Vol. 6, No. 1, 2023

**A. M. Kucherenko[1], I. Gajdos[2], M. Y. Kuznetsova[3], V. S. Moravskyi[1]**
[1] Lviv Polytechnic National University, Department of chemical technology of plastics processing,
[2] Technical University of Kosice, Department of Technologies, Materials and Computer Aided Production,
[3] Lviv Polytechnic National University, Department of heat engineering and thermal and nuclear power plants
volodymyr.s.moravskyi@lpnu.ua

# CHECKING THE POSSIBILITIES OF THE CLASSIC TECHNOLOGY OF CHEMICAL METALIZATION OF POLYMER GRANULES

https://doi.org/10.23939/ctas2023.01.148

**The possibility of obtaining metallized granules of high-tonnage polymers using classical metallization technology was studied. It is shown that this technology is not effective during the metallization of polyethylene and polypropylene. Certain positive points during metallization were achieved only in the case of polyvinyl chloride granules. It was established that the treatment of granules with etching agents of different nature does not lead to a significant change in surface properties, which can explain the low efficiency of classical technology during the metallization of polyethylene, polypropylene and polyvinyl chloride granules.**

**Key words: metallization; copper; surface tension; polyethylene; polypropylene; polyvinyl chloride.**

## Introduction

Polymer composites as a basis for creating modern structural materials have significant prospects. This is caused by the possibility of combining in one material high strength, low weight and a number of unique and specific properties, which creates conditions for their possible use and implementation in various and very wide areas of application. In particular, already now, such materials are used in medicine, space, aviation and defense industries. Polymer composite materials with dielectric fillers have good heat-conducting properties, which allows them to be used in heat removal and dissipation systems [1–3]. Research conducted with a polymer composite containing a filler based on graphene and silver showed that high values of thermal conductivity of the material can be achieved even with a filler content of 15 % [4]. The use of new fillers based on biofibers makes it possible to obtain composite materials characterized by higher mechanical properties compared to conventional materials [5, 6] and good tribotechnical properties [7]. Polymer composites can be used as a new generation of materials with shape memory [8]. Wood flour [9], marble dust [10], and graphene oxide [11] are considered promising fillers in polymer composite materials. polyoxometalates, metals organic-frameworks, perovskites and metal oxides [12].

**Purpose of the work** is to check the possibility of using the classic technology of chemical metalization of polymer granules for their further processing into products.

Among the considered composite materials, metal-filled polymer composites also have a significant perspective. Such materials combine the low mass of the polymer matrix with the plastic and strength properties of metals, which allows their use as a light and highly efficient material for industrial use [13–15]. The combination of a low-density polymer matrix with plastic and strong metals makes it possible to obtain a composite material with flexibility and increased mechanical properties of the resulting hybrid structure, which is impossible for individual components. However, obtaining metal-filled composites with predictable mechanical properties using traditional production methods is a complex technological task. This is caused by the difficulty of controlling the distribution of the filler in the polymer matrix and the low interfacial interaction between the system components. In metal-filled polymer composites, the distribution boundary between the metal and the polymer matrix, as a rule, determines the mechanical properties of the resulting hybrid structure. Accordingly, the development of new methods of introducing a metal filler into a polymer matrix with the possibility of a predictable effect on the final mechanical properties of the material is an urgent task.

We are developing a technology for the production of metal-filled polymer composites, the basis of which is the production of metallized polymer granules and their subsequent processing into products [16–19]. At the same time, the introduction and uniform distribution of metal in the polymer matrix is ensured as a result of processes that are not used in traditional industrial methods.

## Materials and research methods

In order to obtain metallized polymer raw materials, it was decided to use the classic technology of polymer metallization. This technology has long been and successfully used to apply a metal layer on a polymer surface, however, the number of polymers that are used for metallization on an industrial scale is insignificant and does not include a number of high-strength polymers. During the development of the scheme of metallization of polymer raw materials, the multi-stage nature of the classical technology was taken into account, which includes the stages of surface degreasing, its etching, sensitization, activation and the stage of metal deposition itself. Polymer raw materials used for research were high-tonnage granulated polymers: polyethylene (PE), polypropylene (PP) and rigid polyvinyl chloride (PVC).

