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ACTIVATION OF POLYETHYLENE GRANULES BY FINELY DISPERSED ZINC

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The results of experimental researches of features of mechanical activation of polyethylene granules with finely dispersed zinc in a ball mill, and also results of research of chemical copper plating of activated polyethylene granules are given. The influence of the ratio of polyethylene granules and fine zinc, the speed of rotation of the ball mill and the duration of activation, as well as the degree of loading of the components in the activation process of polyethylene granules was studied. It is established that the condition of activation of polyethylene granules with finely divided zinc has a significant impact on the metallization process and the copper efficiency of activated polyethylene granules.

Key words: activation; ball mill; granules; polyethylene; zinc; chemical metallization.

Introduction

Composite materials obtained by combining polymers and metals are characterized by high values of the ratio of strength to mass, which are characteristic of polymers, and high electrical and thermal conductivity, wear resistance and shielding properties of metals. One of the methods of combining the properties of such materials is the metallization of polymers. Metallization allows in the final product to combine high manufacturability of polymers and their low cost of production with operational properties of metals: electrical conductivity, wear resistance, reflectivity, good appearance. Thus, the metallization of polymers is widely used in industry, both in the production of high-tech products [1, 2] and for decorative coatings.

The traditional process of chemical metallization of the polymer includes three stages: preparation of the polymer surface, its activation and deposition of metal. The first stage is mainly designed to clean the surface of the polymer and increase the adhesion of the metal to it. The activation stage is designed to form active centers on the polymer surface. At such active centers, a redox reaction of metal deposition will take place. In the third stage, the activated polymer surface is metallized as a result of autocatalytic surface-selective reaction between the metal complex and the reducing agent contained in the chemical metallization solution [3]. The most common methods of imparting catalytic properties to a polymer surface include the formation of active centers as a result of physical or chemical deposition of activator particles. Such activators are transition metals, usually Pd [4, 5]. However, the high cost of palladium makes us look for ways to replace it with cheaper metals [6, 7].

Recently, metallization technologies have been developed that allow not to use harmful and expensive materials [5, 8]. For example, to prepare the surface instead of using harmful chromium compounds, treatment with a mixture consisting of acids and hydrogen peroxide [9], ozonated water [10] or chlorine dioxide radical [11] is proposed. A separate area can be considered the use of physical fields for the preparation of the polymer surface before chemical metallization [12, 13], as well as the use of the process of laser activation [14, 15].

Activation of the polymer surface by grafting polyacrylic acid with it, followed by sorption of the catalytically active metal provides high adhesion of the copper coating to the polymer base [16]. In this case, there is a sorption of copper sulfate from its alkaline solution with a layer of polyacrylic acid, followed by reduction of copper with sodium borohydride. Thus activated polymer surface is used for chemical coating of the metal method [17].

Another direction of giving the polymer surface catalytic properties can be considered the method of introduction into the melt of the polymer of organometallic compounds, which during mixing decompose thermally with the formation of metal particles of the corresponding metals [18]. The formed metal particles act as activators in the subsequent reduced copper. This method allows you to control the speed and amount of reduced copper on the polymer through the use of metals of different nature, as well as their number. When using palladium and nickel, the recovery rate is higher than in the case of copper [19]. A logical continuation of this technology is the method of providing catalytic activity to the polymer surface of products obtained using 3D printing [20]. In this case, for 3D printing of the product, which will be further metallized, used ABS plastic thread containing palladium chloride.

Thus, the stage of activation of the polymer surface will directly affect the efficiency and cost-effectiveness of the metallization process as a whole. Therefore, research aimed at developing new methods and technologies for giving the polymer surface catalytic properties before its chemical metallization is promising and necessary.

Materials and methods of the study

Liten PL-10 (Unipetrol) polyethylene granules and PC-2 zinc powder were used for the research.

Activation of polyethylene granules was performed in a laboratory ball mill with a volume of 4 liters with ceramic cylindrical grinding bodies, rotation speed – 45–125 rpm. Loading of polymer in a mill of 50–300 g, fine zinc of 0.5–30 g, weight of grinding bodies of 1.5 kg.

Activated granules of two types were used for the research: 1 – after unloading from the mill and sieving on a sieve (sifted) and 2 – after unloading from the mill, sieving on a sieve and intensive washing in water followed by drying (washed). The activation efficiency was determined by the amount of zinc contained in the granules after treatment in a ball mill. To do this, the activated granules were 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 zinc on the activated granules was calculated from the difference between the masses of the granules before and after etching in acid.

