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PECULIARITIES OF METALLIZATION OF POLYVINYL CHLORIDE GRANULES

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The results of experimental studies of copper plating of polyvinyl chloride granules in a chemical precipitation solution are presented. The influence of the surface area of polyvinyl chloride granules on the kinetic regularities of copper reduction and the copper content on metallized granules has been studied. It is established that the surface area of polyvinyl chloride granules has a significant effect on the rate of reduction of copper ions and does not affect the amount of reduced copper. The thickness of the layer of the obtained copper shell on polyvinyl chloride granules of different sizes depending on the metal content is calculated.
Key words: polyvinyl chloride, granules, chemical metallization, copper, shell.

Introduction

The main task of modern science is to create new materials and develop on their basis composites with multifunctional properties for the needs of technology. Along with this, a theoretical substantiation of purposeful search and an explanation of the relationship composition-structure-properties-function of new materials is necessary. Polymer composite materials have wide practical use in various fields and elements of mechanical and instrument making [1, 2], which is caused by a set of valuable properties, such as high strength, chemical resistance, increased thermal and electrical insulating properties, ability to form into products without large costs for high-performance equipment, reliability in operation.

Improving the technological and operational properties of polymer composite materials is mainly achieved when the filler has increased technological compatibility with the polymer matrix [3–6]. In addition, the form of the filler also plays a significant role in the obtained materials of the required quality [7-9].

Metals can be considered as promising fillers for the creation of new polymer composites. The presence of metal particles in the polymer matrix contributes to a higher density, better thermal stability of composite materials, creates a barrier to high-frequency radiation [2] and ensures the presence of magnetic properties [10]. Metal-filled materials are used as sensors and sensors, it is also promising to use such material as highly efficient heat storage systems [11].

Materials and methods of the study

Polyvinyl chloride granules were used for research DANVIL® RST 5635 (Padana Chemical Compounds LLC). Before metallization, the polyvinyl chloride granules were activated with fine zinc [12]. For activation used a laboratory ball mill in which was loaded ceramic grinding bodies, granules of polyvinyl chloride and fine zinc. The speed of rotation of the mill is 125 rpm, the weight of the loaded polyvinyl chloride is 200 g, the fine zinc is 20 g, the weight of the grinding bodies is 1.5 kg, the processing time is 1 hour.

Regularities of reduction of copper ions on activated polyvinyl chloride granules were investigated by volumetric method by the amount of released hydrogen [13, 14]. For copper plating used a solution of chemical precipitation of the following composition (mmol/l): $CuSO_4 \cdot 5H_2O$ – 60, EDTA-Na_2 ($C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$) – 67, NaOH – 375, formalin – 366. When studying the patterns of metallization in all cases used the same initial mass of granules of polyvinyl chloride (20 g).

The metal content on the copper granules of polyvinyl chloride was set as follows. A portion of the copper granules of polyvinyl chloride was weighed to the nearest 0.00005 g, treated with 50%

nitric acid for 5 min, washed, dried to constant weight and weighed again. The percentage of copper on the granules of polyvinyl chloride was calculated by the difference in weight of the granules before and after etching in acid.

Results of the studies and their discussion

There are a large number of technologies that allow the introduction of a metal filler in the polymer matrix, each of which has both advantages and disadvantages [15, 16]. We proposed to introduce the metal into the polymer matrix due to the preliminary metallization of the polymer particles. The result of metallization is to obtain a layer of metal on the polymer surface. The metal layer on the polymer surface is obtained as a result of chemical reduction of metal ions in a solution of chemical deposition [17]. Such polymeric raw materials, in the form of granules, with a metal shell formed on them can be directly processed into products. Thus, the introduction of metal into the polymer matrix will occur as a result of the destruction of the metal shell during the viscous flow of the molten polymer or its deformation. The proposed technology involves the use of different polymers, which requires research to study the patterns of their metallization. Such information is necessary for development of the recommendation and technological conditions of carrying out metallization processes in the controlled conditions that will allow to receive metallized polymeric raw materials of necessary quality.

Obviously, one of the main factors influencing the metallization process in the proposed technology is the area of the activated polymer surface in contact with the chemical deposition solution and on which the metal is reduced. In turn, the surface area of the granules depends on their size.

To study the effect of surface area, polyvinyl chloride granules were used in their original form and after their division into two and four parts (Fig. 1).