According to the classic technology of metallization, at the first stage, it is necessary to clean and degrease the polymer surface with ethyl alcohol. The residence time of polymer granules during mixing in ethyl alcohol was 30 minutes. After degreasing, the polymer granules were dried and used for etching in order to change the structure of the polymer surface. $CCl_4$, chromium mixture and boiling concentrated $HNO_3$ were used as etching agents. The etching time in $CCl_4$ was 30 min, in chromium mixture and nitric acid – 10 min. The etched polymer granules were washed polymer granules were washed with distilled water and dried. The next stage was sensitization, which consists in processing the granules obtained as a result of previous manipulations in an acidic tin chloride solution (50 g/l $SnCl_2{\cdot}2H_2O$ and 50 ml/l HCl) with stirring for 2 minutes. After soluble sensitization, the polymer granules were immediately washed with hot distilled water and transferred to the activation solution. An ammonia solution of silver nitrate (2 g/l $AgNO_3$ and 20 ml/l $NH_{3(25\%)}$) was used as the activation solution. The stay time of the polymer granules in the activation solution was 5 min. After sensitization and activation of the surface of the polymer granules, they were dried again. The final stage was the metallization of activated polymer granules in a solution of chemical precipitation, which consisted of $CuSO_4{\cdot}5H_2O$(12 g/l), EDTA-$Na_2$ (25 g/l), NaOH (10 g/l), formalin (25 ml/l).

The efficiency of metallization of polymer granules was calculated as the ratio of copper deposited on them to the theoretical content that can be obtained on polymer granules in the case of recovery of all copper ions that were introduced into the chemical deposition solution. The amount of copper deposited on the polymer granules was determined by the difference in mass of the granules after metallization and after their treatment in nitric acid in order to dissolve the deposited copper.

## Results and discussion

The obtained results of metallization of the surface of the granules of the used polymers according to the classical technology showed its low efficiency. When carbon tetrachloride was used as an etching agent, it was possible to obtain an almost continuous copper coating on the surface of all granules only for rigid PVC (Fig. 1). In the case of PE and PP, it was possible to form a copper coating only on a small amount of granules, while the resulting coating is not continuous and does not cover the entire surface of the granules.


*PVC* *PE* *PP*

*Fig. 1. Photographs of polymer granules after metallization using classical technology. The pickling agent is carbon tetrachloride*

The use of a more aggressive solution as an etching agent, namely, a chromium mixture, also did not show a positive effect, and, on the contrary, even during the metallization of rigid PVC, it was not possible to obtain a continuous copper coating. In this case, the use of a chromium mixture affected the deposited copper on the polymer surface in the form of a loose metal layer that does not cover the entire surface of the granules (Fig. 2). The copper coating formed on the granules of rigid PVC interacts weakly with the surface of the granules and is easily separated from it in the form of powder. Etching of PE and PP granules in a chromium mixture also did not allow obtaining a continuous copper coating on all granules, and also, in this case, copper deposition on the polymer surface occurs in the form of a loose layer of metal.

The use of boiling concentrated nitric acid for etching the surface of the proposed polymers also did not allow obtaining polymer granules with the required characteristics. In the case of PE and PP, the copper coating is formed only on a small number of granules, with the impossibility of obtaining a continuous coating on the entire surface of the granules (Fig. 3). The copper coating formed on hard PVC granules, as in the case of the chrome mixture, is loose and easily separated from the polymer surface.

Certain differences in the effect of the etching agent on the result of the metallization of the proposed polymers according to the classical technology can be explained by the different chemical structure of the macrochains. All considered polymers are chemically stable materials that are difficult to surface modification. And for successful metallization, it is necessary to give the polymer surface a certain structure (etching) and ensure hydrophilic properties (sensitization). The hydrophilicity of the polymer surface guarantees good wettability of the surface with aqueous chemical deposition solutions.


*PVC* *PE* *PP*

*Fig. 2. Photographs of polymer granules after metallization using classical technology. The pickling agent is a chromium mixture*


*PVC* *PE* *PP*

*Fig. 3. Photographs of polymer granules after metallization using classical technology. The pickling agent is $HNO_3$*

In the classical technology of metallization, the stage of etching and sensitization corresponds to the change of the structure and rendering the surface hydrophilic. As a result of sensitization, tin hydroxides are formed on the polymer surface. The next stage of activation only saturates the surface of the polymer with catalytically active centers. Thus, it can be stated that the nature of the etching agent will have a significant effect on the obtained structure of the polymer surface and on the next stage of sensitization, and therefore on the hydrophobicity of the polymer surface.