A similar technique was used to evaluate the efficiency of copper plating. Copper granules of polyethylene were used for treatment in nitric acid. The difference between the masses of copper and after etching in acid granules was expressed as a percentage of the theoretically possible amount of reduced copper that can be recovered from a solution of chemical metallization.

Studies of the kinetic regularities of copper reduction on activated polyethylene were performed by the volumetric method according to the amount of hydrogen released [21, 22]. Copper plating of activated polyethylene granules was performed in a solution of chemical reduction with vigorous stirring on a magnetic stirrer. The composition of the chemical reduction solution (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.

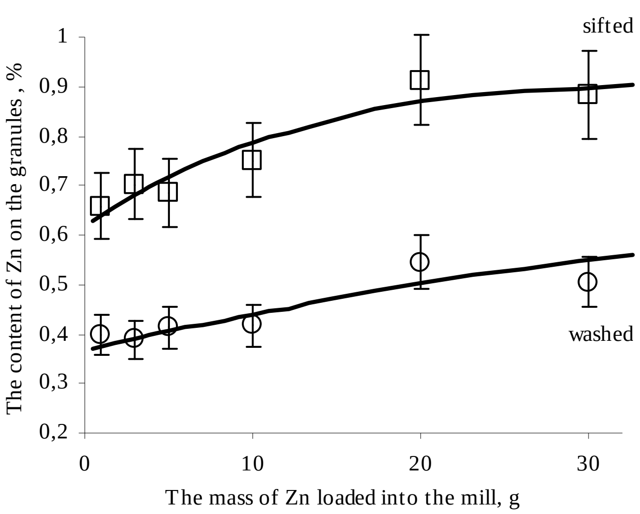
Results of the studies and their discussion

The process of activation of the polymer surface before its chemical metallization is crucial for obtaining products of the required quality. We have proposed a method of activating the polymer surface, which consists in the joint processing in a ball mill of polymer granules and fine powder of activator metal [23]. Previous studies have shown that such processing allows to obtain activated polymer raw materials that can be successfully used for chemical metallization [22, 24].

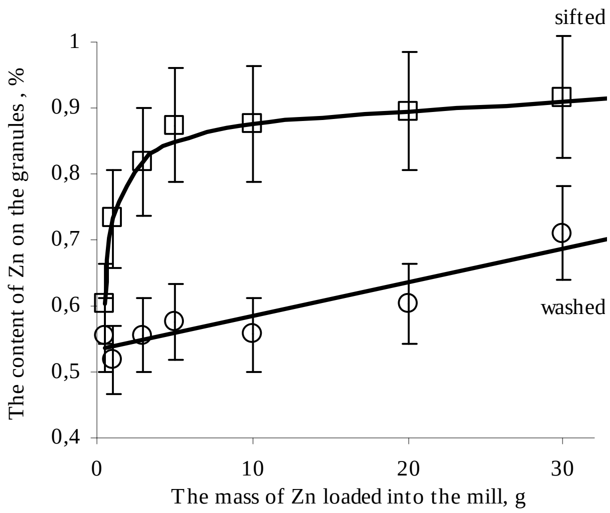
During activation in the ball mill are grinding ceramic bodies, polymer granules and fine metal activator. As a result of rotation of the mill there is an interaction of fine metal of the activator with a polymeric surface. The consequence of such an interaction should ultimately be a strong fixation of the activator metal on the polymer surface. Obviously, the strength of the activator metal on the polymer surface will depend on a number of conditions, such as the speed of rotation of the mill, the degree of loading of the mill with polymer and metal activator, the ratio between polymer and metal activator, activation time, etc. To establish the influence of these factors on the process of activation of polyethylene granules with fine zinc, a number of studies were conducted.

In Fig. 1–3 shows the effect of the ratio between the polymer and the metal activator and the speed of rotation of the ball mill on the final zinc content on the activated polyethylene granules.

