1. Introduction

In today’s conditions of fluctuating market and consumer demands, there is a need for the creation of new high-quality products, the production of which takes minimal time and costs compared with conventional processing methods. Polymers are widely used as structural and engineering materials, mainly due to the properties that make such materials more technologically viable than metals. Polymers have high corrosion resistance, low specific weight, aesthetic appearance, etc. In recent years, such a class of structural and engineering materials is thoroughly studied and widely used in various branches of industry including such most advanced technologies as information, computer production, environment protection, etc.

However, polymer materials have a number of disadvantages that are not inherent to metals. Compared to metals, polymers have less mechanical strength, relatively low thermal stability, etc. Thus, it is logical to combine polymers and metals into materials that will have the advantages of starting materials with a minimum number of their disadvantages.
Metal-filled polymer composites as materials combining the best polymer and metal properties are characterized by a number of new properties that are absent in raw materials. Such composite materials consist of two or more components that are diametrically different in their chemical composition and are separated by a distinct polymer layer. Composite materials are heterogeneous in the microscale and homogeneous in the macroscale. Composition, form, and distribution of components of such composite materials can be predicted at the design and production stages. The properties of the final metal-filled polymer composite are in some way related to each component.

Application of the developed method for introducing a metal filler into a polymer matrix at the stage of production of a final product as a result of metallization of the surface of the initial polymeric raw material [1, 2] is interesting in terms of the possibility of obtaining high-tech materials. The obligatory stage of development of an effective technology of metallization of polymeric raw materials is the research aimed at establishing optimal composition of chemical metallization solutions. Such information is necessary for the production of products from metal-filled polymer composites characterized by advanced and predicted technological and service performance.

The principles that underlie the developed technology make it possible to obtain highly filled polymer composites. A higher content of metal in the final material can be achieved by increasing concentration of components of chemical metallization solutions. Information on the influence of concentration factors on the process of production of metallized polymeric raw materials is necessary for increasing efficiency of the developed technology of metallization of powdered polymeric raw materials and the amount of metal that can be introduced into the polymer composite.

2. Literature review and problem statement

The polymer composite materials containing metal fillers are widely used in electrotechnical [3] and electronic [4, 5] industries and as materials for technical services [6].

The presence of metal particles in the polymer matrix contributes to higher density, better thermal stability of the material based on ABS [7], low density polyethylene [8], polypropylene and high-density polyethylene [9], creates a barrier for high-frequency radiation [10] and ensures presence of magnetic properties [11]. Such materials are used as pickups and sensors [11, 12]. Introduction of metal fillers into a polymer matrix becomes more complicated in the case of use of a filler in a form of fibers, scales, or other elongated forms, however, it guarantees higher performance properties [13].

The promising field of using metal-filled polymeric composites is production of shielding materials. This is due to the ever-growing number of small size sources of electromagnetic radiation including mobile phones, tablets, laptops and other devices requiring a connection to the nets of mobile communication. Protection of such devices against electromagnetic radiation is a prerequisite for maintaining their normal operation. The problem with creating such composites is that to provide the required level of protection, a significant amount of filler material should be introduced in the polymer matrix to achieve percolation threshold [14–16]. The high concentration of filler not only increases the product weight and cost but also reduces the material manufacturability [17, 18].

The high content of filler at which the percolation phenomenon becomes achievable is primarily brought about by the peculiarities of the conductivity mechanism which is realized in the metal-filled polymeric composites. In such materials, the metal filler content has a decisive influence on the composite conductivity. At low filler content, the composite conductivity practically does not change compared with conductivity of the polymer matrix and increases with the increase in the filler content [19, 20]. At the same time, two mechanisms of realization of conductivity are possible: tunneling or percolation [21]. The tunneling mechanism consists in the transfer of electrons between individual metallic particles which is the result of the effect of tunneling electrons through a very thin insulating layer. In this case, the conductive particles remain separated in space but must be very close to each other. Percolation is the conductivity resulting from the direct physical contact between surfaces of the conductive particles. An essential condition for occurrence of the percolation phenomenon is the sufficient content of a conductive filler to form an interconnected conductive net extending through the entire composite body. When the percolation threshold is achieved, conductivity increases sharply.

