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ANALYSIS OF PROCESSES WHICH OCCUR DURING THE DESTRUCTION OF A COPPER SHELL ON POLYETHYLENE GRANULES

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The geometric dimensions of the copper shell formed by chemical deposition on a spherical polyethylene granule were calculated. It is shown that the main factor determining the thickness of the formed copper layer is the initial size of the polyethylene granule. The processes of destruction of the copper shell formed on the polyethylene granule during thermal expansion of the polymer are considered. The values of the limit temperatures in which the copper shell still retains its integrity depending on its thickness are calculated.

Key words: metal-filled polymer composites; metallization; metal coating; shell; polyethylene; copper.

Introduction

Polymers and metals are used in various applications due to their insulating and electrically conductive properties. The creation of metal-filled polymer composites is promising and interesting because it allows you to combine components with diametrically opposite properties in the same material. In this case, with the right combination of components during the production of composite material, you can get a new material. This composite material will combine the positive properties of the components, which will allow you to use it to create new high-tech products and introduce them into new applications.

There is a large number of metal-filled polymer composites, which differ by the polymer matrix and the metal filler. The polymer matrix can be done of thermosetting resins [1–3] and thermoplastic polymers [4, 5]. Metal fillers in the vast majority of studies are copper, aluminum, tin, nickel, although not limited to them [3, 6–9]. The properties of metal-filled polymer composites depend not only on the type of matrix and filler used. The shape of the metal filler and the method of obtaining the composite also have a significant effect on the properties [6, 10]. The main task is to ensure uniform distribution of the metal filler in the polymer matrix, as well as the formation or direct contact between the filler particles or the formation of structures in which a different conduction mechanism is possible [3, 11]. Thus, the process of obtaining metal-filled polymer composites with the required properties is not limited to the choice of polymer matrix and metal filler. It is necessary to take into account other factors that affect the properties of the final composite and that must be taken into account while developing technology for such materials.

We are developing a technology for producing metal-filled composites, which includes the activation of a polymer surface, its metallization, and the processing of metallized polymer raw materials into products. Thus, this technology consists of three stages. The first stage includes obtaining an activated polymer raw material. Activation of the polymer surface occurs as a result of the joint processing of polymer granules and finely dispersed activator metal in a ball mill [12]. This treatment is responsible for fixing the activator metal on the surface of the polymer granules, which is necessary for the second stage of the process - metallization. Metallization of activated polymer granules occurs in chemical precipitation solutions, which main component is copper sulfate. The use of such solutions provides fast and high-quality metallization of the surface with the production of polymer granules uniformly coated with a metal layer [13]. The final stage is the processing of metallized polymer raw materials to obtain metal-filled products.

Materials and methods of research

Calculation of the characteristics of the copper sheath obtained on a polyethylene granule

The obtaining processes of the metal-filled composites as a result of the processing of metallized polymer granules also require an understanding of mechanisms that occur in the material during their processing by various methods. In particular, the properties of the resulting composites will be significantly affected by the geometric characteristics of the metal filler, which depend on the features of the destruction of the metal shell on polymer granules. The mechanism of destruction of the metal shell obtained on the polymer granule will depend on its thickness, as well as the method of processing.

Determination of the properties of the metallized raw material obtained by the developed technology and understanding the mechanisms occurred during the destruction of the metal shell during its processing, the geometric dimensions of the metal filler were calculated depending on the size of the polymer granule. The thickness of the obtained metal layer on the polymer granule was calculated for a spherical particle, which is uniformly covered with a metal layer (Fig. 1).