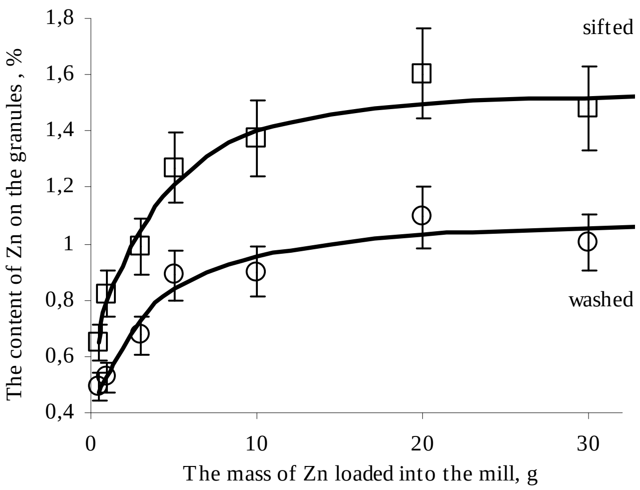
The analysis of the obtained results allows us to state that the zinc content that we can get on polyethylene granules after processing in a ball mill significantly depends on the ratio between polymer and activator metal, and on the speed of rotation of the ball mill. In all cases, as the mass of zinc loaded into the mill increases (the mass of polyethylene is constant), the zinc content of the polyethylene granules increases. At the same time it is necessary to note various dependence for the sifted and washed granules of polyethylene. For sieved granules, regardless of the speed of rotation of the mill, you can see some slowdown in the amount of zinc on the activated granules at a weight of zinc loaded into the mill 5–20 g. At lower speeds, there is an increase in the amount of zinc on the activated polyethylene granules with increasing mass of zinc loaded into the mill.



The speed of rotation of the mill – 45 rpm



The speed of rotation of the mill – 80 rpm



The speed of rotation of the mill – 125 rpm

Fig. 1. The dependence of the amount of zinc on activated polyethylene granules on the ratio between polymer and activator metal. The weight of polyethylene loaded into the mill is 100 g, the duration of activation is 60 minutes

Obviously, the process of fixing zinc particles on the surface of polyethylene requires some energy. In the case of low speeds (45–80 rpm), the kinetic energy developed by the grinding balls is low and to fix more zinc, given the same duration of activation, requires a higher initial mass of activator metal. With increasing speed of rotation is more efficient use of activator metal and saturation of the entire surface of the granule with fine zinc occurs at an initial mass of zinc of about 10 g

To confirm this, we can study the effect of the duration of activation and the speed of rotation of the mill on the amount of zinc on the activated polyethylene granules (Fig. 2). In this case, both the increase in the duration of activation and the increase in the speed of rotation of the mill affect the increased amount of zinc on the obtained activated polyethylene granules. In this case, the decisive influence is the speed of rotation of the mill. Thus, at a speed of 125 rpm and a duration of activation of 5 min, it is possible to achieve almost the same values of the amount of zinc on the activated granules, as well as for activation lasting 1 h at a mill speed of 45 rpm As in the previous case, the decisive factor is the energy developed by the grinding bodies and which is spent on fixing the zinc particles on the polymer surface.

It should also be noted that to construct these dependencies it was necessary to conduct a significant number (8–10) of parallel experiments, which is caused by a significant error of the experiment, which can be estimated at 12 %.

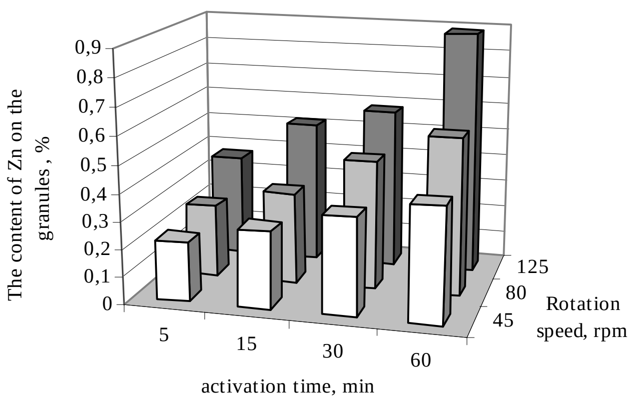


Fig. 2. The effect of the duration of activation and the speed of rotation of the ball mill on the zinc content on the washed activated polyethylene granules The ratio of PE: Zn – 100: 5, the weight of polyethylene loaded into the mill – 100 g

The next factor studied in order to influence the process of activation of polyethylene granules with fine zinc is the change in the degree of loading of raw materials into the mill (Fig. 3).

In this case, the amount of zinc on the obtained activated polyethylene granules decreases with increasing degree of loading of the ball mill with polyethylene. Given that the ratio of polymer - metal activator remains constant, the decrease in the amount of zinc on the activated granules can be explained using the previous assumptions. The energy of the grinding balls, which is spent on fixing the zinc particles on the polyethylene, is distributed to a larger amount of polyethylene, which affects the reduced amount of zinc fixed on the granules of polyethylene.

