21. Krasinskyi, V. Operational properties of nanocomposites based on polycaproamide and modified montmorillonite [Text] / V. Krasinskyi, O. Suberlyak, Yu. Klym // Acta Mechanica Slovaca. – 2016. – Vol. 20, Issue 1. – P. 52–55.
22. Krasinskyi, V. V. Termohravimetrychni doslidzhennia polivinilpirolidonu, modyfikovanoho montmorylonitom [Text] / V. V. Krasinskyi, V. V. Kochubei, Yu. V. Klym, I. Haidos // Visnyk NU "Lvivska politekhnika". – 2015. – Issue 812. – P. 378–382.
23. Suberlyak, O. V. Vliyanie kompleksoobrazovaniya na polimerizatsiyu 2-oksietilenmetakrilata v prisutstvyi polivinilpirrolidona [Text] / O. V. Suberlyak, V. Y. Skorohoda, I. G. Thir // Vysokomolekulyarnye soedineniya. – 1989. – Vol. 31. – P. 336–340.

UDC 691.175.743; 621.793.3
DOI: 10.15587/1729-4061.2017.108462

RESEARCH INTO KINETIC PATTERNS OF CHEMICAL METALLIZATION OF POWDER-LIKE POLYVINYLCHLORIDE

V. Moravskyi
PhD, Associate Professor*
E-mail: vmoravsky@gmail.com
I. Dziaman
PhD, Junior Research*
E-mail: iradzyaman@gmail.com
S. Suberliak
Engineer*
E-mail: Sophiia.A.Suberliak@lpnu.ua
M. Kuznetsova
PhD, Associate Professor**
E-mail: kuznetsovam83@gmail.com
T. Tsimbalista
Specialist of the highest category, Chairman of the cyclic Commission of chemical technology and engineering
State higher educational institution
"Kalush Polytechnic College"
B. Khmelnicky str., 2, Kalush, Ukraine, 77301
E-mail: tetyana975@ukr.net
L. Dulebova
PhD, Associate Professor
Department of Automobile Production
Technical University of Kosice
Letniaya str., 9, Kosice, Slovak Republic, 04200
E-mail: ludmila.dulebova@tuke.sk
*Department of Chemical Technology of Plastics Processing
Department of Thermal Engineering and Thermal Power Stations*
***Lviv Polytechnic National University
S. Bandery str., 12, Lviv, Ukraine, 79013

Представлені кінетичні закономірності металізації механічно активованого цинком порошкоподібного полівінілхлориду в розчинах хімічного відновлення. Досліджено вплив pH середовища та кількості металу активатора на швидкість осадження міді на активованій полімерній поверхні. Встановлено, що зміною pH середовища можна ефективно впливати на процес металізації. Волюметричним методом, за кількістю виділеного водню, показано, що оптимальним pH розчинів хімічної металізації, для проходження реакції відновлення міді формальдегідом, є 12. Зростання pH розчинів, а також кількості металу активатора, збільшує кількість відновленої міді в результаті обмінної реакції з цинком

Ключові слова: металополімерні композити, функціональні композити, полівінілхлорид, хімічне відновлення, швидкість реакції, металеві наповнювачі

Представленные кинетические закономерностях металлизации механически активированного цинком порошкообразного поливинилхлорида в растворах химического восстановления. Исследовано влияние pH среды и количества металла активатора на скорость осаждения меди на активированной полимерной поверхности. Установлено, что изменением pH среды можно эффективно влиять на процесс металлизации. Объемным методом, по количеству выделенного водорода, показано, что оптимальным pH растворов химической металлизации, для прохождения реакции восстановления меди формальдегидом, является 12. Рост pH растворов, а также количества металла активатора, увеличивает количество восстановленной меди в результате обменной реакции с цинком

Ключевые слова: металлополимерные композиты, функциональные композиты, поливинилхлорид, химическое восстановление, скорость реакции, металлические наполнители

1. Introduction

Despite their distinctive complex of high technical properties, polymers in some cases demonstrate significant disadvantages. One of the major shortcomings that limits the scope of application of polymeric materials is the low capacity to conduct electric and thermal energy. It is the high insulating properties of polymers regarded as their main advantage that stand in the way of possible expansion of the areas of use.

The simplest case, which can be employed to eliminate the mentioned shortcomings, is the development of new materials based on traditional polymers. In particular, creation of polymeric composites in which electricity and heat-conducting materials are used as fillers. The most common materials applied to improve the conductivity of polymers are different materials with electron conductivity, namely: metals, graphite, black, in the form of powders, fibers, or continuous fillers.

The wide spread of composite polymeric materials is also due to the high manufacturability, which is characteristic for a polymeric base of such composites. Basic technologies of processing the polymers is the injection molding and extrusion, which are high-performance, single-stage and practically waste-free methods. High manufacturability of the filled polymeric composites is a significant advantage in the case of using such materials to replace products that are made of metals. The replacement of metal parts with the polymeric ones makes it possible to significantly reduce the cost of the product and its weight, and, in some cases, to improve certain characteristics. Another advantage of polymeric products over the metal ones is their high chemical and corrosion resistance, elasticity, and low density.

In order to obtain polymeric composite materials, traditionally used methods are those that employ high-performance mixing equipment. Such methods, despite their widespread, exhibit several shortcomings. That is why finding the ways to create new methods of introducing fillers to the polymeric matrix is a relevant task.

