

Some Properties and Structural Features of Poly(Vinyl Chloride)/Cu Films with Copper Nanoparticles Obtained by Exploding Wire Method

V.V. Krivtsov^{1,*}, V.V. Kukla², V.V. Krivtsov³, A.I. Shidlovskiy¹, M.A. Bordyuk⁴

¹ Rivne State University of Humanities, 12, Stepana Bandery St., 33028 Rivne, Ukraine

² Rivne Regional Institute of Postgraduate Education, 74, Viacheslava Chornovola St., 33028 Rivne, Ukraine

³ National University of Water and Environmental Engineering, 11, Soborna St., 33028 Rivne, Ukraine

⁴ Rivne Medical Academy, 53, M. Karnaukhova St., 33028 Rivne, Ukraine

(Received 17 April 2020; revised manuscript received 15 August 2020; published online 25 August 2020)

The paper presents complex investigation results of preparation condition influence and nanocomposite polymer materials modification on their relaxation state, structure formation processes, viscoelastic, thermostable, antibacterial etc. properties. Composite films that consist of Poly(vinyl chloride) matrix filled with copper nanoparticles and obtained by exploding wire method have been investigated. Thermally stimulated depolarization method, resonance vibrating-reed method, infrared, raman, photoluminescence spectroscopy, antibacterial activity examination, derivative thermogravimetry, differential thermal analysis and other methods of thermal analysis have been used. With the help of spectroscopic and other methods, the reaction of nanofilled Poly(vinyl chloride) systems on external fields' influence of different origin such as stable electric field, temperature field and ultraviolet has been studied. Specific stretching of Poly(vinyl chloride) structure elements under these modification factors has been found. Nanofillers function in the formation of composite complex properties has been set. It has been proved that stable thermoelectrets of Poly(vinyl chloride)/Cu systems have better electret properties than traditional Poly(vinyl chloride) materials. Besides, the obtained metal nanocomposites are quite thermally stable as regards their dynamic viscoelastic properties. It has been established that copper nanoparticles in Poly(vinyl chloride) systems fulfill the role of photostabilizer and antirad slowing down the aging process and polymer destruction in ultraviolet. The obtained metal nanocomposites possess stable indexes of high-energy radiation field absorbing capacity that allows to use them as outer radiation protection materials. High antibacterial activity of Poly(vinyl chloride)/nanoCu films to *Staphylococcus aureus* has been substantiated.

Keywords: Poly(vinyl chloride), Nanoparticles, Exploding wire method, Ultraviolet radiation, Thermoelectret, Antibacterial activity.

DOI: [10.21272/jnep.12\(4\).04032](https://doi.org/10.21272/jnep.12(4).04032)

PACS numbers: 77.22.Ej, 61.82.Pv

1. INTRODUCTION

Unique physical and chemical properties of filled composites, possibilities of creation of new materials on their basis lead to a rapid growth in this field [1]. As a matter of fact, the addition of nanoparticles to Poly(vinyl chloride) (PVC) changes their physical, mechanical as well as operational properties and produces synergistic effect [2]. One of the promising methods of obtaining nanodispersed particles is exploding wire method, which allows to obtain nanofiller in a wide range of sizes with equal particle distribution in the whole volume of polymer matrix. Purpose of the investigation is to estimate how PVC structure and properties can hold control over changes with the help of copper nanoparticles.

2. EXPERIMENTAL PROCEDURES

The paper considers some properties and structural features of industrial PVC KARVINYL KSR-67 produced by «Karpatnaftochim Ltd» filled with nanodispersive copper powder obtained as a result of electric explosion of copper conductors in PVC. PVC metal nanocomposites with different volume content of copper nanoparticles were obtained by varying dispersed PVC mass and a number of conductor explosions in it, followed by hot pressing of obtained blend compound in T-p mode.

2.1 Sample Preparation Technique

Exploding wire method is a rather promising technique of getting nanodispersive particles. It is cost-effective and efficient and allows nanodispersive metal particles size regulation. Thus, nanodispersive metal (Cu) can be inlet with the size of metal nanoparticles from 20 to 80 nm in polymer (PVC powder) with the help of exploding wire method.