The established kinetic regularities of metallization of granules of different area showed that the rate of reduction of copper ions largely depends on their initial size (Fig. 2).

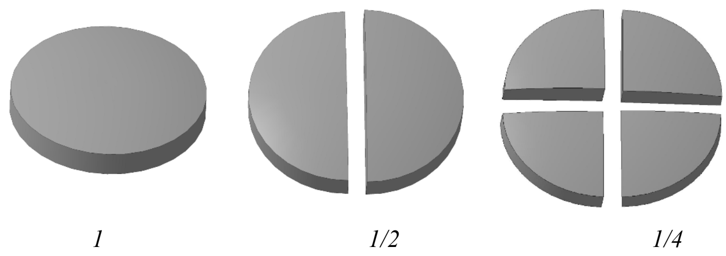

Fig. 1. The scheme of obtaining granules with different initial surface area

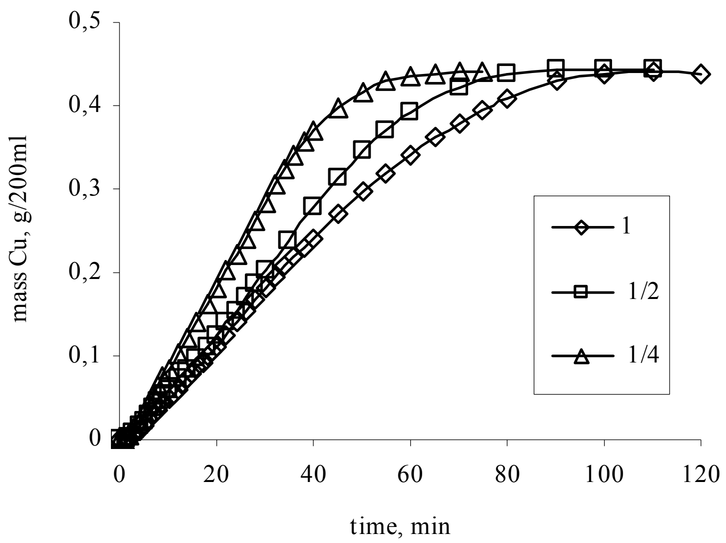

Fig. 2. Kinetic regularities of reduction of copper ions on granules of different size

Since, in all cases, the same initial mass of polymer was used for metallization, it is obvious that the area of the metallized surface increases with a decrease in the size of the granules. It is the increase in the area in contact with the chemical deposition solution and on which the interaction between the reagents takes place that can explain the increase in the rate of reduction of copper ions on the surface of the granules with a decrease in their size.

The used technology of metallization of polymer granules is offered as one of the stages of creation of metal-filled composites, therefore it was of interest to investigate the possibility of obtaining materials with different metal content. The use of a solution of chemical metallization allows to deposit on the polymer surface only a certain amount of metal, because increasing the concentration of salt from which the reduction of the metal above the limit value leads to a loss of stability of the solution. An increase in the amount of metal on the surface of the metallized granules can be achieved either by reducing the amount of polymer that is metallized or by re-metallization.

The study of the kinetics of reduction of copper ions on PVC granules and their re-metallization (Fig. 3) shows that both in the case of the first metallization of zinc-activated granules and re-metallization, the process rate remains high.

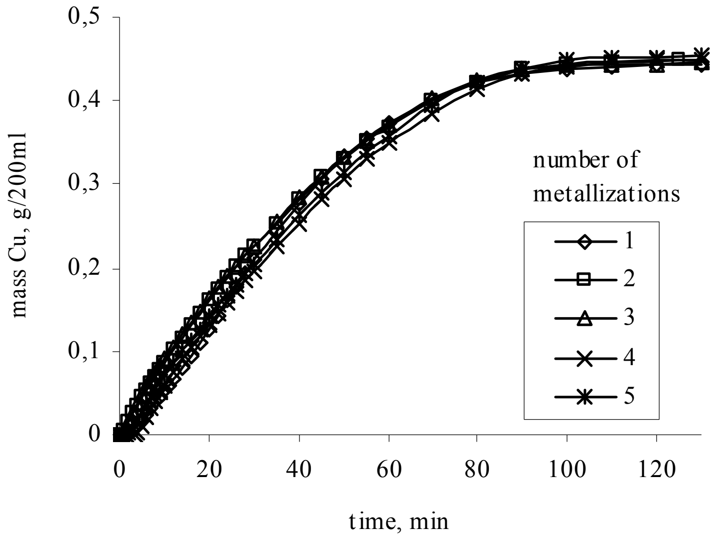

Fig. 3. Influence of the number of metallizations on the kinetic curves of reduction of copper ions on the surface of the original granules of polyvinyl chloride