In order to reduce the amount of filler needed to reach the percolation threshold, various anisotropic and elongated metal fillers have been widely studied in recent years. Reduction of the amount of copper filler required for achievement of the percolation threshold was obtained using polyacrylonitrile based foam granules [22]. Copper was chemically precipitated on such foamed pellets with their subsequent pressing. This enabled obtaining of a composite material including metal filler in a form of two-dimensional flattened ellipsoids. This filler structure provides high shielding properties to the composite. A method involving the use of solvents was used to create an effective shielding composite on the basis of polystyrene and copper nanowires. The method involves preparation of solutions of polystyrene and copper nanowires, mixing of solutions, ultrasound processing and drying [23]. Also, metal nanowires for creation of screening materials were used in [24]. An example of polyvinylidene fluoride and nanoparticles of copper [25] and aluminum [26] has shown that polymer composites have a good balance between screening power and weight and can really be competitors of metals for protection against electromagnetic radiation. Thus, we can state that the operational properties of metal-filled polymer composites depend not only on the quantity and nature but also on the form of the metal filler used.

Undoubtedly, in addition to the content and shape of the metal filler, properties of metal-filled composites are also determined by the production method. The transition to elongated filler particles can increase basic functional performance of composites only in the case of formation of a certain structure in the polymeric composite which is difficult to implement with the use of classical mixing methods. In addition, the costs of obtaining 1D and 2D fillers remain high up to now. The use of solvents and solutions in production of metal-filled composites makes it possible to cope with a number of problems. However, at present, the vast majority of publications on metal-filled composites are only focused on the study of the relationship between the properties of finite materials and the content and form of the filler. There
is no information about the effect of concentration factors on the process of forming metal fillers and the properties of materials obtained from them.

### 3. The aim and objectives of the study

This work objective was to establish the effect of concentration of components of the chemical metallization solution on the efficiency of copper deposition on the activated polymeric surface.

To achieve this objective, the following tasks were addressed:
- to study the influence of concentration of components of the chemical metallization solutions on the kinetic regularities of copper reduction on the polyvinylchloride surface mechanically activated with zinc;
- to study the peculiarities of formation of copper coating on activated powdered polyvinylchloride;
- to establish optimal concentrations of components of the chemical metallization solutions for the production of metallized powdered polyvinylchloride.

### 4. Materials and methods of the study

Suspension of powdered polyvinylchloride [27] activated with finely-dispersed zinc was used for the study.

Copper was deposited in non-stabilized chemical reduction solutions [28]. They consisted of copper sulfate, trilon B and formalin as a complexing and reducing agent. Variation of concentration of reagents in chemical metallization solutions was within the following limits (mmol/l): 48.07–192.26 for CuSO₄; 250.02–1000.08 for NaOH; 13.43–268.64 for trilon B and 366.3–1465.20 for formaldehyde.

To plot kinetic curves, experimental studies were carried out to measure the volume of hydrogen released during metallization of the activated polymeric surface in time. The process of coating activated PVC with copper was investigated using the volumetric method based on measuring the volume of gas released in chemical reaction.

The measuring device consisted of a reaction vessel, a gas burette, and a counterbalance syringe. The gas volume of the burette was connected by means of hoses to the reaction vessel and the water volume with a counterbalance syringe. The gas volume of the burette was chosen based on the maximum possible amount of hydrogen.

The volume of hydrogen formed in reduction of copper was determined by the amount of water displaced from the burette. According to the literature [28], when one mole of copper is reduced in trilon chemical metallization solutions, one mole of hydrogen is released which enables obtaining the change in copper concentration in the chemical metallization solution in time, that is, the kinetic curves of copper reduction. The presented kinetic curves are the averaged result of a series of measurements. The relative error did not exceed 2 %.