The method was proposed for obtaining metal-containing composites by introducing a metallic filler to the polymeric matrix as a result of metallization of the surface of the starting polymeric raw material [1, 2]. The main stage of this method is the process of metallization of the polymeric surface, which will define resulting properties of the composite material. That is why the information about kinetic patterns of reducing a metal on the polymeric surface is essential in order to obtain composites with controlled and preassigned properties.

2. Literature review and problem statement

Polymeric materials with conductive fillers comprise a separate group of highly technological composites, research into which has recently attracted much attention [3–7]. A combination of the polymer and such fillers sets the aim to receive new materials, which are characterized by a set of unique properties and have considerable potential for practical application. Such composites can be used as anti-static materials, flexible heaters, shielding materials from electromagnetic radiation, electrodes, sensors, etc. [8–12]. A significant group among these materials is made up of the metal-containing polymeric composites.

Metal-containing composites contain in the polymeric matrix a certain amount of metallic filler in the form of a dispersed powder, chips, cut or continuous fibers, etc. [13, 14]. Using metals as a filler, it is possible to obtain polymeric composites that are characterized by interesting electric conductive properties while maintaining high manufacturability [15]. A choice of the filler and the polymer will determine the properties of the resulting composite. High-tonnage industrial thermoplastics are mainly used as a polymeric matrix: polyethylene [16], ABC [17], polyvinyl chloride [18], polystyrene [19]. Despite numerous studies that addressed the use of such fillers as carbon nanotubes [20] or graphene [21], metallic powders still remain the main fillers for obtaining advanced polymeric composites. Metals that are the most widely used as fillers are copper [18], nickel [18, 22], silver [23], iron [17].

In addition to affecting the electric or heat-conducting properties of polymers, metallic fillers also change other properties. In paper [24], authors examined the influence of ratio of copper filler on the relaxation properties of composites based on polydimethylsiloxane. The ability to absorb mechanical energy during cyclic loading of composites with such a filler increases when applying nanometer-sized copper particles [25]. The effect of fillers on the rheological properties of polymeric composites is considered in detail in article [26]. Using aluminum powder as an example, it is shown that the presence of a metallic filler in polysopren increases the polymer crystallinity, elevates the temperature of glass transition, and improves mechanical properties [27]. On the contrary, the use of zinc powder as a filler for polyethylene with high density [28] results in the worsening of mechanical properties of the composite in comparison to a non-filled polymer.

Obtaining metal-filled polymer composites is a complicated technological process, which greatly affects the properties of the resulting materials. From a practical point of view, it is the properties of such composites that are of primary interest. Despite a significant number of publications dealing with the creation and study of metal-filled polymeric composites, there are no universal approaches to the creation of highly technological metal-filled composites. Given this, of considerable scientific interest are the studies into creation of new technological methods for obtaining the metal-filled composites.

3. Research goal and objectives

The goal of present work was to establish kinetic patterns of reducing copper in the solutions of chemical metallization on the polyvinylchloride surface that was mechanically activated with zinc. Conducting such a research opens up prospects for the substantiation of fundamentals of the technology for obtaining metal-filled polymeric composites through the metallization of polymeric raw materials.

To accomplish the set goal, the following tasks must be solved:

– to establish a possibility for the metallization of mechanically-activated powder-like polyvinylchloride surface in the solutions of chemical reduction;

– to examine the influence of pH of the solution of chemical reduction and the amount of metal in the activator on the kinetic regularities of copper reduction on the activated polymeric surface.

4. Materials and methods for studying the kinetics of copper plating of the activated polyvinylchloride surface

During studies, we used powder-like suspension polyvinylchloride activated with zinc powder. The activation of polyvinylchloride (PVC) was carried out in a laboratory ball mill with ceramic cylindrical milling bodies. The mill was loaded with suspension PVC and zinc powder of brand PC-2. During rotation of the mill, a strong attachment of metal of the activator to the polymeric surface took place.

The copper plating of the activated PVC was conducted in the non-stabilized solutions of chemical reduction [29], which consist of copper sulphate, trilon-B, and formalin as a complex-forming agent and a reducer. Concentrations of the components in the solution of chemical reduction were: copper sulfate – 48 mmol/l, trilon-B – 74 mmol/l, formalin – 250 mmol/l, sodium hydroxide – 150–1500 mmol/l. The loaded activated PVC made up 25 g/l.

Kinetic patterns of copper plating of the activated PVC were examined using a volumetric method by the amount of isolated hydrogen [22]. We used gas burettes for measurements, their volume was chosen based on the maximum possible amount of isolated hydrogen. A relative error of measurements during construction of the kinetic curves does not exceed 2 %.

