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Electretic State and Radiative Absorption of Polyvinyl Chloride Metal Nanocomposites

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Electretic state and radiation absorption of nanocomposites consisting of polymer matrix and metal particles filler obtained in result of electric explosion are investigated. Stable thermoelectrets of polymer metal-filled systems that have better electert properties than traditional polymer materials are obtained. Suggested method of composite polymer system creation enables to obtain shielded materials with better radiative absorption, resistant to external actions, cost-efficient.

Keywords: Nanocomposite, Electret, Thermal stimulated depolarization, Polyvinyl Chloride, Beta-radiation.

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1. INTRODUCTION

The development of modern polymer Physics and Chemistry looks for new methods of obtaining polymer composite materials with programmable set of properties. Traditionally, the priority is for new polymer synthesis, but modifications of already existing high-molecular compositions combined with different additional components in heterogeneous systems take an important place in polymer materials technology. Popular modification components are different fillers that allow changers in physical and chemical characteristics of polymer materials. And, as a rule, impact efficiency of such fillers is inversely related to their geometric dimensions [1]. Therefore, change-over to nanodimension scale makes significant theoretical and applied interest.

This paper introduces a promising area of changes of electrophysical properties of polymer materials that is a creation of nanocomposite films using nanodimension inclusions. Origin and way of improvement of stability of electretic state as well as increase of radiative absorption in such polymer materials are under-investigated, preferable fillers and their optimum concentration are not defined.

The investigation of electretic state of polymer materials is determined by their increasing penetration in all spheres of human activities. Along with traditional spheres of their application such as electroacoustic transducers, filters etc, appear new ways of their usage, that is medicine, packing, biotechnology. On this regard, fundamental and applied investigations are currently held, focused on examination and search of ways of improvement of electretic properties of polymer materials [2]. The majority of investigations concerns materials of heterogeneous structure with developed interface: dispersed filled polymers, laminated composites.

Lately tendency of usage electretic polymer as metal-filled materials takes place and have in some cases better electretic characteristics than traditional polymers.

As we know, high-density metals, concrete, and materials such as paraffin are typically used for radiation protection [3]. Such radiation protection materials possess certain disadvantages; metals, in particular, have corrosive action, plasticity, high price. Unlike high-density metals, high-molecular compositions are characterized by lower absorption capacity and specific behavior in radiation field. The majority of them is of high radiation resistance and can modify their properties.

Task, which this paper can solve, is to create protective (shielding) material resistant to radiation, with low density, suitable to be used in fixed protection shields and in individual protective gear. Besides, a problem to work out is to reduce the cost of the material at its high efficiency [4].

2. EXPERIMENTAL PROCEDURES

The paper investigates electretic state and beta-radiation absorption of industrial polyvinyl lchloride (PVC KARVINYL SR-67 produced by «Karpatnaftochim Ltd») filled with nanodispersive Cu powder obtained in result of electric explosion of copper conductors in PVC.

2.1 Samples' Preparation Technique

Electric conductor explosion method is a rather promising technique of getting nanodispercive particles. It is cost-effective and efficient and allows nanodispersive metal particles size regulation. Thus, in polymer (PVC powder) with the help of electric explosion nanodispersive metal (Cu) can be inleted with the size of metal nanoparticles from 20 to 80 nm [5].

Electric explosion of copper conductors took place in a special basin directly in dispersed PVC mass. PVC metal nanocomposites with different volume content of nanodispersive Cu particles were obtained by varying dispersed PVC mass and number of conductor's explosions in it, followed by hot pressing of obtained blend compound in T-p mode. To determine quantitative composition and mean size of nanodispersive particles in PVC metal nanocomposites X-ray phase analysis was used. X-ray diffraction patterns of PVC metal nanocomposites with film thickness $6{,}8\cdot10^{-4}$ m and powder standard α-Al_2O_3 with particle size $(1\div4)\cdot10^{-5}$ m were performed under identical conditions on diffractometer DRON-3 in step-by-step scanning mode of photon counter with the help of β-filter CuKα-radiation with a wave length $\lambda = (1{,}542 \pm 0{,}002)$ Å at an operation voltage $U = 24$ kV and power of anode current $I_a = 20$ mA in the range of angles $34° \le 2\theta \le 78°$. There are diffraction peaks on all X-ray diffraction patterns of all investigated samples according to X-ray powder standard JCPDS

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PDF2, which correspond to Cu chrystals and indicate the absence of CuO and Cu_2O chrystal in PVC metal nanocomposites. Statistical analysis of the results was performed with the help of X-Ray Scanner program, X-Ray Graphic and ORIGIN.