The experimental data with the highest value of validity (r=0.99, S=0.009) were approximated by the Gompertz function of the form

\[ y = a \exp(-\exp(b - cx)) \]

The given function (Gompertz Relation) was obtained in the CurveExpert 1.4 software environment.

### 5. Results obtained in the study of influence of concentration of the chemical metallization solution components on the process of copper reduction

Analyzing the possible reactions which result in reduction of copper ions in the chemical reduction solution [27]:

\[
\begin{align*}
2\text{CH}_2\text{O} + \text{Cu}^{2+} + 4\text{OH}^- & \rightarrow \\
& \rightarrow \text{Cu} \downarrow + \text{H}_2 \uparrow + 2\text{HCOO}^- + 2\text{H}_2\text{O} \quad (1) \\
\text{CuSO}_4 + \text{Zn} & \rightarrow \text{Cu} \downarrow + \text{ZnSO}_4 \quad (2)
\end{align*}
\]

it can be stated that concentration of CuSO₄ is the main concentration factor that determines the reaction rate. In this case, concentration of other reagents in the reaction (2) will not have any effect. Trilon B is another reagent that does not take part in the reaction but without which it is impossible to form a high-quality metal coating on the polymeric surface [28].

The studies of kinetics of copper reduction depending on concentration of trilon B have shown that this reagent has a significant effect on the reaction (Fig. 1).

![Fig. 1. Kinetic curves of copper reduction on activated PVC surface. Concentrations (mmol/L): 250.02 for NaOH; 48.07 for CuSO₄; 366.3 for formaldehyde. Zinc content: 15.3 wt. %](image)

Depending on concentration of the complexing agent, two groups of kinetic curves can be distinguished. They differ in the rate of copper reduction reaction. The first group was characterized by a low concentration of the complexing agent (13.43–40.30 mmol/l), the corresponding figure for the second group was (53.73–67.16 mmol/l). The kinetic curve obtained in the chemical metallization solution with concentration of the complexing agent of 47.01 mmol/l is worth of separate consideration.

Such an effect of trilon B concentration on copper reduction kinetics can obviously be explained by complexation with copper ions. Low concentrations of trilon B are not sufficient to bind all Cu²⁺ ions into a complex preventing formation of insoluble copper hydroxide in alkaline medium. The growth of trilon B concentration affects reduction of a portion of copper in a form of hydroxide (colloidal solution) and formation of true solutions.

This dependence is more pronounced for chemical metallization solutions with different contents of the complexing agent at higher pH (Fig. 2).

In this case, there is a significant relationship between concentration of the complexing agent and the amount of copper reduced by formaldehyde. At the same time, the
initial reaction rate is practically the same throughout the concentration range and does not depend on the complexing agent concentration. At up to 40.3 mmol/l of trilon B in the metallization solution, formation of insoluble copper hydroxide is observed. Its content decreases with an increase in the content of the complexing agent. It is the presence of copper hydroxide and low stability of the solution that can be attributed to the high percentage of copper reduction with formaldehyde taking part in reaction.

Fig. 2. Kinetic curves of copper reduction on activated PVC surface. Concentration (mmol/l): 562.54 for NaOH; 48.07 for CuSO₄; 366.3 for formaldehyde Zinc content: 15.3 wt. %

Like for the solutions with lower pH, the presence of insoluble copper hydroxide and a low stability of solutions contribute to the reaction of copper reduction in the solution volume. Since the metal activator firmly adheres to a polymeric surface, only the reaction of copper reduction with the use of formaldehyde is possible in the volume of chemical metallization solutions.

An increase in concentration of the complexing agent enables obtaining of stable true solutions. For such systems, reduction of copper in the solution volume is unlikely which leads to the reduction of copper on the activated polymeric surface with the participation of zinc. This, in turn, affects decrease in the amount of copper reduced by formaldehyde. It amounts about 17 % of the theoretical content.