5. Results of examining the kinetics of copper plating of the activated polyvinylchloride surface

The basis for the choice of method for examining the kinetics of copper reduction by the volume of the isolated hydrogen is the fact that in the trilon solutions of chemical copper plating, 1 mole of hydrogen is isolated per 1 mole of the reduced copper [29]. Reduction of copper ions with formaldehyde occurs according to the following scheme:

$$2CH_2O + Cu^{2+} + 4OH^- \rightarrow$$
$$\rightarrow Cu\downarrow + H_2\uparrow + 2HCOO^- + 2H_2O. \qquad (1)$$

It should be noted that the classical technologies of copper plating, in order to activate a polymeric surface, employ methods (reduction of precious metals salts on the polymeric surface) that do not affect the amount of isolated hydrogen at all. The proposed technology for the activation of a polymeric surface uses zinc, which reduces a less active copper from salt by the reaction that proceeds without hydrogen separation:

$$CuSO_4 + Zn \rightarrow Cu\downarrow + ZnSO_4. \qquad (2)$$

Thus, in the solution of chemical copper plating, there will simultaneously or sequentially take place two competing reactions, which result in the reduction of copper ions.

The results obtained when studying the kinetics of copper reduction show significant dependence of the character of resulting kinetic curves on the starting pH of the solution (Fig. 1).

It is possible to distinguish three groups of kinetic curves, which are united by the value of starting pH of the solution (the amount of introduced NaOH). The first group of kinetic curves is united by the pH values of 10.928–11.444, which corresponds to 152.5 mmol/l NaOH, the second group – 11.918–12.059, which corresponds to 250–268.8 mmol/l NaOH, and the third group – 12.160–12.338 corresponding to 562.5–1500 mmol/l NaOH.

According to equation (1), the reaction of ion copper reduction by formaldehyde proceeds in line with the scheme during which 4 moles of alkali is spent per 1 mole of the reduced copper. The concentration of $CuSO_4$ in the solution is 48 mmol/l. In this case, a sodium hydroxide concentration of 152.5 mmol/l is not sufficient for a full course of the reaction. And such concentration does not provide the required pH magnitude for the reaction to proceed (pH≈12–12.5 [29]). In this case, we observe the low speed of reaction and a small amount of the reduced copper (by the volume of the separated hydrogen), which is also demonstrated by a dark blue coloring of the solution, maintained after the reaction is over. With an increase in the content of alkali to 250–268.8 mmol/l, its concentration is sufficient for the reaction to proceed, as well as to maintain the required pH level. The reaction occurs at high speed and large separation of hydrogen. The solution received after 20 minutes of reaction is colorless and transparent. Further substantial increase in the content of alkali to a concentration of 562.5–1500 mmol/l manifests itself in a slight growth of the solution's pH, but the result is an increase in the reaction rate and a decrease in the period over which the solution becomes colorless and transparent (10 minutes).

Similar results (Fig. 2) were also obtained for the activated PVC containing 23.1 % by weight of zinc.

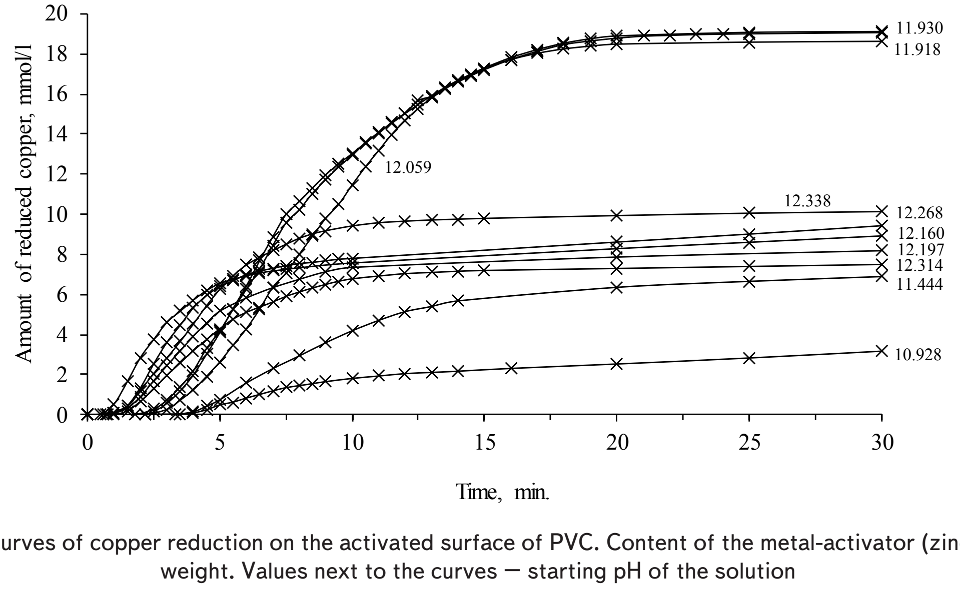


Fig. 1. Kinetic curves of copper reduction on the activated surface of PVC. Content of the metal-activator (zinc) – 15.3 % by weight. Values next to the curves – starting pH of the solution