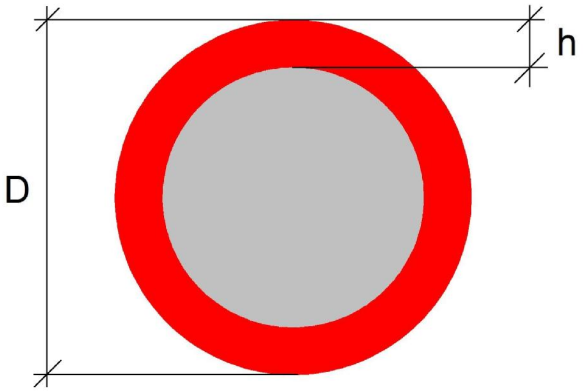

Fig. 1. Metallized spherical polymer pellet

The calculation algorithm was as follows:

1) the given diameter of the polymer particle was used to calculate its volume and mass (1, 2);

2) in accordance with the obtained value of the mass of the polymer particle and the specified value of the metal content, the mass of the metal, its volume, and the diameter of the metallized particle were calculated (2, 3).

Polymer particle volume:

$$V = \frac{4}{3}\cdot\pi\cdot r^3, \qquad (1)$$

where r is the radius of the polymer particle.

The mass of the polymer particle and the volume of the metal from the dependence:

$$\rho = \frac{m}{V}, \qquad (2)$$

where ρ is the density, V is the volume, and m is the mass of the polymer and metal.

The diameter of the metallized particle is calculated using the value of the metal volume that makes up the shell:

$$V = \frac{4}{3}\cdot\pi\cdot\left(R^3 - r^3\right),$$

where r is the radius of the inner sphere (given radius of the polymer particle), R is the radius of the outer sphere (the radius of the metal shell);

where:

$$D = 2\cdot\sqrt[3]{\frac{3V}{4\pi} + r^3}\ . \qquad (3)$$

The difference between the calculated value of the diameter of the metallized particle and the specified value of the diameter of the polymer particle is the thickness of the metal layer on the metallized particle.

Initial data for calculation:

resin particle diameter, mm – 1, 3, 5.

metal content, wt. % – 1, 5, 10;

polymer – polyethylene (ρ = 0.94 g/cm^3);

metal – copper (ρ = 8.96 g/cm^3).

The calculation of the thickness of the copper layer on a spherical polyethylene granule shows that the thickness significantly depends on both the size of the initial granule and the metal content (Table 1). Such difference of the thickness of the copper coating is explained by an increase of the specific surface area of polymer particles during a decrease of their diameter (with the decrease of the diameter of a spherical polyethylene particle from 5 mm to 1 mm, the specific surface area increases from 1.3 to 6.7 m^2/kg).

Table 1

The calculated results of the thickness of the copper layer obtained on a spherical polyethylene granule

The diameter of the spherical granule $d\cdot10^3$, m	Copper content wt. %	The thickness of the obtained copper layer $h\cdot10^6$, m	Specific surface area S_{SSA}, m^2/kg	(R/h > 10)
1	1	0.17	6.7	2994
	5	0.84		598
	10	1.67		300
3	1	0.5	2.2	2988
	5	2.51		598
	10	5.01		300
5	1	0.84	1.3	2988
	5	4.18		598
	10	8.34		300

It is clear that such a significant difference of the thickness of the copper layer will significantly affect on properties of the obtained metal-filled polymer composites. Also, the behavior of the copper layer during the processing of such raw materials will be different.

Research results and their discussion

The mechanism of destruction of the copper shell obtained on a polyethylene granule

The main processes that occur during the processing of polymers are melting and plastic deformation of the material. In this case, depending on the chosen processing method, the conditions of plastic deformation will be different, and the simplest option occurs during the thermoplastics pressing. In this case, plastic deformation occurs without significant shear rates and can be represented by a change in the initial shape of a sphere to the shape of a cube. In this case, regardless of the chosen processing method, heating of the material always takes place. The effect of temperature on each material determines its thermal expansion, which, given the different coefficients of thermal expansion of metals and polymers, will have a certain effect on the destruction of the metal shell.

To calculate the increase in the volume of a spherical polyethylene particle when it is heated, we use the formula:

$$V' = V\cdot(1+\alpha_V\cdot\Delta t), \quad (4)$$

where V is the initial volume of the polymer; α_V is the coefficient of volumetric expansion; Δt – temperature rise.