In order to investigate the influence of the nature of the used etching agent on the hydrophobic properties of polymers before their chemical metallization, a study was conducted to determine the change in the marginal wetting angle of the polymer surface (Table 1). In Fig. 4 shows the change in the marginal angle of wetting on the example of polyethylene.

Analyzing the data shown in Table 1, it can be stated that as a result of preparatory operations before chemical metallization, the hydrophilicity of the polymer surface changes insignificantly and in any case remains low.

Thus, on the basis of the conducted research, it can be concluded that precisely due to the combination of the complexity of changing the structure and the hydrophobicity of the surface of the used polymers, it was not possible to obtain a copper layer of satisfactory quality on the polymer granules using the classic metallization technology.

In the case of polyvinyl chloride granules, certain positive points in the metallization results can be explained by the polarity of the polyvinyl chloride macromolecule and, as a result, possibly better adsorption of catalytically active ions at the activation stage.

It is also necessary to note the low efficiency of using classical technology for the purpose of metallization of the proposed types of polymers (Table 2). At the same time, it can be noted that during the metallization process, copper ions are fully recovered from the chemical reduction solution, which is indicated by the discoloration of the solution at the end of the metallization process (Fig. 5).

*without pickling agent* *$CCl_4$* *chromium mixture* *$HNO_3$*

*Fig. 4. Influence of the nature of the etching agent on the marginal wetting angle of the polyethylene surface*

*Table 1*

**The value of the marginal wetting angle of the polymer surface**

| No. | Pickling Agent | Polymer | | |
|---|---|---|---|---|
| | | PVC | PE | PP |
| 1 | – | 84.4 | 90.8 | 81.7 |
| 2 | $CCl_4$ | 68,5 | 89.3 | 86.9 |
| 3 | chromium mixture | 71.1 | 82.8 | 77.4 |
| 4 | $HNO_3$ | 72.2 | 89.1 | 75.0 |

*Table 2*

**The effectiveness of the metallization of polymer granules depending on the nature of the etching agent (mass %)**

| No. | Pickling Agent | Polymer | | |
|---|---|---|---|---|
| | | PVC | PE | PP |
| 1 | $CCl_4$ | 35.8 | 22.3 | 19.0 |
| 2 | chromium mixture | 31.2 | 13.8 | 15.9 |
| 3 | $HNO_3$ | 26.1 | 15.9 | 13.3 |

*a* *b* *c* *d*

*Fig. 5. Photographs of the chemical metallization solution corresponding to various stages of the metallization process of polyethylene granules: a – initial solution; b – solution corresponding to the beginning of the process of metallization and washing of active centers; c – solution corresponding to the recovery of copper ions in the volume of the solution; d – solution after the end of metallization*

The low efficiency of the process of chemical metallization of polymer granules with complete reduction of copper ions can be explained by the fact that the vast majority of active centers that are formed on the polymer surface at the stage of activation, as a result of its high hydrophobicity, are easily washed off it and pass into the volume of the solution. The result of such washing is that only a small number of active centers remain on the polymer surface, which catalyze the process of recovery of copper ions on the granules, and the main amount of copper ions is recovered in the volume of the solution on the washed active centers. As a result, during the metallization of polymer granules according to the classical technology, most of the copper ions, which do not interact with the polymer surface, are recovered in the volume of the solution. This feature of the recovery of copper ions in the volume of the solution is well illustrated by the photographs of the chemical metallization solution at various stages of the process (Fig. 5).

After the beginning of the metallization process (which is evidenced by the release of gas on the polymer granules), there is a rapid clouding and a change in the color of the solution to a brown color, which indicates the recovery of copper ions in the volume of the solution. At the final stage, the agglomeration of the copper particles recovered in the volume of the solution takes place among themselves and their precipitation.

Somewhat higher values of the efficiency of metallization of PVC granules compared to other polymers when all etching media are used are probably caused by the lower value of the washout of active centers in the chemical metallization solution due to their stronger interaction with the surface, which was noted above.