Electric explosion of copper conductors took place in a special basin directly in dispersed PVC mass. 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 a film thickness of $6.8 \cdot 10^{-4}$ m and powder standard $\alpha\text{-Al}_2\text{O}_3$ with a particle size of $(1 \div 4) \cdot 10^{-5}$ m were performed under identical conditions on diffractometer DRON-3M in step-by-step scanning mode of photon counter with the help of β -filter CuK α -radiation with a wavelength $\lambda = (1.542 \pm 0.002)$ Å at an operation voltage $U = 24$ kV and power of anode current $I_a = 20$ mA in the range of angles $34^\circ \leq 2\theta \leq 78^\circ$.

There are diffraction peaks on all X-ray diffraction patterns of all investigated samples according to X-ray powder standard JCPDS PDF2, which correspond to Cu crystals and indicate the absence of CuO and Cu₂O crystal in PVC metal nanocomposites.

* labor.relax@gmail.com

2.2 Infrared, Raman and Photoluminescence Spectroscopy

Infrared spectra of investigated samples were obtained by a Fourier transform infrared spectrophotometer IRAffinity-1S (Shimadzu) and spectrophotometer SPECORD 75 IR (Carl Zeiss). Spectra records were made in frequency range $400\text{--}4000\text{ cm}^{-1}$. Measurement error of wave number was $< \pm 1\text{ cm}^{-1}$.

Raman scattering spectra were excited with the 514.5 nm line of an Ar^+ -ion laser and registered with a Horiba Jobin Yvon T64000 micro-Raman spectrometer equipped with optical polarizers and Peltier cooled CCD detector. All measurements were performed in backscattering geometry. The spectral resolution did not exceed 1 cm^{-1} .

Photoluminescence spectra of PVC composites with copper nanoparticles were investigated to define the mechanism of electronic structure changes. The spectra were obtained in reflection geometry at ambient temperature by means of spectrofluorophotometer RF-1501 (Schimadzu).

2.3 Thermally Stimulated Depolarization Method

The investigated samples with diameter $(29 \pm 1)\text{ mm}$ and thickness $(0.2 \pm 0.02)\text{ mm}$ were made by means of hot press 403 K 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 indoor temperature in the same tension field. TSD current changes and parameter calculations of electric relaxation of the composites were conducted according to GOST 25209-82. Discharge current was recorded by means of electrometric amplifier $U\ 5\text{--}9$ [3].

2.4 Resonance Vibrating-Reed Method

Forced resonance vibrating-reed oscillation method is for investigational study of polymer viscoelastic properties and implies amplitude oscillation measurements of a loose end of the cantilevered viscoelastic pivot at frequency force change that is attached to another fixed end. According to sample's transverse amplitude oscillation measurements $|A|$ at different frequencies, resonance curves are built. Their data of resonance frequency ϑ and width of resonance curves $\Delta\vartheta$ are taken at $|A_{\text{max}}|/\sqrt{2}$ enabling us to determine Young's modulus E' and factor of mechanical losses $\text{tg}\delta = E''/E'$.

Test installation is fitted with noncontact sensors and is fully computerized. PC proper software for OS Windows was developed that makes absolute two-dimensional recognition of body movements and determines the amplitude of samples oscillation [4]. Measurement error does not exceed 1.5% (at minimum amplitude).