Based on the assumption that the thermal coefficient of linear expansion in the temperature range below the temperature of phase transitions is linear [14], it is possible to calculate the thermal coefficient of volume expansion ($\alpha_V \approx 3\cdot\alpha_L$). This made it possible to calculate the change in the volume of a spherical polyethylene granule during its heating (Fig. 2).

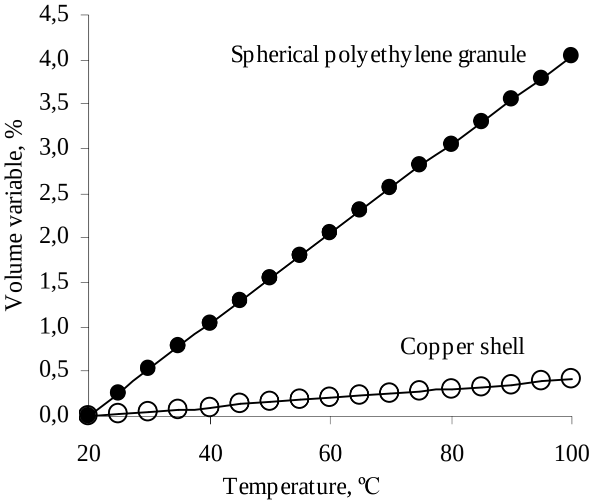

Fig. 2. Change in the volume of a spherical polyethylene granule and a copper shell during heating (For polyethylene $\alpha_L = 1.75\cdot10^{-4}$ K^{-1}, for copper $\alpha_L = 17\cdot10^{-6}$ K^{-1})

The increase in the volume of a spherical polyethylene particle in the considered temperature range, as well as the coefficient of thermal expansion, has a linear dependence. However, it is necessary to pay attention to the significant difference in the volume change values for polyethylene and copper sheath. Heating of polyethylene in a closed volume of a copper sheath is accompanied by its thermal expansion, which will cause an increase in stress in the copper layer and, as a result, will lead to its destruction. In this case, the destruction of the copper sheath will be caused by a significant increase in pressure that acts on the sheath.

To calculate the maximum pressure of a substance in a closed volume when it is heated, you can use the formula [15]:

$$P^{(M)} = P_0 + \frac{\alpha_{\mathrm{L}}}{\alpha^{(P)}} \cdot \Delta t \qquad (5)$$

where P_0 is the initial pressure, Pa; $\alpha^{(P)}$ – compressibility coefficient, Pa^{-1}.

Thermoplastic melts are a low compressible medium, while the value of the compressibility coefficient and thermal linear expansion for polyethylenes of different grades are 10^{-9} Pa^{-1} and 10^{-4} K^{-1}, respectively. These coefficients are very small. Thus, it can be assumed that the assumption of the constancy of the properties of polyethylene and the independence of the values of the coefficients from pressure and temperature will introduce an insignificant error into the calculations.

Formula (5) allows you to calculate the maximum pressure that polyethylene will create in a closed volume when it is heated, but it does not take into account the thermal expansion of the copper sheath. Simultaneous thermal expansion of the copper sheath during the heating of the polymer will lead to lower values of the maximum pressure acting on the sheath. The value of the maximum pressure, taking into account the thermal expansion of the metal shell, can be calculated using the formula:

$$P^{(M)} = P_0 + \left(\frac{\alpha_{\mathrm{LPP}}}{\alpha^{(P)}_{\mathrm{PE}}} - \frac{\alpha_{\mathrm{LCu}}}{\alpha^{(P)}_{\mathrm{Cu}}} \right) \cdot \Delta t \qquad (6)$$

here the coefficients for polyethylene and copper are denoted respectively by indices PE and Cu.

Using formula (6), the maximum pressure in a closed volume was calculated during the thermal expansion of polyethylene (Table 2). The following parameters were used in the calculations: $\alpha_{LPE} = 1.75 \cdot 10^{-4}$ K^{-1}; $\alpha^{(P)}_{\mathrm{PE}} = 1.4 \cdot 10^{-9}$ Pa^{-1}; $\alpha_{LCu} = 1.7 \cdot 10^{-5}$ K^{-1}; $\alpha^{(P)}_{\mathrm{Cu}} = 7.3 \cdot 10^{-9}$ Pa^{-1}. Initial conditions: $P_0 = 0.1$ MPa; $t_0 = 20$ ºC.

