance measurement, sorption capacity measurement were used in the work.

The luminescence spectra were recorded on a spectrofluorimeter «Fluorolog». The diffraction patterns were measured on an x-ray diffractometer «Empyrean» (Panalytical BV) in the Bragg-Brentano geometry; CuKα radiation was used. Photomicrographs were obtained using a Motic DMBA 300 optical microscope. Layer resistance measurements were made using a multimeter MS8233E. from HYELEC

Measurement of the adsorption capacity for the absorption of vapors and liquid benzene and hexane was carried out by the weight method.

Synthesis of materials with Layer 1 was carried out according to the following procedure.

Initially, a coal suspension (hereinafter «sol») with sorbed PVC was prepared in a mixture of tetrahydrofuran, benzyl alcohol and triethanolamine with a different ratio of coal and PVC. For this, a solution containing 10.5 g of PVC resin in a mixture of 400 ml of THF, 55 ml of benzyl alcohol, and 5.1 ml of triethanolamine was placed in a shredder of type of blender with a four-blade stirrer and 8.75 g, 17.5 g or 35 g of coal were added with grinding it to stable suspension state. After that, the volume of the sol was brought to 500 ml by adding THF. To determine the particle size in the sol, an approximate 0.5 ml of sol was applied to the tensioned transparent PVC film, and after evaporation of THF, microphotography was carried out on the gleam. It was established that spherical and elliptical particles with diameters from 0.5 to 4 μm and associates of two or three particles. The percentage of associates increases with the increase in the coal content.

The PVC film was clamped in the cuvette holder. 1 ml of the sol was added to one side of the film, and by means of the vibrating of the holder, a uniform distribution of the sol over the surface of the film bounded by the walls of the holder was achieved. The film was then held in the holder in air until the tetrahydrofuran evaporated, and then heated at 105-110 ° for an hour. Under these conditions, according to [1], there is a grafting of PVC to the surface of the crushed particles and sewing a layer of particles with grafted PVC to the surface of the film occurs. After that, the film with the layer in the holder was kept at 100 - 105 ° in a 96% solution of monoethanolamine before the PVC sections were converted to cyclic ethanolamines. The film with Layer 1 in the holder was boiled in water until benzyl alcohol was removed, washed with a solution of hydrochloric acid to remove the sorbed ethanolamine, washed with sodium hydroxide solution and water to pH ≈ 7; then dried at 90 ° to constant weight. The Layer 1 obtained from the sol with a coal content of 8.75 g is designated as Layer 11, from the sol with a coal content of 17.5 as Layer 12, and a sol with 35 g of coal as Layer 13. The conversion of grafted PVC to cyclic ethanolamines was monitored with the help of luminescence spectra.

The **Figure 1** shows the luminescence spectrum of Layer 11 from the layer side and from the film side.

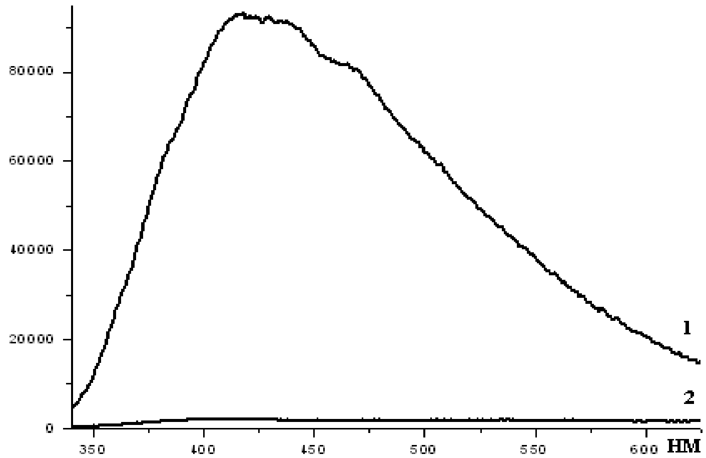

Figure 1 Luminescence spectrum of Layer 11. (1) — layer, (2) — PVC film

The film does not luminesce. In the spectrum of the layer there is a complex band with three maxima of about 416, 429 and 470 nm. It correlates with the spectra of organic luminophors - derivatives of naphthalene and anthracene [4], as well as carbon nanotubes with substituents including hydroxy and amino groups [5]. Consequently, groups of conjugated carbon radicals and associated radicals with oxy and amino groups form the grafting zone.