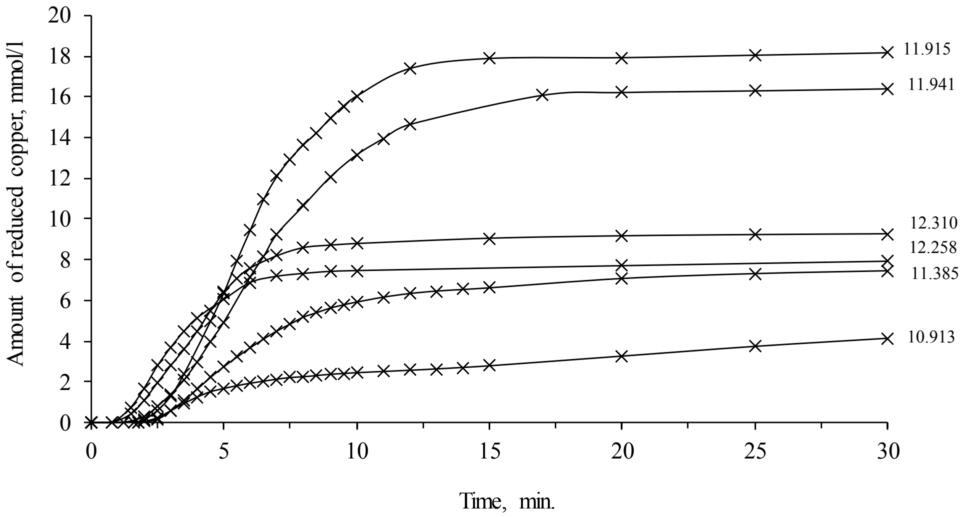


Fig. 2. Kinetic curves of copper reduction on the activated PVC surface. Zinc content — 23.1 % by weight. Values next to the curves — starting pH of the solution

Measuring pH of the solution after the reaction was over also revealed an interesting pattern (Fig. 3). The biggest difference between the starting and resulting pH occurs in the solutions with a low concentration of alkali. This is explained, as mentioned above, by the consumption of alkali in the course of the copper ions reduction reaction. The same pattern is also observed for the solutions of group 2, however, in this case a change in the pH magnitude is much smaller. For the solutions of group 3, we observed the opposite dependence, pH of the solutions after the reaction is over is somewhat higher than that of the starting pH of the solution. In this case, it is caused by a significant excess of alkali, which increases pH after the exhaustion of reagents that reduce pH of the solution ($CuSO_4$, formaldehyde).

In the case of low concentrations of alkali, we also observe a considerable influence of the content of metal-activator on the pH value of the solution after the reaction is completed. A more substantial decrease in pH of the solution is observed during copper plating of the activated PVC that contains less amount of metal-activator. This feature can be explained by a deeper course of the copper reduction reaction involving formaldehyde and alkali (1). And vice versa, with a growth in the content of metal-activator, the amount of copper that is reduced as a result of exchange reaction with zinc (2) increases, thus the consumption of alkali during first reaction is less, and pH of the solution when the reaction is completed is thehighest.

A confirmation of the assumption we made on that with an increase in the content of metal-activator the amount of copper, which is reduced as a result of exchange reaction with zinc, slightly increases, is the kinetic curves of copper reduction, shown in Fig. 4.

Because the amount of reduced copper was assessed by the volume of the separated hydrogen, the kinetic curves presented show the share of copper, which was reduced as a result of the interaction with formaldehyde according to reaction (1). The amount of copper reduced by reaction (1) decreases with increased content of metal-activator. This peculiarity is better observed at higher pH values of the solution.

A significant impact should be noted of the solutions' pH on the mechanism of reduction of copper ions (Fig. 5). The maximum hydrogen isolation is observed for a pH of the solution close to 12. This allows us to state that at the given pH there are the best conditions for the reduction of copper ions by formaldehyde. Increasing pH of the solution to values above 12.1 reduces the amount of copper reduced by formaldehyde and contributes to the course of exchange reaction with zinc (2).

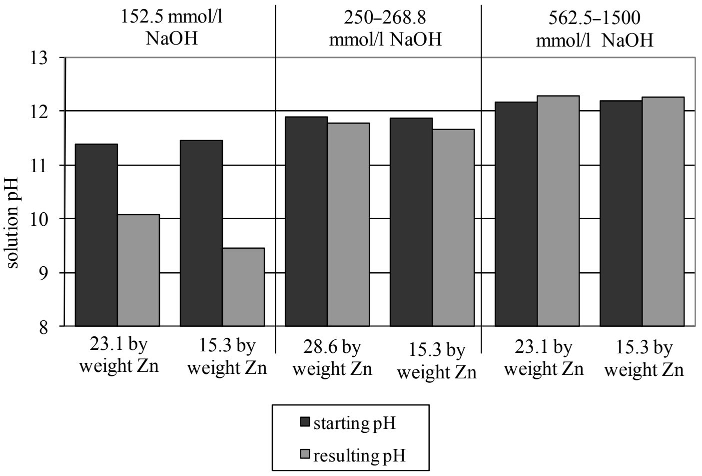


Fig. 3. Influence of the content of metal-activator on the pH value of the solution when the reaction is completed

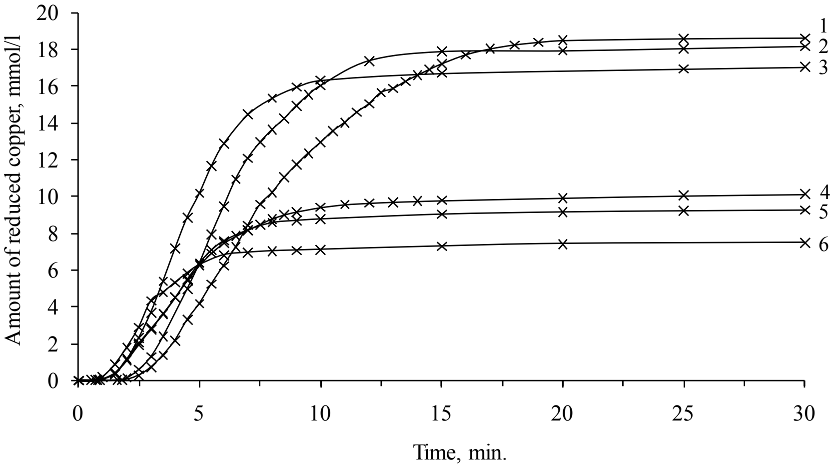


Fig. 4. Kinetic curves of copper reduction on the activated PVC surface. Zinc content: 1, 4 – 15.3 % by weight; 2, 5 – 23.1 % by weight; 3, 6 – 28.6 % by weight. 1 – 3 – starting pH of the solution ≈11.9; 4–6 – starting pH of the solution ≈12.2

