ABSTRACT

of dissertation of Serikbayeva Bagdagul Saduyekhasovna
on the topic “Development of technology for modifying the surface of thermoplastic polymers by applying copper- and silver-containing films”
for the degree of Doctor of Philosophy (PhD) in the study program
8D07160 – “ Chemical technology of inorganic substances”

One of the most popular materials on the world market in many industries are polymer-based materials. In Kazakhstan, polymeric materials are produced in significant volumes, among which the most common are polypropylene and polyethylene. The areas of application of these polymers are related to both their physical and chemical characteristics and the possibility of imparting new functional properties to them. This allows to obtain the most widely used polymeric materials by developing new methods for modifying surfaces by metallization of the polymer matrix. One of these processes for modifying polymers is the creation of metal films on their surfaces. It is economically advantageous to introduce into production an innovative modification technology by changing the surface properties of polymers.

In Kazakhstan, there is currently a significant demand for research in the field of developing specialized technologies for creating products with unique properties based on polymers. One of the main tasks of the complex processing of hydrocarbon raw materials in Kazakhstan is the production of various polymeric materials that are in high demand in the domestic and international markets. Metallization of the surface of polymers using metals (copper, silver, gold) is becoming increasingly relevant for the production of composite materials. This is due to the fact that by replacing metal products with products made of metallized polymer, it is possible to rationally use metals, using them only in such quantities and in those cases where their metallic properties are required.

Metallization of polymers hides the polymer’s shortcomings under a metal layer, which serves as a functional shell. This imparts new properties that are not inherent to either the polymer or the metal. Such a coating improves the electrical, thermal, and mechanical properties, as well as the chemical and photochemical wear resistance of the surface, thereby increasing the strength and stability of the coating. New capabilities of metallized polymers, including phenomenological, chemical, mechanical, and electrical reactions, have inspired innovations in various fields.

Currently, there are several methods for producing metallized polymers that are widely used in the world market. Chemical electrolytic metallization (CEM) has become widespread in industry. Chemical metallization methods are effective because they allow obtaining metal films, have small direct energy losses from metal compounds, and often have small losses of the metal itself. However, there is a need to improve the chemical metallization method, which is the leading method of polymer metallization from an environmental and economic point of view. Currently proposed alternative methods require expensive special equipment or are suitable only for certain types of dielectric surfaces. One of the main

processes in chemical electrolytic metallization is the activation of the dielectric surface. Usually, sensitization with tin (II) chloride solutions is carried out before activation. Then the sensitized surface is treated with solutions of palladium compounds. The main disadvantages of this method are the use of expensive palladium compounds for activating the dielectric surface and the implementation of processes in significant volumes of sensitization and activation solutions. During the work, by-products of the ongoing reactions accumulate in the solutions, creating problems during the regeneration of these solutions. In addition, the process of chemical copper plating is not currently used due to the presence of environmental problems in the treatment of wastewater generated after the chemical process. This is due to the fact that the technological solutions of chemical copper plating, containing copper salts, complexing agents and formaldehyde, are highly toxic. Wastewater treatment is complicated by the presence of chelate compounds, which are formed from copper ions and organic residues of complexing agents. These compounds prevent the release of metals from wastewater, which makes the process of their treatment very labor-intensive and, therefore, expensive. This was also facilitated by environmental protection legislation adopted in most countries.

Therefore, the objective is to replace expensive palladium compounds with relatively cheap copper and silver compounds and eliminate the sensitization stage in this technology.

It was previously shown that after preliminary preparation of polymeric materials, the photochemical activation process is carried out during chemical metallization.

The development of an innovative technology for the process of metallization of polymeric materials by photochemical reduction is of great and current importance.

The objective of the research is to develop a technology for modifying the surface of thermoplastic polymers by applying copper- and silver-containing films.

The tasks of the research:

- development of optimal conditions for imparting the required surface roughness by etching;
- development of technology for activating the surface of thermoplastic polymers with electromagnetic waves of sunlight;
- application of an electrically conductive layer to the activated surface of polymers by direct metallization for further galvanic build-up;
- study of the mechanism of formation of metal films obtained on the surface of thermoplastic polymers and determination of the physicochemical properties of the obtained metal films;
- establishment of the main laws of the photochemical process used to obtain copper and silver films on the surface of thermoplastic polymers;
- development of technology for obtaining copper-silver films on the surface of thermoplastic polymers suitable for obtaining metallized material;

- mathematical optimization of the main parameters of the process for obtaining metallized polymers.

Methods and objects of the research. The research objects are thermoplastic polymers: polypropylene and low-density polyethylene, copper, silver and gold films. The research methods: IR Fourier spectroscopy (Shimadzu JR Prestige-21), X-ray phase analysis (EDX-7000, "Shimadzu corporation" and D8ENDEAVOR "Bruker") were carried out using electron microscopy devices with energy-dispersive analysis. To measure the roughness of the original sample and the resulting coating surface, Mitutoyo Surftest SJ-310 Profilometer was used. When measuring the electrochemical potential of the silver film, P-4 potentiostat device (Russia) was used to determine the electrode potentials of the electrochemical cell. To process the results of experimental studies, methods of mathematical modeling and statistical data processing were used.

The main provisions submitted for the defense:

- optimal parameters of the surface preliminary preparation process for metallization of thermoplastic polymers;
- results of the study of photochemical processes in thin layers of solutions of halogenides of copper subgroup elements;
- the mechanism of formation of a catalytic layer of copper particles as a result of photochemical processes;
- physical and chemical principles and features of the proposed technology for producing copper, silver and gold films;
- results of the study of photochemical reduction of copper, silver and gold films on the polymer surface, caused by both electromagnetic waves of sunlight and the action of the reducing capacity of ascorbic acid;
- technology of metallization of thermoplastic polymer with copper and silver coatings.