The composition of Layer 11, Layer 12 and Layer 13 was established as follows. Before the beginning of the synthesis, the mass of the original film (m1) was measured, and the mass of the coated film after evaporation of THF prior to heating (m2) and the mass of the film with Layer 1 (m3) were measured during the course of the synthesis. The masses of the coating consisting of PVC, coal and benzyl alcohol were calculated from the difference (m2 - m1), and based on the ratio of the masses of PVC and coal in the ash, the mass of coal (m4) in the material was calculated, the mass fraction of the film W(film) = m1 / m3, and also the mass fraction of coal in the layer W(coal-in-layer) = m4 / (m3 - m1). It was found that in Layer 11 W(film) = 39%, W(coal-in-layer) = 49% in Layer 12 W(film) = 30%, Wy(coal-in-layer) = 67%, and in Layer 13 W(film) = 24%, W(coal-in-layer) = 75%.

Results and Discussion

The structure of the materials and the determination of the layer thickness were investigated by the method of microphotography of sections. On a micrograph (**Figure 2**), as an example, section of the Layer 11. A fibrous structure characteristic of plastic PVC materials is traced in the film. The layer is continuous. Between the layer and the film there is no clear boundary. This can be explained by the fact that when the sol is applied some swelling of the film surface occurs due to tetrahydrofuran. At the same time, individual sections of sorbed PVC are associated with PVC sections located in the area of the film surface. With the action of ethanolamine, cyclic ethanolamines are formed with the participation of these sections of PVC. At the same time, some coal particles are infiltrate into this zone and the layer with the film becomes a single unit. Therefore, it is not possible to mechanically divide the materials into a layer and a film. For the thickness of the layer (h), the distance from the surface to the middle of the transition zone was assumed. It depends on the coal content: h = 0.43 mm for Layer 11, 0.89 mm for Layer 12 and 1.22 mm for Layer 13.

Figure 2 The microphotograph of Layer 11 section

Investigation of the effect of grafting on carbon structures in coal particles was carried out by X-ray diffraction. Based on the fact that reflection signals from planes in PVC and in coal are found in the region θ ≈ 18-28TEA, and in the region θ ≈ 40-48TEA are only in coal [6]. Diffractograms of Layer 12 and Layer 13 are shown in **Figure 3**.

It is seen that in the diffractograms of both materials there is a complicated band with a maximum at θ ≈ 23TEA. The maximum of the band related to coal in Layer 12 is at 42.5 TEA, and in Layer 13 at 45 TEA. The change in the position of the maxima indicates changes in the structure in the coal particles. According to the conditions of synthesis, the number of groups from carbon radicals and associated cyclic amines in single particle of coal in Layer 12 is greater than in Layer 13. On this basis, it can be assumed that the grafting of macromolecules affects the internal structure of coal particles. Perhaps this is due to the fact that in the grafting zone there are stresses of conjugated structures from carbon, which affect the geometry of the adjacent structures inside the particles.

The determination of the bulk electron conductivity of the layers was carried out as follows. The resistance of the layer between the parallel plates of copper was measured, which was pressed with clamps. The width of the plates is 26 mm, the distance between the plates is 16 mm. It is established that the resistances of Layer 11, Layer 12 and Layer 13 are 3.53, 1.56 and 0.59 kOm. Based on these values, the area of the layer between the plates and the thickness of the layer, bulk electronic conductivity was calculated. For Layer 11, it is equal to $1.29 \cdot 10^{-4}$ S/cm, for

Layer 12 is 1.85·10^{-4} S/cm and for Layer 13 it is 3.34·10^{-3} S/cm. The electronic conductivity values correlate with the coal content in the layer. According to the synthesis conditions Layer 11, Layer 12 and Layer 13, the numbers of carbon atoms coming to it are 1.16, 2.14 and 4.27. Consequently, with an increase in the coal content, the number of coal particles that are combined by the same number of cyclic ethanolamines increases. In this case, an increase in the electron conductivity indicates the convergence of coal particles by macromolecular networks between them.