Table 2

The results of calculating the maximum pressure acting on the copper shell obtained on a spherical polyethylene granule

T, ºC	*P(M)*, Pa	*T*, ºC	*P(M)*, Pa
20	0.10	60	5.01
25	0.71	65	5.62
30	1.33	70	6.23
35	1.94	75	6.85
40	2.55	80	7.46
45	3.17	85	8.07
50	3.78	90	8.69
55	4.39	95	9.30

The calculation results show that heating polyethylene in a closed volume, which does not allow its expansion, leads to an increase in pressure. In this case, the pressure that acts on the walls of the metal shell can lead to its destruction. It should be noted that the calculations do not take into account the initial geometric dimensions of the polymer granule and heat transfer processes in it. The obtained values show only the maximum pressure in the set thermal regime.

The pressure that polyethylene creates during thermal expansion in a closed volume will act on the copper sheath. In this case, tensions arise in the copper shell, the magnitude of which can be determined using the calculation of spherical shells according to the momentless theory [16]. The use of this theory is based on the fact that a metal shell on a spherical polymer granule can be considered as a body of revolution with an insignificant wall thickness (Fig. 3). In this case, it can be assumed with high accuracy that only normal stresses (tensions) are present in the shell walls, which are uniformly distributed over the thickness of the shell wall. Calculations based on such assumptions are agreed with experimental data only in the case of thin-walled shells. For such shells, the ratio of the smallest radius of curvature at a given point to the thickness of the shell wall exceeds 10 $\left(\frac{R}{h} > 10 \right)$. According to the accepted restrictions regarding the size of the granules and the metal content, the copper sheath obtained on spherical polyethylene granules can in all cases be considered thin-walled (Table 1).

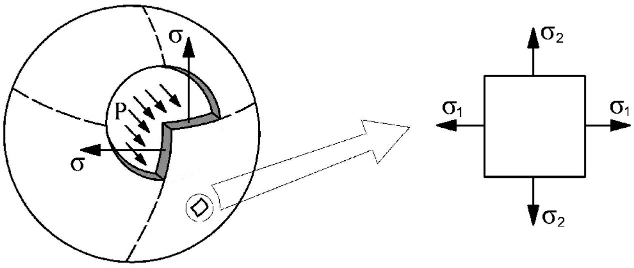

Fig. 3. Scheme of stress state formation in a copper shell

The tension that are acted on the shell have the properties of axial symmetry. The shell itself also has central symmetry. The consequence of this is $\sigma_1 = \sigma_2 = \sigma$, and $\rho_1 = \rho_2 = d/2$, where d is the diameter of the sphere. For this case, the Laplace formula takes the form [16]:

$$\sigma = \sigma_1 = \sigma_2 = \frac{P \cdot d}{4 \cdot h}.$$

Since in this case under consideration there is a plane tension state, the strength can be calculated using the third strength hypothesis and the assumption that there is no pressure between the layers of the shell, i. e. $\sigma_3 = 0$. Principal tensions matter in this case: $\sigma_1 = \sigma$; $\sigma_2 = \sigma$; $\sigma_3 = 0$ and in accordance with the third hypothesis of strength, the tension calculation is carried out as in the case of a uniaxial tension state:

$$\sigma = \frac{P \cdot d}{4 \cdot h} \qquad (7)$$

where P is the internal pressure acting on the shell; d is the shell diameter; h is the shell wall thickness.

An analysis of the formula used to calculate the tensions in the shell shows that the tension value depends on the ratio of the shell diameter and its wall thickness. Since this ratio is the same for granules of different diameters with the same metal content (Table 1), the calculation can only be made for granules of the same size. Thus, the initial data for calculating tensions in a spherical shell are pressure and shell thickness. Based on the condition that the metal layer on the polymer surface is formed at a pressure of 0.1 MPa, the excess pressure that is created during the thermal expansion of a polyethylene granule is defined as $P = 0{,}1 – P^{(M)}$ (Table 3).