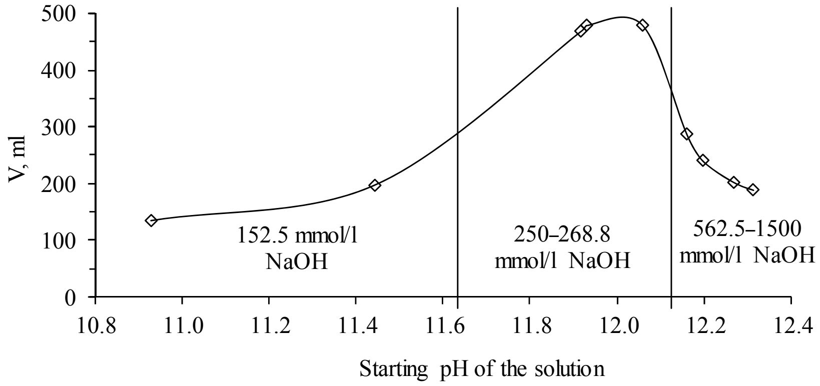
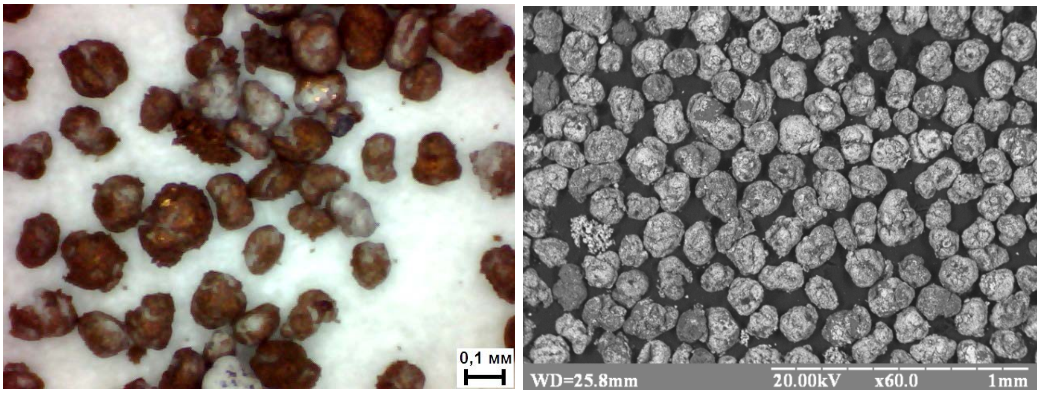


Fig. 5. Dependence of the amount of isolated hydrogen on the starting pH of the solution. Zinc content – 15.3 % by weight

The proposed technology for copper plating the polymeric raw materials can be applied in order to create metal-containing composites. The introduction of metal to the polymeric matrix will take place directly at the stage of the formation of the product. The obtained samples of copper-plated polyvinylchloride are distinguished by a high degree of particle coating with metal, which can be seen in the microphotographs acquired using the optical and electron microscopes (Fig. 6). In the microphotographs of particles of the powder-like PVC one can identify areas both covered and not covered with copper.

Detecting a spectrum of characteristic x-ray radiation during electron microscopy in a contrast mode (Fig. 7) confirms the absence of solid metallic coating on the surface of the polymer. This is indicated by the presence of a chlorine peak in the spectrum of characteristic x-ray radiation, which can be attributed only to the surface of the polymer.



a *b*

Fig. 6. Microphotographs of the copper-plated powder-like polyvinylchloride:
a – optical microscopy; *b* – electron microscopy in a contrast mode