2.5 TG-DTG-DTA Complex Method of Thermal Analysis

Derivatograph system Paulik-Paulik-Erdey type «3427-1000 °C» (MOM, Hungary) combines all the above-mentioned methods of investigation and can distinguish

direction and enthalpy variation value (ΔH), heating value and speed of samples' mass loss. Quantity and numerical related forecast of TG, DTG, DTA curves enables to distinguish glass transition temperature T_g as well as onset temperature of thermal oxidative degradation (TOD) process of PVC systems. To get energy of activation E_a of TOD process, Reich-Fuoss method was used. Having constant heating speed R_H , activation energy value E_a of polymer decomposition process reaction order n , one can depend on equation:

$$R_T \cdot d(W_i / W) / dt = (A / R_H) \cdot e^{-E_a / RT} (W_i / W)^n$$

$$\text{or } \Delta \lg R_T = n \Delta \lg (W_i / W) - (E_a / 2,303R) \Delta (1 / T),$$

where R_t is the reaction rate; W , W_i are the samples mass at temperatures T , T_i ; A is the preexponential factor.

The value of $\Delta \lg (1 / T)$ is constant, so $\Delta \lg R_T$ and $\Delta \lg (W_i / W)$ are linearly related. Accordingly, angle of inclination is determined and corresponds to reaction order n . Line segment on the y -axis is E_a value.

2.6 Antibacterial Activity Examination

Antibacterial action of original and modified films based on gram-positive prokaryote (firmicutes) of *Staphylococcus aureus* origin was studied. *Staphylococcus aureus* was used as test-bacteria. Investigation was undertaken by traditional evaluation method of antibacterial activity [5]. Films were inserted onto solid medium surface in Petrie dish and inoculated by test-bacteria. Following 24-hour thermostatic control at 310 K temperature, bacteriostatics area around sample films was determined. While inserting sample films in liquid medium, bacteria and fungi growth in the testing tube with plain broth, incubation test culture and film sample at 310 K temperature and 24-hour thermostatic control were taken into consideration. The amount of grown bacteria was estimated by spectrophotometer i.e., oxidation haze decreased according to bacterial destruction. Having compared optical depth of liquids, bacteriostatic interset was determined. PVC and PVC/nanoCu films were investigated.

3. RESULTS AND DISCUSSION

3.1 PVC Macromolecules Structural Properties

To distinguish PVC macromolecules structural properties, a complete set of normal oscillations (position of vibrational energy level) of a polyatomic molecule in Infrared and Raman spectra should be set. All PVC IR-lines can be identified. Moreover, $600\text{--}700\text{ cm}^{-1}$ range is considered to be the most sensitive to stereochemical changes, as it relates to frequency of macromolecular chain. It was established that there are characteristic bands of starching vibrations C–Cl in PVC spectral region $600\text{--}700\text{ cm}^{-1}$. In this spectral region of investigated PVC KSR-67, 615 , 635 , 693 cm^{-1} can be emphasized.

PVC syndiotacticity index was determined as correlation of optical density lines 635 cm^{-1} and 693 cm^{-1} i.e. D_{635}/D_{693} . It proves to be low (1.4). Since PVC syndiotacticity index belongs straight to the degree of crystallinity of PVC (only PVC macromolecules with

syndiotactic period not less than 12 monomer units can be crystallized), PVC KSR-67 can be considered as amorphous with a number of specific defects, conformational and configurationally irregular.

Determination of PVC crystalline structure, which was conducted with the help of X-ray diffractometer DRON-3M, acknowledges that PVC KSR-67 is an amorphous polymer, thus with insignificant content of crystalline phase. It is obvious that for PVC KSR-67 certain interferential maxima take place, which decomposing on crystalline and amorphous constituents enable us to obtain the degree of crystallinity in this particular sample $< 10\%$.

Investigated PVC could be considered as copolymer which consists of izo- and syndiotactic structures that interlace. Along with izo- and syndiotactic structures atactic structure occurs and is transitive between izo-tactic and syndiotactic ones.

3.2 PVC-systems Reaction on Outer Electric Field

One of the methods of PVC structure and properties modification is processing them by electric field. Most polymers under rather strong electric field and high temperatures generate electrets condition, which is characterized by the presence of surface chargers.