Such a mechanism of copper reduction in true and colloidal solutions of chemical metallization is confirmed by microphotographs obtained with the help of a scanning electron microscope (Fig. 3, 4).

The point reduction of copper on a polymeric surface and the absence of a continuous metal layer can be judged from the analysis of microphotographs (Fig. 4). Besides, it is necessary to note significantly larger sizes of metal particles (agglomerates) formed in the solution volume in comparison with those reduced on the polymeric surface.

Fig. 3. Microphotographs of metallized PVC obtained in a contrast mode by the mean atomic number: metallization in a true solution (a); metallization in a colloidal solution (b)

The spectrum of the characteristic X-ray radiation of the polyvinylchloride particle surface coated with copper obtained by combination of the spectra corresponding to dark and light regions (polymer and metal) was characterized by the presence of chlorine and copper peaks (Fig. 5). The absence of zinc peaks indicates a deep interaction between zinc and copper ions during restoration of the latter.

Obviously, CuSO₄ is the main component that has the greatest influence on kinetics of copper reduction (Fig. 6, 7).
There was a direct relationship between the concentration of CuSO$_4$ in solution and the rate and the amount of copper reduced by interaction with formaldehyde. In the case of true solutions ($C_{CuSO_4}$=48.07 and 60.08 mmol/l), the rate and amount of copper reduced by formaldehyde were the smallest and respectively amounted to 15 % and 24 % of the theoretical amount of copper in the solution. As for colloidal solutions, both rate and the amount of copper reduced by formaldehyde increase. The amount of copper reduced at various CuSO$_4$ concentrations was 41 % for 80.11 mmol/l, 43 % for 90.12 mmol/l and 47 % for 100.14 mmol/l. It should be noted that virtually identical results were obtained in the case of the use of activated polyvinylchloride containing more metal activator (Fig. 7).

It is interesting that the solutions with low alkaline concentration featured a significant dependence of the induction reaction period on CuSO$_4$ concentration (Fig. 8) and practically complete absence of dependence of the amount of reduced copper on CuSO$_4$ concentration in the reaction with formaldehyde.

The increase in the induction period with increase in concentration of CuSO$_4$, can be obviously explained by the influence of copper sulfate on the magnitude of initial and especially final pH of these solutions (Table 1). As it is known [28], the rate of copper reduction in chemical metallization solutions is very sensitive to pH variations. Besides, at such concentrations of copper sulfate, solutions lose their stability and insoluble copper hydroxide is formed which also consumes a portion of alkali. It can be assumed for such conditions that the main factor controlling the copper reduction reaction is alkali concentration. Significant decrease in its content brings about termination of the reaction of copper reduction by formaldehyde.

### Table 1

<table>
<thead>
<tr>
<th>Item No.</th>
<th>CuSO$_4$ concentrations, mmol/l</th>
<th>pH of chemical metallization solutions</th>
<th>Zinc content: 15.3 wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>48.07</td>
<td>11.915</td>
<td>11.678</td>
</tr>
<tr>
<td>2</td>
<td>60.08</td>
<td>11.875</td>
<td>10.526</td>
</tr>
<tr>
<td>3</td>
<td>80.11</td>
<td>11.703</td>
<td>8.902</td>
</tr>
<tr>
<td>4</td>
<td>90.12</td>
<td>11.556</td>
<td>7.597</td>
</tr>
</tbody>
</table>

For these conditions, it results in a practically equal amount of copper reduced which is only determined by alkali.
concentration. With an increase in alkali concentration to 562.54 mmol/l, the concentration factor of alkali ceases to exist and the amount of reduced copper is determined by CuSO₄ concentration in the solution (Fig. 9).