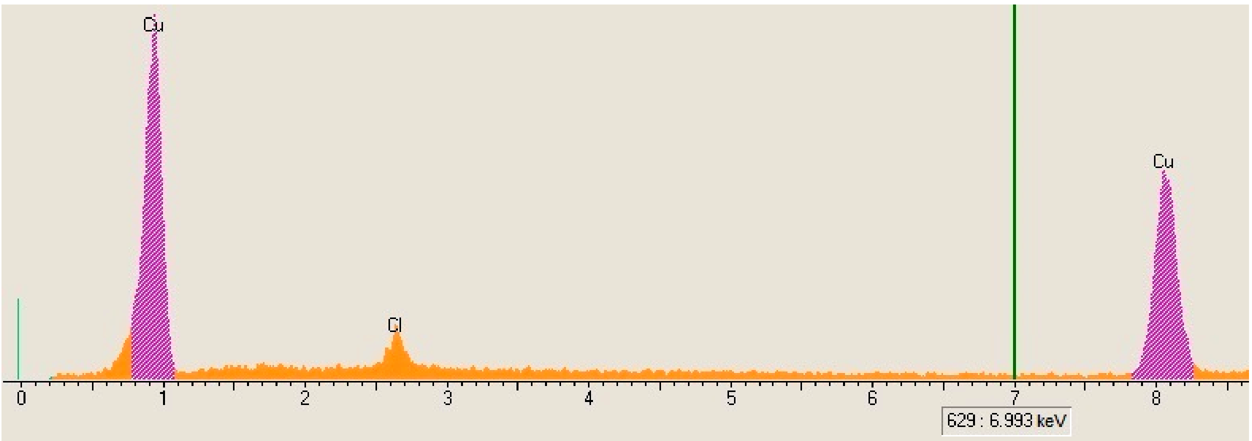


Fig. 7. Spectrum of characteristic x-ray radiation of the surface of copper-plated powder-like polyvinylchloride

We should also note the lack in a spectrum of characteristic x-ray radiation of the peaks corresponding to oxygen. This fact was previously noted by researchers when using trilon solutions of chemical metallization [29] that prevent passivation of the formed copper coating.

6. Discussion of results of examining the kinetics of copper plating of the activated polyvinylchloride surface

Based on the obtained experimental data, we established that the copper reduction rate in the solutions of chemical metallization depends mainly on the medium pH. In the solution, there are two simultaneously proceeding competing reactions, the result of which is the full reduction of copper.

An analysis of possible reactions of copper reduction in the solutions of chemical metallization on the zinc-activated polymeric surface reveals that the amount of reduced copper, which was assessed by the volume of separated hydrogen can be attributed only to the reaction of copper reduction by formaldehyde. Because the exchange reaction with zinc occurs without hydrogen isolation. At pH of the solutions of chemical metallization above 11.6, copper reduction reaction proceeds until full consumption of $CuSO_4$ and appropriate discoloration of the solution. The amount of hydrogen separated according to reaction (1) for the second group of kinetic curves (Fig. 5) is 475 ml on average, which makes up 21 mmol H_2. Under condition on that 1 mole of separated hydrogen corresponds to 1 mole of the reduced copper and at accepted concentration of $CuSO_4$ in the solution of 48 mmol/l, such a volume of separated hydrogen corresponds to about 44 % of the reduced copper according to reaction (1) of the maximum possible. Increasing pH of the solution reduces the volume of the isolated hydrogen and, accordingly, the amount of copper reduced by formaldehyde. At pH of the solution 12.160, the amount of copper reduced by formaldehyde is 27 %, at pH=12.268 – 22 %.

A slight increase in the amount of copper that is reduced as a result of exchange reaction with zinc also occurs with the growth of the amount of metal-activator (Fig. 4). In this case, at pH of the solution close to 11.9, in line with reaction (1), 44 % of copper are reduced, at a content of metal-activator of 15.3 % by weight, 40 % of copper, at a content of metal-activator 28.6 % by weight.

The obtained results of copper reduction through the interaction with formaldehyde made it possible to establish the amount of copper that is reduced as a result of exchange reaction with zinc. The amount of such copper is always larger. At a content of metal-activator of 15.3 % by weight, the amount of zinc, which is introduced to the solution of chemical metallization is 58.1 mmol/l. Such a quantity of zinc cannot be completely replaced with copper, even under condition that the solution undergoes the exchange reaction only. It is logical to assume that part of metal of the activator remains unused and it will enter the composition of metallic coating. The higher the content of zinc in the activated PVC, the larger the amount of such metal.

A volumetric method applied when exploring the kinetics of metallization of the powder-like PVC activated with zinc can, obviously, be combined with chemical or gravimetric methods, for the purpose of accurately account of the amount of copper that is reduced as a result of interaction with zinc. The volumetric method, however, remains a convenient tool for monitoring the process of metallization and for establishing the time the reaction is completed. The results of research revealed that the hydrogen separation termination means the end of copper reduction.

The application of mechanically activated powder-like polyvinylchloride makes it possible to obtain the metal-containing raw material that could be used to create metal-filled composites. An analysis of spectrum of characteristic x-ray radiation of the surface of the copper-plated powder-like polyvinylchloride and the obtained microphotographs of the surfaces of such PVC allow us to state that the reduction of copper occurs directly on the activated polymeric surface. The formed copper coating is not solid. The presence of regions on the surface of PVC that are not coated with metal provides for the possibility of employing plastisol technology, which would expand the range of resulting materials and products.

The results obtained will form the basis of further research in order to optimize the compositions of solutions for chemical metallization, to develop a technology for obtaining metal-filled composites, and to study their properties.

7. Conclusions

1. We obtained kinetic patterns of copper reduction in the solutions of chemical metallization on the zinc-mechanically-activated powder-like polyvinylchloride. It was found that the bulk of copper is reduced as a result of exchange reaction with zinc. The optimal value for the copper reduced as a result of interaction with formaldehyde is pH of the

solutions close to 12. Under such a condition, the amount of copper reduced as a result of interaction with formaldehyde is not larger than 44%.

2. The ratio of quantities of the reduced copper as a result of exchange reaction with zinc and reduced by formaldehyde is determined by pH of the solutions of chemical reduction and the amount of metal-activator. The course of exchange reaction with zinc is facilitated by an increase in pH of the solutions of chemical reduction and an increase in the amount of metal-activator.