It is known that depending on the temperature in electric field, certain macromolecule sections acquire the capacity to be oriented, if they possess dipole moment. While temperature increases, the capacity to be oriented acquires: pendent groups (radicals), then 2-4 atoms relative to molecule's axis, after that segments with length of 50-100 atoms (this corresponds to glass transition temperature T_g) and finally, the whole macromolecule. Investigation of the external orientation field influence on local mobility of polymer chain showed that external electric field with $E \leq 2.5 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$ when $T \geq T_g$ does not affect infrared spectrum of investigated PVC. Under the influence of electric field with $E = 3 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$, conformational changes in the PVC infrared spectrum are observed. The number of stable TGTG izotactic diads decreases in PVC macromolecules owing to the increase of quotient of TGTG'T defects in convolved TG-conformations. Consequently, thermoelectret effect in PVC polymer with oriented dipole polarization is conditioned

by the mobility of chain sections as a whole in electric field where $E \leq 2.5 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$. However, $E = 3 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$ causes the displacement of chain sections in electric field. This is because of overcoming the positional barriers and is conditioned by the transformation of kinesthetic elements of PVC structure from one power state to another quasi-stable state as a result of conformational change of macromolecule section.

In case of filled samples PVC + 0.1 vol. % nanoCu, such conformational changes take place under less E value of constant electric field (starting from $1.0 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$). Those distinctions in PVC systems' reactions on external electric field could be explained by the fact that adding dispersed electrically conducted fillers in PVC causes supplementary power sources in electric field when composite is obtained in T-p mode. TSD results show that filled electrets have more initial surface charge density σ_{eff} meaning than not filled PVC electrets. So, investigated electrets PVC + 0.1 vol. % nanoCu gain σ_{eff} almost twice larger than initial PVC σ_{eff} and from 1 to 2 years charge relaxation. Investigation showed the advantages of Cu nanodispersed polymer composites in comparison with other systems. When electric field is applied to such composites, the charge of certain quantity and sign are induced on the surface of metal fillers [6]. Composites acquire electric charge that remains stable after external electric field removal, because the mobility of polymer segments is restrained not only by steric but also by energetic effects in a boundary layer.

3.3 PVC-systems Reaction on Ultraviolet Radiation

Apart from that electric field, the samples underwent ultraviolet radiation. High pressure mercury lamp burner of DRL-250 type was used as an ultraviolet radiation destructive source with the most intensive lines 184.9499 nm, 253.6517 nm (rough ultraviolet, C type) and 435.8328 nm (G line, blue).

External electric field and ultraviolet radiation impact on syndiotactic period of the polymer chain was not found. Under ultraviolet radiation the number of stable TGTG izotactic diads in PVC increases owing to the decrease of quotient of TGTG'T defects in convolved TG-conformations.