It should be noted that in the case of re-metallization of the catalytically active metal in the reduction reaction of copper ions from a solution of chemical deposition is pre-precipitated copper and it was possible to expect differences in the rate of the reduction reaction. However, as we see, there is no significant difference in the rate of metallization of both raw materials and subsequent metallizations. The obtained values of the kinetic curves lie within the error of the experiment.

Examining the amount of metal that can be obtained on polyvinyl chloride granules by the method of repeated metallizations showed that the efficiency of copper reduction remains high (Fig. 4) and such a method is justified for obtaining highly filled composites.

It should also be noted that the use of granules of different sizes does not affect the content of metal deposited on them (Fig. 5), which is logical, because the use of the proposed solution of chemical deposition allows to deposit almost all theoretically possible amounts of copper.

The use of granules of different initial sizes will also affect the characteristics of the metal layer obtained on their surface, in particular, its thickness. Since, when using granules of smaller size, the total surface area to be metallized will increase, it is clear that the thickness of the metal layer on such granules will be smaller compared to larger granules (Fig. 6).

Since the polyvinyl chloride granules used for research have a simple geometric shape, which is as close as possible to the shape of the disk, it allowed to measure the geometric dimensions of a large sample of granules (500 pcs), to calculate the geometric dimensions of the average granule. The following 3D modeling established the surface area (S_{on}) of the initial granule and the granules obtained by its separation (Table).

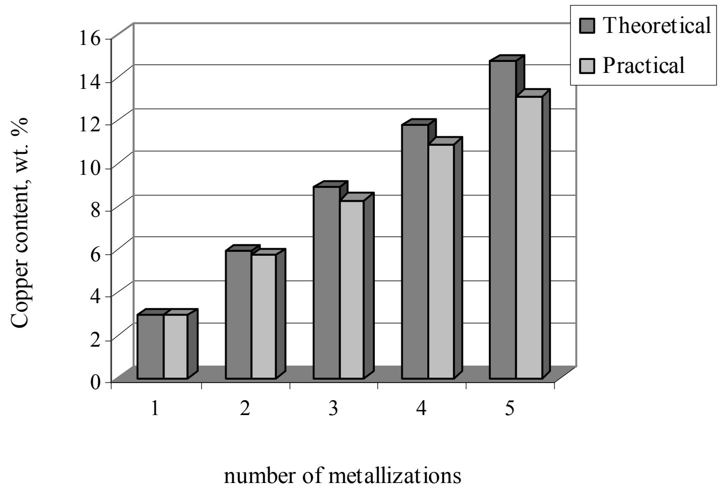

Fig. 4. The dependence of the content of copper deposited on the original granules of polyvinyl chloride on the number of metallizations

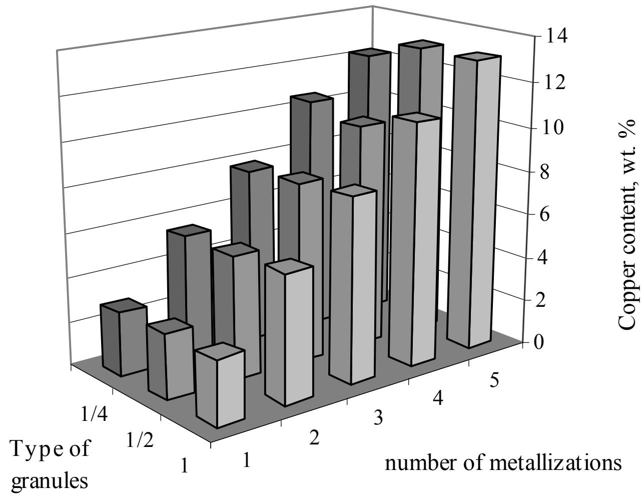

Fig. 5. The dependence of the content of precipitated copper on the size of the granules of polyvinyl chloride and the number of metallizations