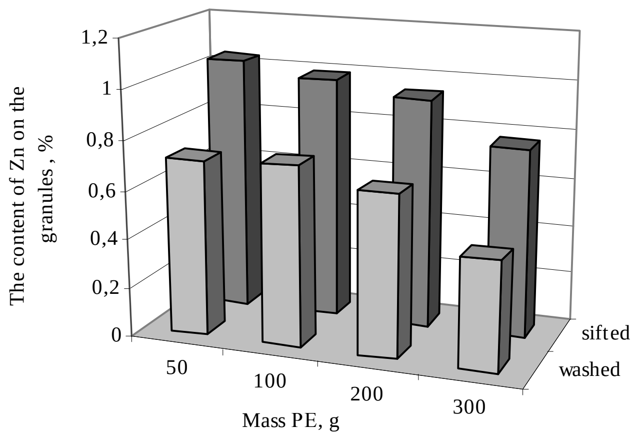


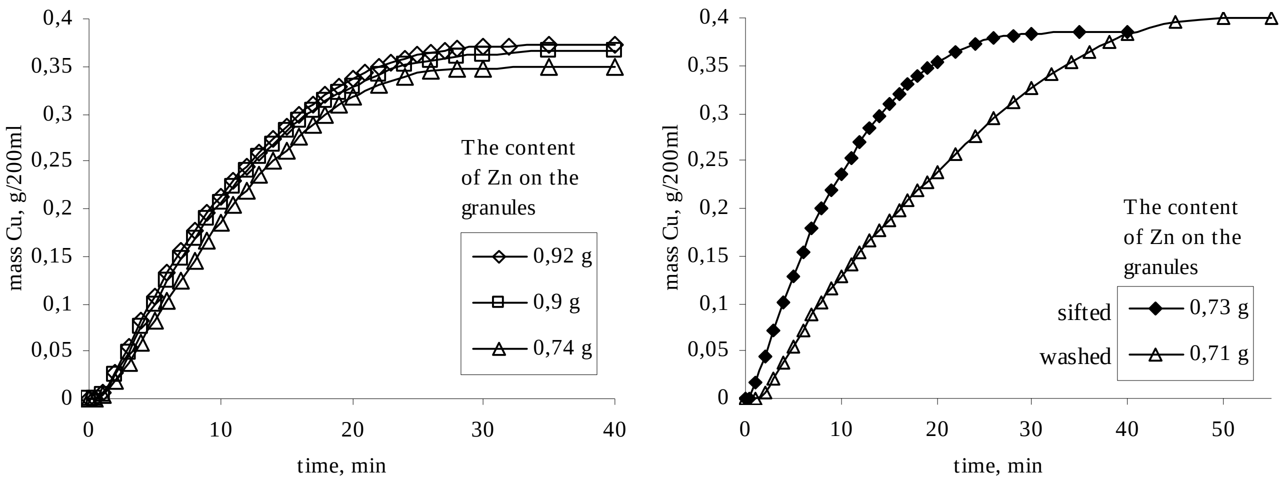
Fig. 3. The influence of the degree of loading of the ball mill with polyethylene on the zinc content on activated polyethylene granules. The ratio of PE: Zn – 100: 5, the speed of rotation of the mill – 125 rpm, activation duration – 60 minutes

Thus, the studies suggest that when using the method of activation of polyethylene granules with fine zinc in a ball mill, it is possible to obtain activated polymeric raw materials. The properties of such raw materials can be changed in a wide range by the parameters of the process of activation of polyethylene granules in a ball mill.

Since activated polyethylene granules were obtained for the purpose of their subsequent metallization in chemical copper plating solutions [22], it is necessary to establish the influence of activation parameters on the copper plating process of activated polyethylene granules (Fig. 4).

Analysis of the obtained kinetic curves shows that the type of granules used has the greatest influence on the rate of reduction of copper ions on the activated surface of polyethylene granules. Even in the case of almost the same zinc content on the surface of the granules, the metallization rate is significantly lower when using washed granules (Fig. 4, *b*). In the case of sieved granules, the effect of zinc content on the surface of the granules on the reduction rate of copper ions is almost absent (Fig. 4, *a*).