2.2 Thermally Stimulated Depolarization Method

With the help of thermally stimulated depolarization method (TSD) the impact of electrical conductive fillers (nanodispersive Cu, dispersive powders of wolfram, zinc) and fillers-dielectrics (dispersive powders of talcum, emery) on the electrets effect in PVC is investigated. We managed to get the electrets with volumetric substance of electrical conductive filler 0,5 vol. % where effective size of the particles doesn't exceed 7 μm. We could not receive electrets of PVC composition with 0,5 vol. % Cu because of the inner electric breakdown – particles size Cu ~ 14÷18 μm [6].

The investigated samples with diameter (29 ± 1) mm and thickness (0,2 ± 0,02) mm were made with the help of the hot press 130 °C temperature and 10,0 MPa pressure. For reaching a reliable electric contact within the electrets and the sample, it was pressed between two aluminum foils.

The sample's polarization was made in electric field with constant intensity for five minutes. After that the sample was cooled for thirty minutes to the indoor temperature in the same intension field. TSD current changes and parameter calculations of electric relaxation of the composites were conducted according to the GOST 25209-82. Current of discharge was recorded with the help of electrometric amplifier U 5-9 (fig. 1).

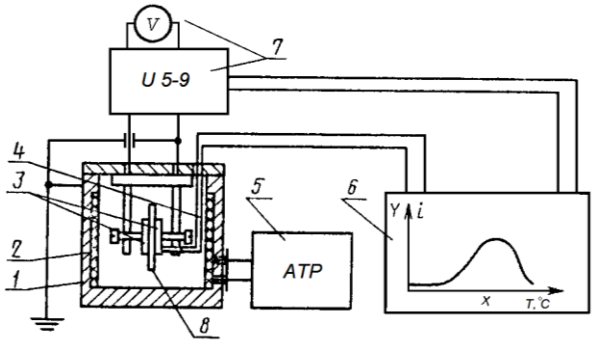

Fig. 1 – TSD pilot unit: 1 – thermo case; 2 – thermo heating; 3 – electrodes; 4 – thermo sensor; 5 – automatic temperature programmer; 6 – personal computer with analog-to-digital signal converter; 7 – current meter (electrometric amplifier U5-9 and digital voltmeter V7-40/4); 8 – electret

2.3 Measuring Beta-radiation Absorption Capacity

The source of radiation is 90Sr + 90Y, BF 90SS-5M type with maximum energy W_{max} = 2,270 MeV, intensity of outlet flow I = 4678 imp/s and half-live time $T_{1/2}$ = 28,7 years. Maximum beam energy before the sample was 2,047 MeV. Source usage enables to get only beta-radiation. Beam of the source goes through the leaded plate with 2 mm hole in the middle (collimator) and orb of appropriate absorber, which is in fine vacuum to minimize currents that appear as a result of atmosphere ionization. Investigation of filled PVC beta-radiation absorption was held by using pilot unit the scheme of which is on fig. 2.

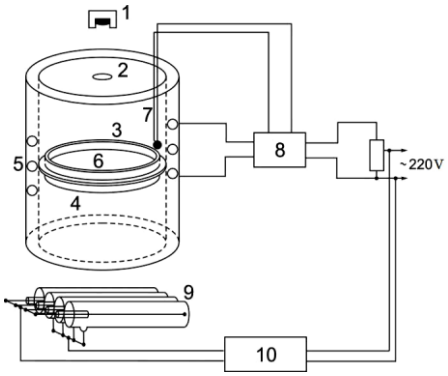

Fig. 2 – Pilot unit for measuring the absorption capacity of beta-radiation: 1 – source of radioactivity; 2 – collimator; 3, 4 – holders of the polymer sample; 5 – thermo heating; 6 – polymer sample; 7 – thermo sensor; 8 – automatic temperature programmer; 9 – Geiger-Muller counter SBT-11A; 10 – device for studying the energy spectrum of electrons FPK-05

3. RESULTS AND DISCUSSION

3.1 Electret Effect in Heterogeneous PVC Systems (Electret Thermal Analysis)

Current curves of TSD for PVC with different fillers are on fig. 3. The parameters of electric relaxation, calculated on the basis of TSD current's curves (speed of heating 3°C/min), are shown in fig. 4, where σ is the surface solidity of an electric charge, τ_e is the minimal time of charge relaxation under exploitation circumstances.