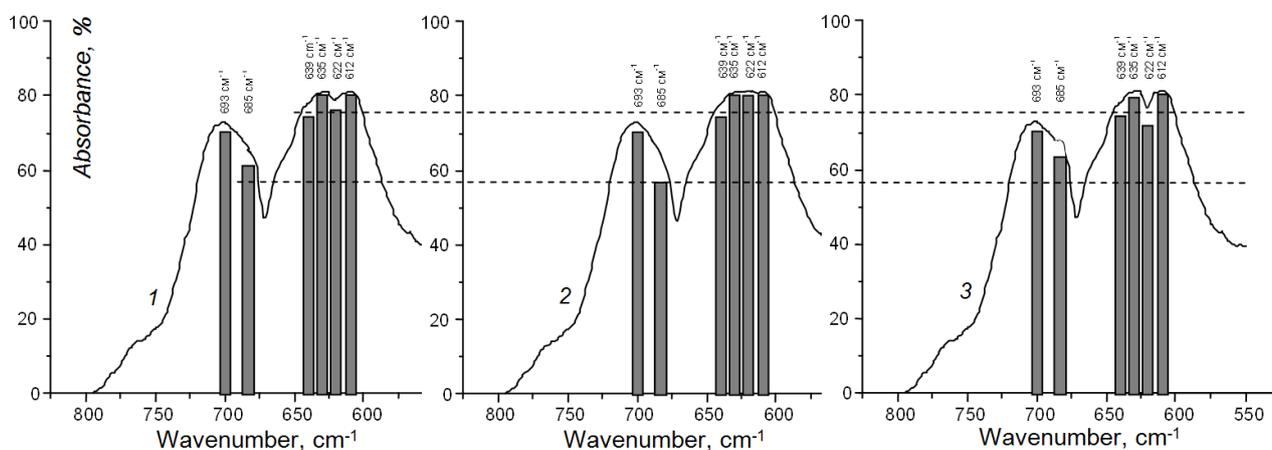


Fig. 1 – IR spectroscopy bands of PVC KSR-67 for region $550\text{-}800 \text{ cm}^{-1}$: 1 – film without influence of outer electric field and ultraviolet radiation; 2 – film under the influence of outer electric field ($E = 3 \cdot 10^6 \text{ V}\cdot\text{m}^{-1}$); 3 – film under UV-radiation influence

Subsequent spectroscopic investigation of PVC conformational changes with further increase in ultraviolet radiation certifies intensive transition of isotactic chains to regular helix conformation. Similar structure of isotactic PVC helix could be observed in ultraviolet spectra of heat treated PVC films. Subsequent samples' heating to the temperature 10-25 % less than T_g of polymer with further slow cooling shows that isotactic chains try to go to regular helix TG-conformation.

Experimental evaluation of viscoelastic properties of PVC systems proved that increasing amount of ultraviolet radiation makes them harder and more fragile. However, nanofilled and pure PVC systems respond to ultraviolet rays in different ways. Thus, pure PVC samples, stood up to ultraviolet rays of duration 360 s, increasing Young's modulus E' up to 60 %. At the same time, nanofilled PVC systems have E' increment only up to 20 %. Being at the initial stage of ultraviolet radiation and not undergoing significant destruction (such as dehydrochlorination, increasing number of C=C connections, molecules splitting) according to IR-spectra, PVC macromolecules in a certain period of time are able to recover their initial relaxed condition. PVC samples filled with metal nanoparticles have less time of relaxation of structure elements and undergo ultraviolet radiation destruction in a more complicated manner (Fig. 2).

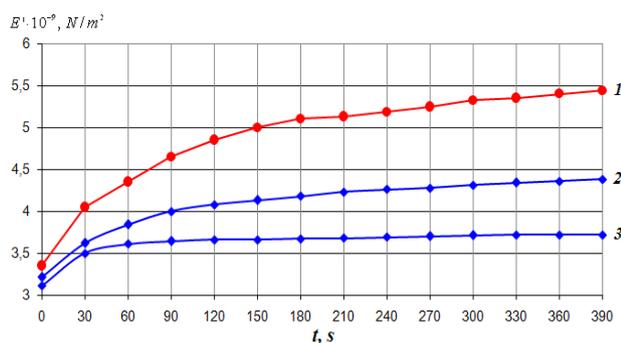


Fig. 2 – Young's modulus E' change of PVC-systems under UV-radiation influence: 1 – pure PVC, 2 – PVC + 0.03 vol. % nanoCu, 3 – PVC + 0.06 vol. % nanoCu

PVC photoluminescence occurrence results from dehydrochlorination of defective structure in a variety of polyene chains of different length. These chains lead to the formation of discrete bonds in PVC and, according to their length, bring out group of maxima depending on π - π^* -transitions.

Apart from polyene, luminescence in PVC can be induced by other defective structures such as unsaturated ketones, allyle chlorine etc. that can be found in PVC as a result of the influence on it. Fig. 3 shows photoluminescence spectra of nanofilled and pure PVC. When photoluminescence excitation with $\lambda = 220$ nm takes place there is photoluminescence in a wide range of wavelengths. The existence of copper nanoparticles causes significant extinction of PVC photoluminescence. Besides, emergence of additional changes in spectra is observed. It is obvious that such photoluminescence spectra transformations are conditioned by certain interaction of PVC macromolecules with copper nanoparticles.