However, it should be noted that in addition to the effect on the rate of reduction of copper ions, the properties and background of activated polyethylene granules have a significant effect on the efficiency of copper plating (Fig. 5).



a *b*

Fig. 4. Kinetic curves of recovery of copper ions on the activated surface of polyethylene granules.
a – the effect of zinc content on sieved activated polyethylene granules,
b – the effect of the method of preparation of activated polyethylene granules

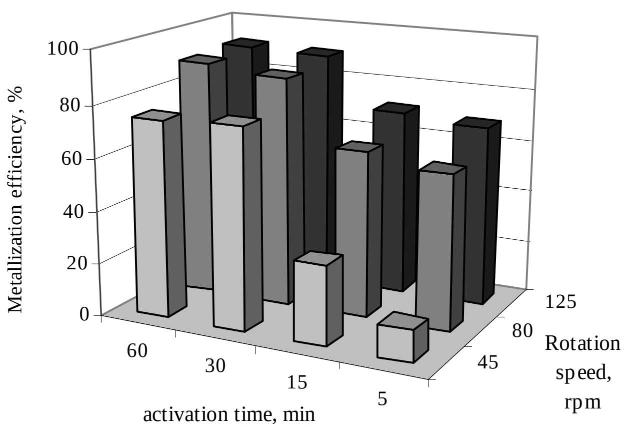


Fig. 5. The influence of the duration of activation and the speed of rotation of the ball mill on the efficiency of copper plating of sifted activated polyethylene granules

The obtained results allow to state that the main factor determining the efficiency of copper plating of activated polyethylene granules is the strength of fixing of activator metal particles on the polymer surface. Activated polyethylene granules obtained at low speeds of rotation of the ball mill and short duration of activation with the subsequent intensive stirring in the chemical reduction solution lose part of the activator metal due to its washing away from the surface of the granules. This means that part of the copper is reduced not on the activated surface of the granules, but in the volume of the solution on the washed zinc particles. Such a metal reduced in the volume of the solution forms a precipitate and reduces the efficiency of copper plating. It is obvious that the residence time of activated polyethylene granules with intensive mixing will determine the amount of zinc that will pass from the surface of the granules into the solution (Fig. 6). The residual zinc content on the activated polyethylene granules is primarily determined by the strength of the fixation of zinc particles on the polymer surface.

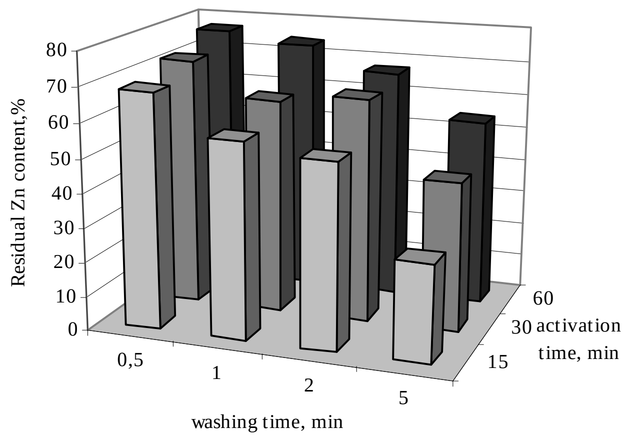


Fig. 6. The effect of the duration of washing the activated granules and the speed of rotation of the ball mill on the residual zinc content on the activated polyethylene granules after washing

Another factor that will affect the efficiency of copper plating is the induction period that occurs at the beginning of the metallization process. The use of solutions with a small induction period will allow copper plating with high efficiency due to the short time during which zinc particles can pass into the solution.

Conclusions

The research results confirm that in the process of mechanical activation in a ball mill of polyethylene granules with finely divided zinc it is possible to obtain activated polymeric raw material suitable for subsequent copper plating in chemical reduction solutions. It is established that the main factors influencing the activation process are the speed of rotation of the ball mill, the duration of activation, the ratio and the number of components loaded into the mill for activation. This information allows you to set the optimal parameters of the process. It is shown that the efficiency of copper plating of activated polyethylene granules directly depends on the conditions of activation.

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АКТИВАЦІЯ ГРАНУЛ ПОЛІЕТИЛЕНУ ДРІБНОДИСПЕРСНИМ ЦИНКОМ

Наведено результати експериментальних досліджень особливостей механічної активації гранул поліетилену дрібнодисперсним цинком у кульовому млині, а також результати дослідження хімічного міднення активованих гранул поліетилену. Досліджено вплив співвідношення гранул поліетилену і дрібнодисперсного цинку, швидкості обертання кульового млина і тривалості активації, а також ступеня завантаження компонентів на процес активації гранул поліетилену. Встановлено, що умови активації гранул поліетилену дрібнодисперсним цинком істотно впливають на процес металізації та ефективність міднення активованих гранул поліетилену.

Ключові слова: активація; кульовий млин; гранули; поліетилен; цинк; хімічна металізація.