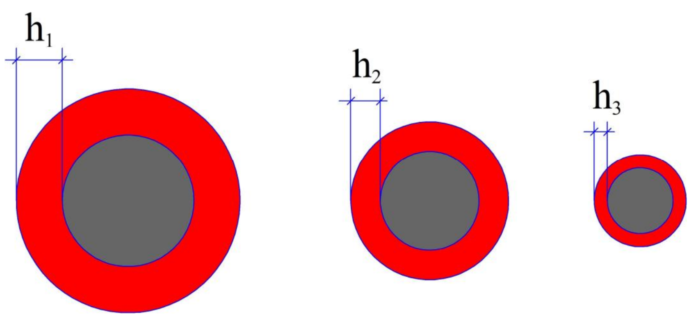

Fig. 6. Reducing the thickness of the metal shell while reducing the size of the granules $h_1 > h_2 > h_3$

Characteristics of metallized granules of polyvinyl chloride

Type of granules	Number of metallizations	S_{on}, mm^2	m_{aver}, g	N_{gr}, pcs	S_{total}, m^2	Copper content, wt.%	V_{Cu}, cm^3	$h \cdot 10^3$, mm
1	1	99.88	0.072	278	0.028	2.9	0.07	2.41
	2					5.7	0.13	4.82
	3					8.3	0.20	7.24
	4					10.9	0.27	9.85
	5					13.1	0.34	12.14
1/2	1	63.26	0.035	572	0.036	2.9	0.07	1.85
	2					5.6	0.13	3.67
	3					8.1	0.20	5.46
	4					10.1	0.25	6.94
	5					13.1	0.34	9.31
1/4	1	38.29	0.017	1177	0.045	2.9	0.07	1.49
	2					5.6	0.13	2.95
	3					7.9	0.19	4.26
	4					10.6	0.26	5.87
	5					12.3	0.31	6.96

Given that the mass of the metal deposited on the granules depending on the number of metallizations and the size of the granules, as well as the initial surface area of the granules, it becomes possible to estimate the thickness of the metal layer deposited on the polymer granules of different sizes. The values of the average weight of one granule (m_{aver}), depending on the initial size, are given in the table. Given that in all cases the same mass of polymer was used for metallization, it is possible to calculate the number of granules is 20 g of PVC (N_{gr}). Knowing the initial area of one granule of each size, we calculate the surface area of all granules used for metallization (S_{total}).

The thickness of the metal layer on the granules was calculated for the following reasons. Since the obtained metallized granules are characterized by the formation of a continuous coating, we assume that its thickness is the same over the entire surface of the granule. Taking into account the density of copper (8.96 g/cm^3) and its content on the granules, the volume of reduced copper (V_{Cu}) can be calculated. This volume, as suggested above, is evenly distributed over the entire surface of the metallized granules, which allows you to calculate the thickness of the copper layer (h).

Analyzing the obtained results, it can be noted that at almost the same copper content on the PVC granules the thickness of the copper layer is significantly different. It is clear that the properties of composites obtained by processing such raw materials will be different, which can be used to obtain materials with different properties.

Conclusions

Thus, the studies allow us to establish that the characteristics of the obtained metallized granules of polyvinyl chloride can be largely controlled by the size of the initial granules and the number of metallizations. It is established that the speed of the metallization process of polyvinyl chloride granules significantly depends on the initial size of the granules used and does not depend on the number of previous metallizations. The proposed method of re-metallization allows to obtain highly filled polymer composites, and its combination with the use of granules of different sizes to obtain raw materials of the required quality with predetermined and controlled properties.

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ОСОБЛИВОСТІ МЕТАЛІЗАЦІЇ ГРАНУЛ ПОЛІВІНІЛХЛОРИДУ

Наведено результати експериментальних досліджень міднення гранул полівінілхлориду в розчині хімічного осадження. Досліджено вплив площі поверхні гранул полівінілхлориду на кінетичні закономірності відновлення міді і вміст міді на металізованих гранулах. Встановлено, що площа поверхні гранул полівінілхлориду має значний вплив на швидкість відновлення іонів міді і ніяк не впливає на кількість відновленої міді. Розраховано товщину шару одержаної мідної оболонки на гранулах полівінілхлориду різного розміру залежно від вмісту металу.

Ключові слова: полівінілхлорид, гранули, хімічна металізація, мідь, оболонка.