3. It is established that the use of solutions of chemical reduction and mechanically-activated polyvinylchloride makes it possible to obtain metal-containing polymeric raw materials suitable for the creation of metal-filled polymeric composites.

Acknowledgement

Present work is carried out within the framework of projects DB/NPK "Creating the technology of obtaining structural dispersal filled polymeric (nano) composites" (State registration number 0116U004410) and KEGA – 059TUKE-4/2016.

References

1. Lee, S. H. Highly anisotropic Cu oblate ellipsoids incorporated polymer composites with excellent performance for broadband electromagnetic interference shielding [Text] / S. H. Lee, S. Yu, F. Shahzad, J. P. Hong, W. N. Kim, C. Park et. al. // Composites Science and Technology. – 2017. – Vol. 144. – P. 57–62. doi: 10.1016/j.compscitech.2017.03.016
2. Moravskyi, V. S. Metalizatsiya polivinilkhlorydnoho plastykatu khimichnym vidnovlennyam v rozchynakh [Text] / V. S. Moravskyi, I. A. Tymkiv, P. T. Bodnarchuk // Visnyk Natsionalnoho universytetu "L'ivska politekhnika": Khimiya, tekhnolohiya rechovyn ta yikh zastosuvannya". – 2016. – Vol. 841. – P. 405–409.
3. Eichner, E. Using dilute spouting for fabrication of highly filled metal-polymer composite materials [Text] / E. Eichner, V. Salikov, P. Bassen, S. Heinrich, G. A. Schneider // Powder Technology. – 2017. – Vol. 316. – P. 426–433. doi: 10.1016/j.powtec.2016.12.028
4. Park, H. J. Experimental study on the thermal and mechanical properties of MWCNT/polymer and Cu/polymer composites [Text] / H. J. Park, A. Badakhsh, I. T. Im, M.-S. Kim, C. W. Park // Applied Thermal Engineering. – 2016. – Vol. 107. – P. 907–917. doi: 10.1016/j.applthermaleng.2016.07.053
5. Panwar, V. Analysis of electrical, dielectric, and electromagnetic interference shielding behavior of graphite filled high density polyethylene composites [Text] / V. Panwar, R. M. Mehra // Polymer Engineering and Science. – 2008. – Vol. 48, Issue 11. – P. 2178–2187. doi: 10.1002/pen.21163
6. Mansour, S. A. Dielectric dispersion and AC conductivity of acrylonitrile butadiene rubber-poly(vinyl chloride)/graphite composite [Text] / S. A. Mansour, M. E. Al-ghoury, E. Shalaan, M. H. I. El Eraki, E. M. Abdel-Bary // Journal of Applied Polymer Science. – 2011. – Vol. 122, Issue 2. – P. 1226–1235. doi: 10.1002/app.34240
7. Mansour, S. A. Thermoelectric Power Properties of Graphite-Loaded Nitrile Rubber/Poly(vinyl chloride) Blends Above the Percolation Threshold [Text] / S. A. Mansour, M. Hussein, A. H. Moharram // Advances in Polymer Technology. – 2014. – Vol. 33, Issue S1. – P. 21439–21448. doi: 10.1002/adv.21439
8. Klason, C. Electrical properties of filled polymers and some examples of their applications [Text] / C. Klason, D. H. Mcqueen, J. Kubat // Macromolecular symposia. – 1996. – Vol. 108, Issue 1. – P. 247–260. doi: 10.1002/masy.19961080120
9. Patent US5902518 A, МПК H01B 1/06 Self-regulating polymer composite heater [Text] / Khazai B., Nichols G. M. – Watlow Missouri, Inc., Northwestern University. – US 08/902,122; declared: 29.07.1997; published: 11.05.1999.
10. Arranz-Andres, J. Hybrids based on poly(vinylidene fluoride) and Cu nanoparticles: Characterization and EMI shielding [Text] / J. Arranz-Andres, E. Perez, M. L. Cerrada // European Polymer Journal. – 2012. – Vol. 48, Issue 7. – P. 1160–1168. doi: 10.1016/j.eurpolymj.2012.04.006
11. Arranz-Andres, J. Lightweight nanocomposites based on poly(vinylidene fluoride) and Al nanoparticles: Structural, thermal and mechanical characterization and EMI shielding capability [Text] / J. Arranz-Andres, N. Pulido-Gonzalez, C. Fonseca, E. Perez, M. L. Cerrada // Materials Chemistry and Physics. – 2013. – Vol. 142, Issue 2-3. – P. 469–478. doi: 10.1016/j.matchemphys.2013.06.038
12. Kim, H.-R. Lightweight nanofibrous EMI shielding nanowebs prepared by electrospinning and metallization [Text] / H.-R. Kim, K. Fujimori, B.-S. Kim, I.-S. Kim // Composites Science and Technology. – 2012. – Vol. 72, Issue 11. – P. 1233–1239. doi: 10.1016/j.compscitech.2012.04.009
13. Nurazreena. Metal Filled High Density Polyethylene Composites – Electrical and Tensile Properties [Text] / Nurazreena, L. B. Hussain, H. Ismail // Journal of Thermoplastic Composite Materials. – 2006. – Vol. 19, Issue 4. – P. 413–425. doi: 10.1177/0892705706062197
14. Sancaktar, E. Electrically Conductive Epoxy Adhesives [Text] / E. Sancaktar, L. Bai // Polymers. – 2011. – Vol. 3, Issue 4. – P. 427–466. doi: 10.3390/polym3010427
15. Bloor, D. A metal–polymer composite with unusual properties [Text] / D. Bloor, K. Donnelly, P. J. Hands, P. Laughlin, D. Lussey // Journal of Physics D: Applied Physics. – 2005. – Vol. 38, Issue 16. – P. 2851–2860. doi: 10.1088/0022-3727/38/16/018
16. Krupa, I. The mechanical and adhesive properties of electrically and thermally conductive polymeric composites based on high density polyethylene filled with nickel powder [Text] / I. Krupa, V. Cecen, A. Boudenne, J. Prokes, I. Novak // Materials and Design. – 2013. – Vol. 51. – P. 620–628. doi: 10.1016/j.matdes.2013.03.067