Filled electrets obtain more initial value of surface charge-density σthan PVC electrets without fillers. Thus accumulated charge has different energy of relaxation process activation. The most stable among filled electrets are metal-filled composites. So, PVC + 0,1 vol. % nanoCu and PVC + 0,1 vol. % W electrets gain σ almost twice a large than initial PVC σ and from 1 to 2 years charge relaxation. PVC-electrets with dielectric fillers obtain lower τ_e and therefore can't be actually used due to their unsteady electret effect. During the formation of PVC + 0,5 vol. % Zn and PVC + 0,5 vol. % W composite, we deal with an active filler, and the mass transfer of PVC macromolecule turns to its surface, that facilitates composites' energy interaction on the brink phase division PVC-metal. Investigation showed the advantages of Cu nanodispersed polymer composites if to compare with systems obtained on the basis of industrial dispersed powder metals. When the electric field is given to such composites, the charge of certain quantity and sign is inducted on the surface of metal fillers [7].

Composites acquire electric charge that remains stable after outer electric field removal, because the mobility of polymer segments is restrained not only by steric but also by energetic effects in a boundary layer. While pressing composites in T-p thermal condition, PVC is melting and filling all the volume around filler's particles, forming for nanometal fillers a system which has a number of improved physical and chemical properties.

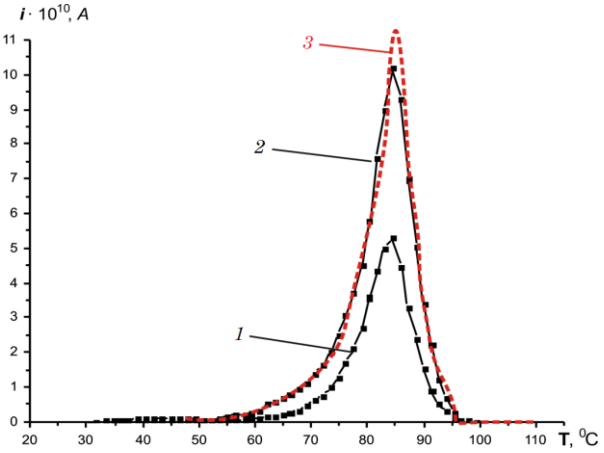

Fig. 3 – TSD current curves of the following samples: PVC (1); PVC + 0,5 vol. % W (2); PVC + 0,1 vol. % nano Cu (3)

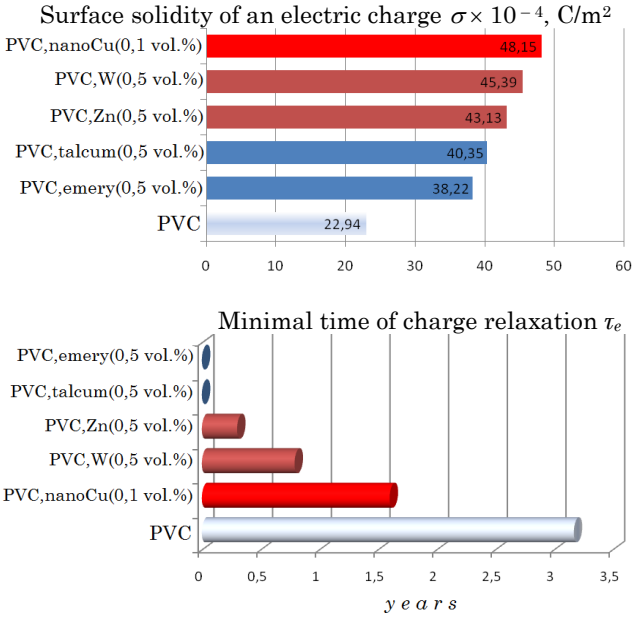

Fig. 4 – Characteristics of electric relaxation of thermoelectret PVC-systems with different fillers

3.2 Filled PVC Beta-radiation Absorption

Laboratory research sets that the most effective radiative absorption takes place when nanofiller is about 40÷45 nm. Fig. 5 presents characteristic curve 1 of layer thickness of complete absorption (h) of PVC + Cu composite's radiation energy of the source 90Sr + 90Y, BF 90SS-5M type [4] against nanofiller size (d) when its concentration is 10 vol. %. The figure shows that there is no intensive growth of magnitude h in range (20÷80) nm of particle filler size.

Fig. 5 (curves 2, 3) shows dependency diagram of layer thickness of complete absorption (h) against filler volume content (φ) when nanoparticles are (45 ± 5) nm and microparticles are 14,5 μm in Cu-filled PVC. It is set that at the same metal radiative absorptivity the amount of nanodispersive material decreases in 45 times at contents 0,02-3,00 vol. % if to compare with microdispersive filler. Especially intensively the effect takes place when contents of nanodispersive metal are low (0,01÷0,1) vol. %.