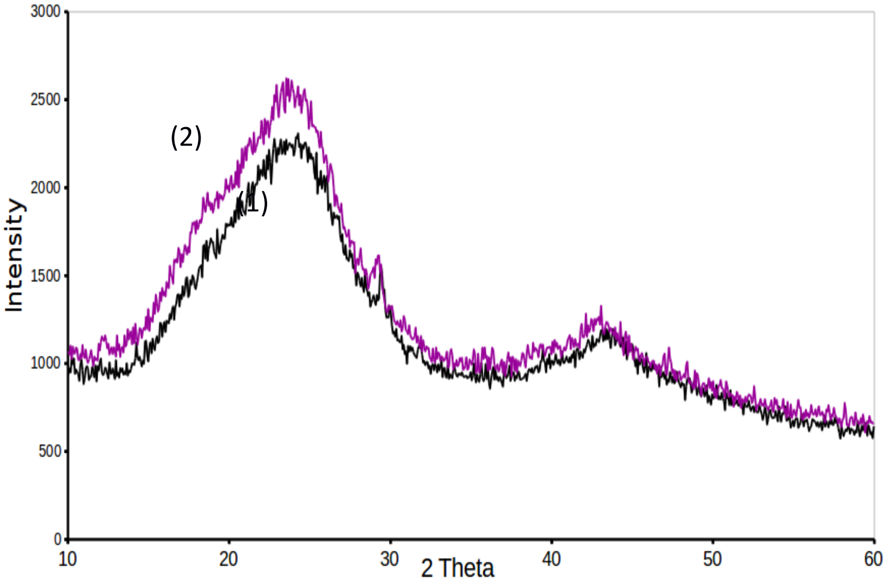

Figure 3 Diffractograms of Layer 12 (1) and Layer 13 (2)

In **Table 1** the measurement data of the sorption capacity of layers in materials are shown. It is seen that they depend on the composition of the layers and the nature of the sorbed molecules with different contents of coal during absorption of vapour and liquid benzene and hexane. As noted above, the filling of the pores of the transition zone occurs through the pores with walls of cyclic ethanolamines, and pores in the coal through the pores of the transitional zone. Judging by the data of Tab. 1 it can be assumed that the molecules of benzene and hexane pass both into the pores of the transition zone and into the pores of the coal. An increase in the content leads to a simultaneous decrease in the pore volume with walls from cyclic ethanolamines and an increase in the pore volume in the transition zone. The capacitance values in Layer 12 are close to capacity in Layer 13, and in some cases more than these values. This suggests that the pores of the transition zone keep the molecules of benzene and hexane more firmly than the pores in the coal.

Table 1 Sorption capacity of layers

Sample	**vapour, mmol/g**		**Liquid, mmol/g**	
	hexane	**benzene**	**hexane**	**benzene**
Layer11	5.18	15.61	10.85	16.61
Layer12	8.38	12.7	12.89	22.95
Layer13	8.61	12.24	12.53	22.53