![Graph showing the dependence of the amount of copper reduced by formaldehyde on CuSO₄ concentration.](image)

**Fig. 9.** Dependence of the amount of copper reduced by formaldehyde on CuSO₄ concentration (mmol/l); 67.16 for trilon B; 366.3 for formaldehyde. Zinc content: 15.3 wt. %

The results obtained in the studies of copper reduction kinetics in concentrated chemical metallization solutions \((C_{CuSO₄} = 100 \text{ mmol/l})\) which did not lose their stability (true transparent solutions) show that the amount of copper reduced by formaldehyde in these conditions is significant: about 46 % of total copper present in the solution. However, reduction of copper in interaction with formaldehyde occurs on the activated surface of the polymer and not in the solution volume as it occurred in the case of colloidal chemical metallization solutions.

The further proportional growth of concentration of components in the chemical metallization solution \((C_{CuSO₄} = 192 \text{ mmol/l})\) (a fourfold increase in concentration compared with the recommended [28]) showed the inexpediency of such a decision.

High concentration of components brings about loss of solution stability: copper reduction starts at a high rate even in the absence of activated polymeric surface. However, in these conditions, efficiency of the process is low as indicated by the blue color of the solution in the end of metallization.

The study of influence of change in formaldehyde concentration on kinetics of copper reduction showed that the growth of formaldehyde concentration brings about growth of the amount of copper reduced by interaction with it. In the case of low alkaline concentrations, this feature is hardly noticeable and increases with increased pH of the solution. At alkali concentration of 562.5 mmol/l, the amount of copper reduced by interaction with formaldehyde is 45 % at 1.98 mol/l versus 17 % at 0.37 mol/l of formaldehyde. This pattern persists when concentration of copper sulfate increases which is also reflected by the growth of amount of copper reduced by formaldehyde (60 % at 1.98 mol/l versus 39 % at 0.37 mol/l of formaldehyde).

6. Discussion of results of studying the influence of component concentrations in chemical metallization solutions on the process of copper reduction

Depending on concentration of trilon B, the considered features of copper reduction can be explained by the fact that a certain portion of copper ions is in a form of insoluble hydroxide and does not take part in the reduction reaction which affects the rate of reduction. In this case, it is necessary to note a fairly high volume of evolved hydrogen which indicates a significant contribution to the reaction of copper reduction with participation of formaldehyde. In these conditions, 1.4–1.5 g/l of copper is reduced which is about 49 % of theoretically available amount (3.05 g/l).

Also, the low stability of chemical reduction solutions at low concentrations of the complexing agent contributes to high efficiency of the reaction of copper reduction by formaldehyde. In these conditions, the reaction of copper reduction is possible in the solution volume and not solely on the activated polymeric surface with the participation of zinc.

At trilon B concentration of 47.01 mmol/l, the rate of copper reduction by interaction with formaldehyde and the amount of hydrogen are highest. The growth of rate of the copper reduction reaction in this case can be explained by a decrease in the amount of insoluble copper hydroxide since the molar concentration of the complexing agent is practically equal to the concentration of CuSO₄. However, a high percentage of reduced copper in reaction with formaldehyde (53.4 %) indicates solution instability and formation of optimal conditions for copper reduction in the solution volume. Under these conditions, copper hydroxide is still present in the solution which together with the high concentration of copper ions leads to an increase in the amount of copper reduced by reaction with formaldehyde.

The further increase in the amount of trilon B in the chemical metallization solutions affects preservation of the high rate of copper reduction and the decrease in the amount of copper reduced by the reaction with participation of formaldehyde. The high rate of reaction of copper reduction can be explained by complete bonding of copper ions in a complex with trilon B and absence of insoluble copper hydroxide, that is, true solutions are formed in these conditions. Also, formation of true solutions promotes a deeper reaction of copper reduction on a polymeric surface with the participation of zinc. At a level of 67.16 mmol/l of trilon B concentration in the chemical metallization solution, the portion of copper reduced with participation of formaldehyde decreases to 39 %.