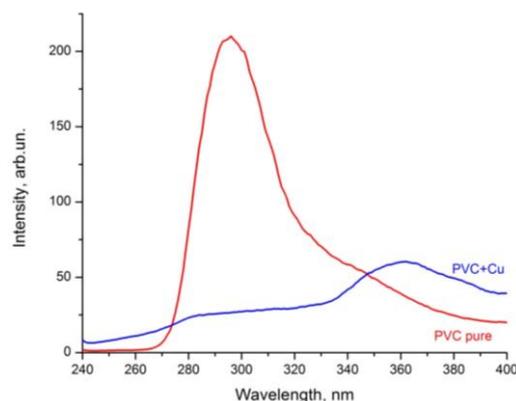


Fig. 3 – Photoluminescence spectra of pure PVC and PVC + 0.06 vol. % nanoCu at a temperature of 293 K ($\lambda = 220$ nm)

3.4 PVC-systems Reaction on Temperature Field

Samples' temperature rise, as well as beta-radiation increase [3], enable a wide range of less efficient conformations and defects with simultaneous reduction of optical density line absorption of energetically more efficient conformations that prevail under normal conditions.

With the help of TG-DTG-DTA complex method of thermal analysis, heat-stable properties of PVC/nanoCu films are investigated. It was considered that thermal-oxidative breakdown of PVC systems at samples' heating speed of 2.5 K/min occurs at the first order reaction. Investigation results show that such composites are distinguished by certain stage of degradation at 448-573 K. Temperature area, where it can be noticed, is almost the same as the temperature when PVC transfers from high elastic to viscoelastic condition. At this stage of dehydrochlorination, activation energy value of thermal-oxidative breakdown of PVC composites is 122-138 kJ/mol depending on the filler concentration. PVC-systems filled with nanoCu possess much lower thermostability in comparison to pure PVC systems. Apparently, it is determined by the increase in unstable groups in PVC systems after being subjected to the filler in the structure formation process. Therefore, the addition of 0.1 vol. % amount of highly dispersed nano-filler does not have much effect on thermostable properties of investigated systems. Frequent cyclical heating and cooling of PVC + 0.1 vol. % nanoCu sample up to 353 K do not influence the elastic modulus value substantially. At the same time, $\text{tg}\delta$ value has been decreased from 0.084 to 0.076.

3.5 Antibacterial Properties of PVC/nanoCu Films

The results of microbiological tests of PVC films bioactivity on solid medium space correlate with the results of bioactivity in liquid medium followed by inoculation. Change in the transmission ratio while testing PVC and PVC/nanoCu and controlling sample out of *Staphylococcus aureus* survivorship rate in liquid medium shows that polymer metal matrix composite, that has been obtained, develops superior bioactivity and arouses test culture growth inhibition. Transmission ratio, that was estimated by spectrophotometer in cuvettes with PVC + 0.1 vol. % nanoCu, was at its peak (94 %) vs 73 % in

pure PVC film. Growth inhibition absence in liquid medium oculation proves high antibacterial potency of PVC/nanoCu films towards *Staphylococcus aureus*.

4. CONCLUSIONS

Implementation of complementary spectroscopic investigation methods of PVC systems structural properties cleared up a crucial role of nanofillers in polymer composite materials production with a predicted set of properties and analyzed ways of control of their physical and chemical qualities in external fields of different origin. For instance, metal nanoparticles presence in PVC system in external electric field leads to creation of additional field sources inside the composite shifting it to higher tensile field and simplifying its transition to electret state. It has been established that metal

nanoparticles in polymer systems fulfill the role of photostabilizer and antirad, slowing down the aging process and polymer destruction in ultraviolet, protecting against destruction under the influence of high-energy radiation. The suggested method of nanocomposite polymer system production gives an opportunity to make protective things with high absorption capacity of radiation field. Besides, the obtained metal nanocomposites are quite thermally stable at their dynamic viscoelastic properties. High antibacterial activity of PVC/nanoCu films to *Staphylococcus aureus* has been substantiated.