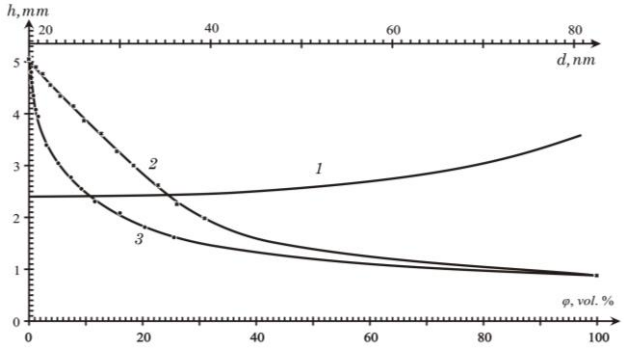

Fig. 5 – Dependence of layer thickness of complete absorption (h) of PVC + Cu composite's radiation energy of the source 90Sr + 90Y, BF 90SS-5M type on nanofiller size (d) – curve 1 and on Cu volume PVC content (φ): curve 2 – PVC filled with microdispersed Cu; curve 3 – PVC filled with Cu nanoparticles

Radiative absorption occurs because of energy dissipation on the edge of structure polymer – high dispersed metal. Therewith, radiative energy doesn't localize on inter- or intra-molecular connections but scatters on account to relaxation processes in the whole system, without damage to the material structure.

Suggested method of composite polymer system creation enables to obtain shielded materials with better radiative absorption, resistant to external actions, cost-efficient.

4. CONCLUSIONS

1. It is set, that inletting into polymer conductive nanodispersive fillers, creates a composite system with better set of physical and chemical properties.
2. Activity of PVC dispersed fillers according to the influence on spectrum character of TSD is classified in a line: nanoCu (0,1 vol. %), microdispersed W, Zn, talcum, emery at $\varphi = 0{,}5$ vol. % and $T \le T_g$. Among filled electrets the most stable electret effect have metal filled composites.
3. Stable PVC thermo electrets with Cu nanofillers are got, that obtain more initial value of surface charge-density σ than PVC electrets without fillers. Conditions of PVC metal nanocomposite electrets' electric relaxation and their radiative absorption are determined by structural composite factors.
4. Investigation of electret condition and radiative absorption showed the advantage of Cu nanodispersed polymer composites if to compare with systems obtained on the basis of industrial dispersed powder metals. Industrial application of such samples will lower their metal consumption in many times, that offer significant economic effect.
5. The obtained results can be used as scientific basis for creation of new polymer composite materials; direction regulation of their structure and set of properties; to improve technology of obtaining and implementation in different scientific and engineering branches.

Електретний стан та радіаційне поглинання полівінілхлоридних металонанокомпозитів

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Досліджено електретний стан та розглянуто радіаційне поглинання нанокомпозитів, що складаються з полімерної матриці та наповнювача у вигляді наночастинок металу, одержаних шляхом електричного вибуху провідника. Отримано стабільні термоелектрети з полімерних металонаповнених систем, які перевершують за своїми електретними характеристикам традиційні полімерні матеріали. Запропонований метод створення нанокомпозиційних полімерних систем дозволяє виготовляти матеріали для захисту від радіоактивного випромінювання з підвищеною поглинаючою здатністю радіаційного поля, які є стійкими до дії зовнішніх впливів та економічно доцільними.

Ключові слова: Нанокомпозит, Електрет, Термічно стимульована деполяризація, Полівінілхлорид, Бета-випромінювання.

Электретное состояние и радиационное поглощение поливинилхлоридных металлонанокомпозитов

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Исследовано электретное состояние и рассмотрено радиационное поглощение нанокомпозитов, состоящих из полимерной матрицы и наполнителя в виде наночастиц металла, добытых путем электрического взрыва проводника. Получены стабильные термоэлектреты из полимерных металлонаполненных систем, превосходящие по своим электретным характеристикам традиционные полимерные материалы. Предложенный метод создания нанокомпозиционных полимерных систем позволяет изготавливать материалы для защиты от радиоактивного излучения с повышенной поглощающей способностью радиационного поля, стойкие к действию внешних влияний и экономически целесообразны.

Ключевые слова: Нанокомпозит, Электрет, Термически стимулированная деполяризация, Поливинилхлорид, Бета-излучение.

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