The analysis of microphotographs of polyvinylchloride metallized in a colloidal solution showed a significant amount of copper agglomerates formed in the solution volume. The following mechanism of agglomerate formation can be suggested: insoluble particles of copper hydroxide present in a colloidal solution of chemical copper coating can act as the nucleation center of copper reduction in the solution volume. Reduction of copper in such centers is only possible by interaction with formaldehyde. It is confirmed by a significant amount of hydrogen.

It should also be noted that in the spectrum of characteristic X-ray radiation of polyvinylchloride coated with copper, there are no peaks corresponding to oxygen. This phenomenon was noticed by other researchers and is explained by the use of trilon B as a complexing agent. It is responsible for the absence of copper passivation [28].

The influence of CuSO₄ concentration in the chemical metallization solutions on the process of copper reduction on the activated polyvinylchloride surface can be explained (as in previous cases) by the loss of solution stability and reduction of a significant amount of copper in the solution volume. This is additionally confirmed by the absence of decrease in the amount of copper reduced by interaction with formaldehyde when the content of the metal activator increases which takes place when using true solutions [27].
When analyzing the dependence of the amount of copper reduced by formaldehyde on the concentration of copper sulfate, it should also be noted that in the case of using higher alkali concentrations and true solutions (CuSO₄ concentration of 48.60 mmol/L), the copper reduction mechanism is different. Less volumes of evolved hydrogen (correspondingly, less copper reduced by formaldehyde) indicate that most of copper is reduced under these conditions as a result of interaction with zinc. Obviously, the higher pH values of the solutions contribute to this reaction.

The regularities of influence of formaldehyde concentration on kinetics of copper reduction can be explained by the growth of formaldehyde concentration which contributes to the reaction. It should also be noted that this feature becomes more noticeable only at higher pH values of the solution. In this case, high pH values probably contribute to the reaction of copper reduction with the use of formaldehyde which does not occur in solutions with a low alkaline concentration.

Information on the effect of concentration factors on the process of metallization of powdered polyvinylchloride is a prerequisite for the production of metal-containing polymeric raw materials which can be used to create high-tech metal-filled composites. The logical continuation of these studies will be a determination of dependence of the properties of final metal-filled polymer composites on the technological parameters of their obtaining including concentration. Such information will enable development of a highly efficient technology for the production of metal-filled polymer composites with properties adjustable at the design stage.

7. Conclusions

1. The influence of concentration factors on the regularities of copper reduction in solutions of chemical metallization on mechanically activated powdered polyvinylchloride has been investigated. It was established that the main condition for optimization of the composition of chemical metallization solutions is ensuring formation of copper coating on the activated polymeric surface and not in the solution volume. It was shown that obtaining of high-quality metallized polymeric raw materials is only possible in the true chemical metallization solutions. An increase in the concentration of components of the chemical metallization solutions results in the loss of solution stability and the formation of ineffective colloidal solutions. The concentration of components of the chemical metallization solution which guarantees production of high-quality metallized polymeric raw materials is as follows (mmol/L): ≈100 for CuSO₄; ≈560 for NaOH; ≈140 for trilon B, and ≈370 for formaldehyde.

2. It was found that in the case of formation of true solutions, the amount of copper reduced by interaction with formaldehyde is insignificant and the bulk of copper is reduced in the exchange reaction with zinc. The condition of existence of true solutions is the higher molar concentration of trilon B compared with the molar concentration of CuSO₄. In these conditions, the complete binding of copper ions in a complex with trilon B occurs. It was shown that the growth of trilon B concentration from 47.01 mmol/L to 67.16 mmol/L results in a reduction of the amount of copper reduced by formaldehyde from 53.4 % to 39 %.

3. The composition of chemical metallization solutions that provides copper reduction on the activated polymeric surface at a high rate and efficiency can be considered optimal. The amount of metal on a metallized polymeric surface can be controlled by changing concentration of reagents in the chemical metallization solutions which makes it possible to produce metallized powdered polyvinylchloride suitable for obtaining metal-filled composites. It was established that the limiting concentration of CuSO₄ in the chemical metallization solution is 190 mmol/L and its further increase is inappropriate.

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