Key findings of the research:

- a technology for direct metallization of polymers by using thin sorption layers was developed, increasing the efficiency of the impact of electromagnetic waves of light radiation;
- the positive effect of copper subgroup metal ions on the process of polymer surface activation was demonstrated;
- a mechanism for photochemical reduction of copper ions (Cu^{2+}) in the presence of ascorbic acid was proposed and substantiated;
- metal films were obtained using photochemical processes and reducing agents of polyvalent metal ions in the surface layer of polymeric materials;
- patent of the Republic of Kazakhstan No. 36399 was received for the current method of obtaining conductive films under the influence of electromagnetic waves of light radiation in the presence of ascorbic acid;
- basic diagram of modification of polymeric materials using copper and silver films;
- mathematical modeling of the main parameters of the process of obtaining conductive silver film.

Justification of the novelty and significance of the results obtained:

- it was proved that the polymer surface is reactive in the process of activation after etching the polymer surface with a solution of the composition: $K_2Cr_2O_7$ 6,5%, H_2SO_4 93,5% for 15 minutes;

- optimal conditions for activating the polymer surface with copper, silver and gold ions by the photochemical method were established: the concentration of the solution $CuCl_2$ – 200 g/l, $AgNO_3$ – 10 g/l, $AuCl_3$ – 10 g/l, exposure to sunlight at a temperature of 20-30°C for 20-40 minutes, the recommended sunlight flux density – 1000-1200 W/m^2 600-800 W/m^2 and 500-600 W/m^2;

- the composition of reagents was selected and the optimal parameters for obtaining a conductive silver film using the method of direct metallization of the polymer surface were determined: the solution with the concentration of 20 g/l $AgNO_3$, the reducing concentration of $C_6H_8O_6$ – 50 g/l, sunlight flux density – 700-1100 W/m^2, time – 10-20 minutes; coating thickness – 0.11-0.48 μm;

- the use of environmentally friendly ascorbic acid as a reducing agent was proposed, and the mechanism for the formation of the electrically conductive film was established;

- it was shown that the silver film can be used for further galvanic build-up of the polymer surface with a hardness on the Vickers scale (1490-1550HV);

- a new composition of reagents was selected and the optimal parameters for direct gilding of polymeric materials were determined: the solution of the composition of 20 g/l $AuCl_3$, the reducing concentration of $C_6H_8O_6$ – 40 g/l, sunlight flux density – 800-1100 W/m^2, time – 15-20 minutes; coating thickness – 5-10 μm;

Relationship with the research plan. The dissertation was completed in accordance with the research activities of Department of Chemical Technology of Inorganic Substances of M. Auezov South Kazakhstan University for 2021-2025: B-21-03-02-section, topic “Development of new promising technologies and improvement of traditional technologies for obtaining inorganic products, environmentally friendly fertilizers and plant growth stimulants based on mineral raw materials and technogenic waste”, 4th section “Photochemical and chemical methods for applying functional films to dielectric materials”.

The scientific data of the dissertation are based on the results obtained by conducting experimental work and physicochemical studies using modern research equipment and devices. The works related to mathematical modeling and data processing were performed using computer technology.

The objectives and tasks of the dissertation were formulated based on the relevance of this problem.

The theoretical and practical significance of the work is substantiated by the fact that an economically efficient and low-stage technology for obtaining an electrically conductive layer on the polymer surface is proposed.

According to the results of testing the metallized polymer obtained using the proposed technology, the metallized film meets the requirements of current regulatory documents (GOST) (Appendix B) in terms of quality indicators, suitable for use in various industries.

Personal contribution of the doctoral student to the preparation of each publication.

All experimental and analytical works were performed by the author of the dissertation. Physicochemical studies and analysis, calculations of the results generalization and publications on the obtained results were performed directly by the author with the participation of consultants. On the topic of the dissertation, 9 scientific works were published, including: 3 articles in international scientific journals included in the Scopus database, 2 articles in journals recommended by Science and Higher Education Quality Assurance Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan, 3 articles were published in collections of international and republican conferences and 1 patent of the Republic of Kazakhstan for an invention was received.

1. In the article "Photochemical Metallization: Advancements in Polypropylene Surface Treatment" published in the journal "Polymers", the doctoral student prepared a review and presented the results of an experiment on obtaining an electrically conductive film on the surface of a polymer.

2. The article "Metal coatings to dielectric materials by photochemical processes" in the journal "International Journal of Chemical Reactor Engineering, Article Online Publishing" presents the results of an experiment on the activation of a polymer surface with copper and silver ions.

3. The article "Studies of the Application of Electrically Conductive Composite Copper Films to Cotton Fabrics" in the Journal of Composites Science presents the results of experiments on obtaining a semiconductor film on the surface of dielectrics using a photochemical process.

4. The article "Direct photochemical silvering of polymers" in the journal "Reports of the National Academy of Sciences of the Republic of Kazakhstan" provides a review and analysis of literature data on obtaining a silver film by direct metallization on the polymer surface.

5. The article "Use of photochemical processes for metallization of polyethylene" in the journal "Bulletin of Shakarim University" provides the results of a study on the activation of the surface of polyethylene by a photochemical method and the processing of the obtained data.

The author's contribution to the preparation of each publication is given in the dissertation and relevant publications.

Structure and scope of the dissertation. The dissertation consists of introduction, four chapters, conclusion, references and appendices. The work is presented on 138 pages, contains 28 tables, 75 figures, a bibliography of 157 titles.