The obtained results could be used as scientific background for new polymer composites inventions; guided regulations of their structure and properties; improvement of development and application of technologies in different areas of science and technology.

REFERENCES

1. C. Harito, D.V. Bavykin, B. Yuliarto, H.K. Dipojono, F.C. Walsh, *Nanoscale* **11**, 4653 (2019).
2. C. Miranda, S. Rodríguez-Llamazares, J. Castaño, M.A. Mondaca, *Adv. Polym. Tech.* **37** No 3, 937 (2016).
3. V.V. Krivtsov, Ye.V. Malinovsky, *J. Nano- Electron. Phys.* **6** No 4, 04029 (2014).
4. V. Maschenko, V. Krivtsov, V. Kvasnikov, V. Drevetskiy, *IAPGOS* **9** No 4, 34 (2019).
5. M. Rai, A.P. Ingle, R. Pandit, P. Paralikar, S. Shende, I. Gupta, J.K. Biswas, S.S. da Silva, *Nanotechnol. Rev.* **7** No 4, 303 (2018).
6. V.V. Krivtsov, *Surf. Eng. Appl. Elect.* **41** No 1, 53 (2005).

Деякі властивості та структурні особливості композитних ПВХ/Си плівок з наночастинками міді, отриманих методом електричного вибуху провідника

В.В. Кривцов¹, В.В. Кукла², В.В. Кривцов³, А.І. Шидловський¹, М.А. Бордюк⁴

¹ Рівненський державний гуманітарний університет, вул. С. Бандери, 12, 33028 Рівне, Україна

² Рівненський обласний інститут післядипломної педагогічної освіти, вул. В. Чорновола, 74, 33028 Рівне, Україна

³ Національний університет водного господарства та природокористування, вул. Соборна, 11, 33028 Рівне, Україна

⁴ Рівненська медична академія, вул. М. Карнаухова, 53, 33028 Рівне, Україна

У роботі представлено результати комплексного дослідження впливу умов отримання та модифікації нанокомпозитних полімерних матеріалів на їхній релаксаційний стан, процеси структуроутворення, в'язкопружні, термостабільні, антибактеріальні та інші властивості. Вивчено композитні плівки, що складаються з полівінілхлоридної матриці та наповнювача у вигляді наночастинок міді, одержаних методом електричного вибуху провідника. Як методи дослідження використано: метод термостимульованої деполаризації, методи ТГ-ДТГ-ДТА термічного аналізу, метод вимушених резонансних коливань на звукових частотах, ІЧ- та КР-спектроскопію, спектроскопічний метод визначення антибактеріальної активності, фотолюмінесцентний аналіз та ін. Досліджена реакція нанопоповнених полівінілхлоридних систем на дію зовнішніх полів різної природи: орієнтуючого постійного електричного поля, температурного поля, ультрафіолетового випромінювання. Оцінено ступінь модифікації полівінілхлоридних систем нанорозмірним наповнювачем та зовнішніми енергетичними полями різної природи. Встановлені особливості поведінки елементів структури полівінілхлориду під впливом цих модифікуючих факторів. З'ясована роль нанопоповнення у формуванні комплексу властивостей композиту. Показано, що термоелектрети з металонаповнених ПВХ-систем за своїми електретними характеристиками перевершують традиційні ПВХ-матеріали. Наночастинки міді у полівінілхлоридних системах відіграють роль фотостабілізаторів та антирадів, сповільнюючи процеси старіння та деградації полімерного матеріалу під впливом УФ-променів. Отримані металонанокомпозити мають стійкі показники поглинаючої здатності високоенергетичного радіаційного поля, що дозволяє використовувати їх як матеріали для захисту від зовнішнього випромінювання. Підтверджено високу антибактеріальну активність плівок ПВХ/наноCu по відношенню до золотистого стафілококу.

Ключевые слова: Полівінілхлорид, Нанопоповнювач, Електричний вибух провідника, Ультрафіолет, Термоелектрет, Антибактеріальна активність.