Table 3

Calculation of tensions in a copper sheath obtained on a spherical polyethylene granule

T, °C	P, MPa	The thickness of the copper layer, 10^6, m		
		0.17	0.84	1.67
		Stress in the shell, MPa		
20	0.00	0.0	0.0	0.0
25	0.61	918.2	183.4	91.9
30	1.23	1836.4	366.8	183.7
35	1.84	2754.6	550.3	275.6
40	2.45	3672.8	733.7	367.5
45	3.07	4591.0	917.1	459.4
50	3.68	5509.2	1100.5	551.2
55	4.29	6427.4	1283.9	643.1
60	4.91	7345.6	1467.4	735.0
65	5.52	8263.8	1650.8	826.9
70	6.13	9182.0	1834.2	918.7
75	6.75	10100.2	2017.6	1010.6
80	7.36	11018.4	2201.0	1102.5
85	7.97	11936.6	2384.5	1194.4
90	8.59	12854.8	2567.9	1286.2
95	9.20	13773.0	2751.3	1378.1

The results show that an increase in temperature leads to a significant increase in tensions in the shell. In this case, the thickness of the shell has a significant influence on the stress value in the shell.

Literature data [17], as well as our microscopic studies of copper coatings obtained by the developed method [18, 19], shows that such coatings have a microcrystalline structure. The microcrystalline structure of the copper coating obtained by chemical deposition affects the fact that such coatings have higher values of ultimate strength compared to the strength of technical copper and its value reaches 400 MPa [17, 20]. For technical copper, this indicator has a value of 225 MPa [21].

Based on the obtained tension results (Table 3), the destruction of the copper shell, depending on its thickness, will begin at a temperature of 22.2 ºC for a shell with a thickness of $0.17\cdot10^{-6}$ m, 31 ºC for a shell with a thickness of $0.84\cdot10^{-6}$ m and 41.7 ºC for a shell with a thickness of $1.67\cdot10^{-6}$ m. These conclusions do not take into account the fact that with an increase in temperature, the tensile strength of copper decreases. Although the temperatures at which the destruction of the copper sheath begins are low, there will be no significant decrease in strength in the range of such temperatures. The plastic deformation of copper with a microcrystalline structure is within 2–3 % [20]. This value of the plastic deformation of the copper shell makes it possible to predict its destruction at a temperature of 60–80 ºC, regardless of the thickness of the shell (Fig. 2).

Conclusions

It is clear that the considered assumptions of the destruction of the metal shell on the polymer granule are far from real conditions. Granules of industrial polymers have an irregular shape and, accordingly, the shape of the metal shell obtained on the surface will be far from spherical. Such shells will fail according to other mechanisms, and in this case, the presence of stress concentration zones will be the decisive factor. However, the considered factors of destruction of the metal shell are interesting from the point of view of determining the main factors that have an impact on the process of destruction of the metal shell. Such information is necessary to understand the processes that occur during the production of metal-filled composites by processing metallized polymer raw materials and the possibility of influencing the properties of the final product.

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АНАЛІЗ ПРОЦЕСІВ, ЩО ВІДБУВАЮТЬСЯ ПІД ЧАС РУЙНУВАННЯ МІДНОЇ ОБОЛОНКИ НА ПОЛІЕТИЛЕНОВІЙ ГРАНУЛІ

Виконано розрахунок геометричних розмірів мідної оболонки, сформованої методом хімічного осадження на сферичній поліетиленовій гранулі. Показано, що основним чинником, який визначає товщину сформованого шару міді, є початковий розмір гранули поліетилену. Розглянуто процеси руйнування сформованої на поліетиленовій гранулі мідної оболонки під час теплового розширення полімеру. Розраховано значення граничних температур, за яких мідна оболонка ще зберігає цілісність залежно від її товщини.

Ключові слова: металонаповнені полімерні композити; металізація; металеве покриття; оболонка; поліетилен; мідь.