17. Thermo-Mechanical Properties of a Metal-filled Polymer Composite for Fused Deposition Modelling Application [Text] / M. Veidt (Ed.) // 5th Australasian Congress on Applied Mechanics, ACAM 2007, 2007. – 836 p.
18. Kurt, E. Preparation and Characterization of Flexible Polyvinylchloride-Copper Composite Films [Text] / E. Kurt, C. Y. Ozçelik, S. Yetgin, F. O. Omurlu, D. Balkose // Polymers and Polymer Composites. – 2013. – Vol. 21, Issue 3. – P. 139–143.
19. Iqbal, M. Z. A study on polystyrene-metal powder conductive composites [Text] / M. Z. Iqbal, G. M. Mamoor, T. Bashir, M. S. Irfan, M. B. Manzoor // Journal of Chemical Engineering. – 2010. – Vol. 25. – P. 61–64. doi: 10.3329/jce.v25i0.7240
20. Burmistrov, I. Mechanical and electrical properties of ethylene-1-octene and polypropylene composites filled with carbon nanotubes [Text] / I. Burmistrov, N. Gorshkov, I. Ilinykh, D. Muratov, E. Kolesnikov, E. Yakovlev et. al. // Composites Science and Technology. – 2017. – Vol. 147. – P. 71–77. doi: 10.1016/j.compscitech.2017.05.005
21. Zakiyan, S. E. Influence of chain mobility on rheological, dielectric and electromagnetic interference shielding properties of poly methyl-methacrylate composites filled with graphene and carbon nanotube [Text] / S. E. Zakiyan, H. Azizi, I. Ghasemi // Composites Science and Technology. – 2017. – Vol. 142. – P. 10–19. doi: 10.1016/j.compscitech.2017.01.025
22. Grytsenko, O. M. Investigation of nickel chemical precipitation kinetics [Text] / O. M. Grytsenko, O. V. Suberlyak, V. S. Moravskyi, A. V. Hayduk // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 1, Issue 6 (79). – P. 26–31. doi: 10.15587/1729-4061.2016.59506
23. Kim, H.-R. Lightweight nanofibrous EMI shielding nanowebs prepared by electrospinning and metallization [Text] / H.-R. Kim, K. Fujimori, B.-S. Kim, I.-S. Kim // Composites Science and Technology. – 2012. – Vol. 72, Issue 11. – P. 1233–1239. doi: 10.1016/j.compscitech.2012.04.009
24. Sonawane, D. Effect of aspect ratio of test specimens on quasistatic compression loading and stress-relaxation of PDMS and a Cu-filled-PDMS composite [Text] / D. Sonawane, S. Oberoi, P. Kumar // Polymer Testing. – 2016. – Vol. 55. – P. 173–183. doi: 10.1016/j.polymertesting.2016.08.022
25. Oberoi, S. Effect of strain rate and filler size on mechanical behavior of a Cu filled elastomer based composite [Text] / S. Oberoi, D. Sonawane, P. Kumar // Composites Science and Technology. – 2016. – Vol. 127. – P. 185–192. doi: 10.1016/j.compscitech.2016.03.006
26. Rueda, M. M. Rheology and applications of highly filled polymers: A review of current understanding [Text] / M. M. Rueda, M.-C. Auscher, R. Fulchiron, T. Perie, G. Martin, P. Sonntag, P. Cassagnau // Progress in Polymer Science. – 2017. – Vol. 66. – P. 22–53. doi: 10.1016/j.progpolymsci.2016.12.007
27. Baboo, M. Mechanical and thermal properties of composites of cis and trans-polyisoprene blends filled with Al-powder [Text] / M. Baboo, K. Sharma, N.S. Saxena // Powder Technology. – 2012. – Vol. 231. – P. 54–62. doi: 10.1016/j.powtec.2012.07.042
28. Rusu, M. Mechanical and thermal properties of zinc powder filled high density polyethylene composites [Text] / M. Rusu, N. Sofian, D. Rusu // Polymer Testing. – 2001. – Vol. 20, Issue 4. – P. 409–417. doi: 10.1016/s0142-9418(00)00051-9
29. Shalkauskas, M. Khymycheskaya metallyzatsyya plastmass [Text] / M. Shalkauskas, A. Vashkyalys. – Lenigrad: Khymyya, 1985. – 144 p.