Investigations of the nature of the interaction of molecules of organic solvents in the pores of the transition zone were carried out proceeding from the fact that pore filling with liquid solvents can lead to partial or complete quenching of the luminescence, and the formation of host-guest complexes between the structural elements of the pore walls and solvent molecules to changes in the structure of the spectra compared with the original. Conclusions were drawn for the example of Layer 11. As an example of solvents, decane, benzene, toluene, 1,4-dioxane and dimethylsulfoxide were used. In **Figure 4** the spectra of the layers after their soaking in liquid solvents, and in **Figure 5 -** layers after exposure to impregnated samples in air at a partial vapor pressure close to zero are shown. It is established that, in comparison with the initial spectrum, saturation with solvents leads to a partial quenching of the luminescence. In the case of the decane, the position of the maxima is generally remained unchanged, but the intensity ratio of the bands has changed. In the case of other solvents, the spectra have one band at 414 ± 416 nm. After exposure to air, the spectra of the layers differ from the spectrum of the original layer. This means that there are host-guest complexes in the walls of the pores of the transition zone. Spectra with complexes with benzene and toluene increased the intensity of the bands, and in the region of 450-460 nm a shoulder appeared. In the spectrum with the decane complex, in addition to increasing the intensities, a shoulder appeared at 389 nm, and the third maximum shifted to the shortwave region to 461 nm. Spectra with complexes with dioxane and dimethylsulfoxide increased the intensity of the band at 414 ± 416 nm. The luminescence of the structures forming the transition zone arises as a result of π*→π transitions in conjugated carbon structures associated with groups with oxy and amino groups through which π electrons are excited. It can be assumed that in the layers with a liquid solvent quenching of the luminescence can be explained by the dissipation of the energy of the excited hydroxy and amino groups due to their solvation. In layers with complexes this dispersion is minimal. The reason for the change in the structure of the spectra can be donor-acceptor or similar interactions of conjugated structures with solvent molecules from the complexes.

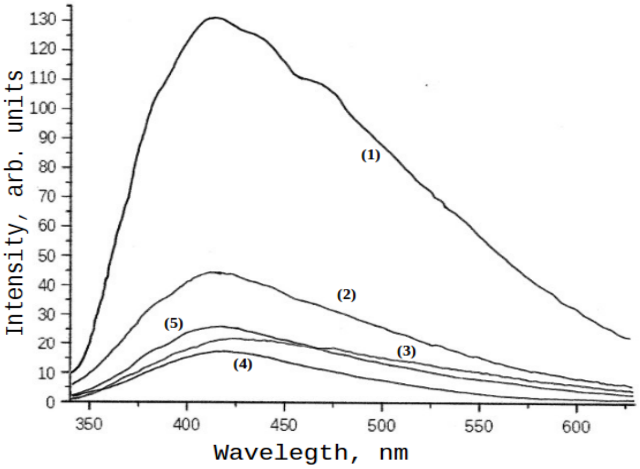

Figure 4 Luminescence spectra of Layer 11, solvated with decane (1), benzene (2), toluene (3), 1,4-dioxane (4), dimethylsulfoxide (5)

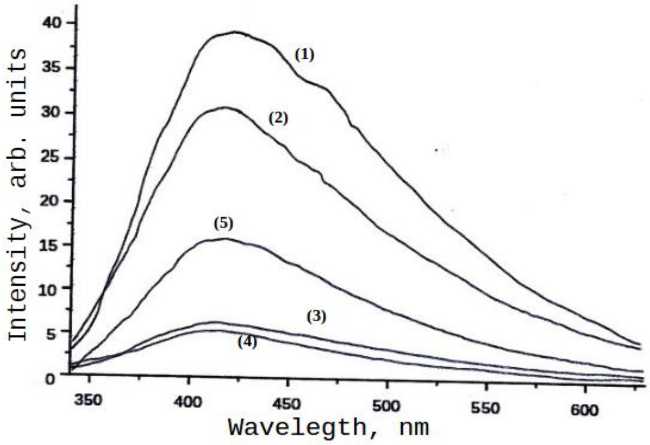

Figure 5 Luminescence spectra of Layer 11 with «host-guest» complexes with decane (1), benzene (2), toluene (3), 1,4-dioxane (4), dimethylsulfoxide (5)

X-ray measurements were carried out on the equipment of the FMI Center of the Institute of Physics and Technology of the Russian Academy of Sciences. The authors thank the professor of the Russian Academy of Sciences, A.A. Shiryaev for these measurements and for valuable consultations.

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