## Conclusions

Thus, on the basis of the obtained results, the low efficiency and fundamental unsuitability of the classic metallization technology for the formation of copper coating on polyethylene, polypropylene and hard polyvinyl chloride granules and the subsequent production of metal-containing composites using the proposed technology have been established. In addition, the classic technology of metallization is characterized by multi-stages, the need to use precious metals, volatile and aggressive environments, and also requires repeated washing and drying of polymer granules.

## References

1. Wang, L., Yang, C., Wang, X., Shen, J., Sun, W., Wang, J., Yang, G., Cheng, Y., Wang, Z. (2023). Advances in polymers and composite dielectrics for thermal transport and high-temperature applications. *Composites Part A: Applied Science and Manufacturing*, 164, 107320. https://doi.org/10.1016/j.compositesa.2022.107320.

2. Kim, K., Ju, H., Kim, J. (2016). Filler orientation of boron nitride composite via external electric field for thermal conductivity enhancement. *Ceramics International*, 42:7, 8657–8663. https://doi.org/10.1016/j.ceramint.2016. 02.098.

3. Wei, Z., Xie, W., Ge, B., Zhang, Z., Yang, W., Xia. H., Wang, B., Jin, H., Gao, N., Shi, Z. (2020). Enhanced thermal conductivity of epoxy composites by constructing aluminum nitride honeycomb reinforcements. *Composites Science and Technology*, 199, 108304. https://doi.org/10.1016/j.compscitech.2020.108304.

4. Guo, H., Hu, B., Wang, Q., Liu, J., Li, M., Li, B. (2023). Horizontally aligned graphene/silver heterostructure for anisotropically highly thermoconductive polymer-based composites by stress-induced assembly. *Applied Surface Science*, 615, 156404. https://doi.org/10.1016/j.apsusc. 2023.156404.

5. Dharani, K. S., Aravindh, M., Manoj, V. K., Madhumithra, C., Kaviya, P., Yaswanth, S. (2023). Fracture toughness of bio-fiber reinforced polymer composites- a review. Materials Today: Proceedings. https://doi.org/10.1016/ j.matpr.2023.01.334.

6. Arun, R. R., Gautham, V., Mavinkere, R. S., Suchart, S. (2023). 5 – Physical modification of cellulose fiber surfaces, Ed: R. ArunRamnath, Mavinkere Rangappa Sanjay, Suchart Siengchin, Vincenzo Fiore. In Woodhead Publishing Series in Composites Science and Engineering, Cellulose Fibre Reinforced Composites, Woodhead Publishing. https://doi.org/ 10.1016/ B978-0-323-90125-3.00016-1.

7. Yadav, V., Singh, S., Chaudhary, N., Garg, M. P., Sharma, S., Kumar, A., Li, C., Eldin, E. M. (2023). Dry sliding wear characteristics of natural fibre reinforced polylactic acid composites for engineering applications: Fabrication, properties and characterizations. *Journal of Materials Research and Technology*, 23, 1189–1203. https://doi.org/10.1016/j.jmrt.2023.01.006.

8. Tan. Q., Li, F., Liu, L., Liu, Y., Leng, J. (2023). Effects of vacuum thermal cycling, ultraviolet radiation and atomic oxygen on the mechanical properties of carbon fiber/epoxy shape memory polymer composite. *Polymer Testing*, 118, 107915. https://doi.org/10.1016/j. polymertesting.2022.107915.

9. Jithin, K. F., Thankachan, T. P., Mathew, J., Mervin, J. T., Kurian, J. (2023). Investigations on mechanical properties of wood composite for sustainable manufacturing. *Materials Today: Proceedings*, 72:6, 3111–3115. https://doi.org/10.1016/j.matpr.2022.09.428.

10. Upadhyay, P., Rajput, V., Rajput, P. S., Mishra, V., KhanI, A., Jha, A., Agrawal, A. (2023). Physical, mechanical and sliding wear behaviour of epoxy composites filled with micro-sized marble dust composites. *Materials Today: Proceedings.* https://doi.org/10.1016/ j.matpr.2023.01.276.

11. Fu, X., Lin, J., Liang, Z., Yao. R., Wu, W., Fang, Z., Zou, W., Wu, Z., Ning, H., Peng, J. (2023). Graphene oxide as a promising nanofiller for polymer composite. *Surfaces and Interfaces*, 37, 102747. https://doi.org/10.1016/j.surfin. 2023.102747.

12. Benltifa, M., Brahmi, C., Dumur, F., Limousy, L., Bousselmi, L., Lalevée, J. (2022). A comparison study of the photocatalytic efficiency of different developed photocatalysts/polymer composites. *European Polymer Journal*, 181, 111660. https://doi.org/10.1016/j.eurpolymj.2022.111660.

13. Kim, K. J., Rhee, M. H., Choi, B. I. (2009). Development of application technique of aluminum sandwich sheets for automotive hood. *Int. J. Precis. Eng. Manuf,* 10, 71–75. https://doi.org/10.1007/s12541-009-0073-5.

14. Sun, G., Chen, D., Zhu, G., Li, Q. (2022). Lightweight hybrid materials and structures for energy absorption: A state-of-the-art review and outlook. *Thin-Walled Structures*, 172, 108760. https://doi.org/10.1016/ j.tws.2021.108760.

15. Pokkalla, D. K., Hassen, A. A., Nuttall, D., Tsiamis, N., Rencheck, M. L., Kumar, V., Nandwana, P., Joslin, C. B., Blanchard, P., Tamhankar, S. L., Maloney, P., Kunc, V., Kim, S. (2023). A novel additive manufacturing compression overmolding process for hybrid metal polymer composite structures. *Additive Manufacturing Letters*, 5, 100128. https://doi.org/10.1016/j.addlet.2023.100128.

16. Kucherenko, A. N., Mankevych, S. O., Kuznetsova, M. Ya., Moravskyi, V. S. (2020). Peculiarities of metalization of pulled polyethylene. *Chemistry, technology and application of substances*, 3:2, 140–145. https://doi.org/10.23939/ctas2020.02.140.

17. Kucherenko, A., Dovha, Y., Kuznetsova, M., Moravskyi, V. (2022). Analysis of processes which occur during the destruction of a copper shell formed on polyethylene granules. *Chemistry, technology and application of substances*, 5:1, 186–192. https://doi.org/10.23939/ctas2022.01.186.

18. Moravskyi, V., Kucherenko, A., Kuznetsova, M., Dulebova, L., Spišák, E. (2022). Obtainment and characterization of metal-coated polyethylene granules asabasis for the developmen to fheatstorage systems. *Polymers*, 14:1, 218. https://doi.org/10.3390/ polym14010218**.**

19. Moravskyi, V., Kucherenko. A., Kuznetsova, M., Dulebova, L., Spišák, E., Majerníková, J. (2020). Utilization of Polypropylene in the Production of Metal-Filled Polymer Composites: Development and Characteristics. *Materials*, 13, 2856. https://doi.org/10.3390/ma13122856.

**А. М. Кучеренко[1], І. Гайдос[2], М. Я. Кузнецова[3], В. С. Моравський[1]**

[1] Національний університет "Львівська політехніка", кафедра хімічної технології переробки пластмас,
[2] Технічний університет в Кошице, кафедра технологій, матеріалознавства та автоматизованого виробництва,
[3] Національний університет "Львівська політехніка", кафедра теплоенергетики, теплових та атомних електричних станцій

## ПЕРЕВІРКА МОЖЛИВОСТЕЙ КЛАСИЧНОЇ ТЕХНОЛОГІЇ ХІМІЧНОЇ МЕТАЛІЗАЦІЇ ГРАНУЛ ПОЛІМЕРІВ

**Досліджено можливість одержання металізованих гранул високотонажних полімерів із використанням класичної технології металізації. Показано, що дана технологія є не ефективною під час металізації поліетилену і поліпропілену. Певні позитивні моменти під час металізації вдалося досягти лише у випадку полівінілхлоридних гранул. Встановлено, що обробка гранул різними за природою травильними агентами не призводить до суттєвої зміни поверхневих властивостей, чим і можна пояснити низьку ефективність класичної технології під час металізації гранул поліетилену, поліпропілену і полівінілхлориду.**

**Ключові слова: металізація; мідь; поверхневий натяг; поліетилен; поліпропілен; полівінілхлорид.**