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Dependence of Permeability and Duration of Dissolution Capsules Forming Polymer Materials from Number of Hydrophilic Groups Available in Polymeric Chain

Key words: *encapsulation, an encapsulating agent, permeability, duration of dissolution, hydrophilic groups, the degree of polymerization.*

Annotation: *the dependence of permeability and duration of dissolution of capsule-forming polymeric materials on the number of hydrophilic groups was investigated. It has been established that a decrease in hydrophilic groups of up to 65% in 3 times reduces the permeability and duration of the dissolution of the polymers of the capsule former. It was determined that this dependence at the beginning of the process has a rectilinear and then parabolic character, which is associated with an increase in the diameter of the polymers between the swollen fiber. The equations describing the dependence of the duration of dissolution (CRC) of granules with different degrees of polymerization are proposed.*

The relevance of the problem. One of the effective ways to increase the time of absorption of mineral fertilizer granules by plants is to coat them with capsule-forming polymeric materials, which are widely used in advanced countries. Capsulated fertilizer granules acquire the property of prolonged action, which allows increasing the degree of utilization of the nutrient elements of fertilizers by plants. The dissolution rate of the coated fertilizer granules significantly depends on the number of elementary units replaced by hydrophilic groups. The change in the number of hydrophilic groups in the primary units of the polymer chain makes it possible to control the prolongation of the action of the granules of mineral fertilizers. Therefore, the study of the dependence of the permeability and duration of dissolution of a polymeric capsule former on the number of hydrophilic groups in the elementary unit of polymeric material is necessary and has theoretical and practical significance.

Formulation of the problem. The article studies the dependence of permeability and duration of dissolution of individual capsule-forming materials on the number of hydrophilic groups contained in the elementary units of the polymer chain.

Experiment and discussion of the results. For the experiment, we used polymers synthesized by us - K-CMC, NH4-CMC, Ca- (CMC) 2 and manufactured in the industry - Na-CMC hydrophilic groups in the polymer chain (later this term will be used as the degree of polymerization) having 65, 70, 75, 85% [3].

Of each (K, NH_4, Ca, Na) CMC having a degree of polymerization of 65, 70, 75, 85%, samples of polymer films were made in a square form in the size of 100x100 mm thick (0.5; 1.0; 1.5; 2, 5) mm (Fig. 1).

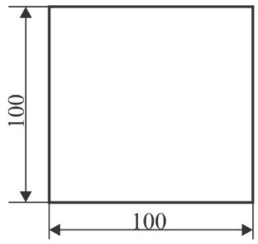

Fig.1. Polymeric films of 100x100 mm in size.

The fabricated samples of each polymer film were wrapped in a conical shape and placed in a funnel mounted on the surface of a 200 ml conical flask. Then distilled water was added to each manufactured funnel in a volume of 100 ml. and including a stopwatch, we determined the time of permeability (Fig. 2).

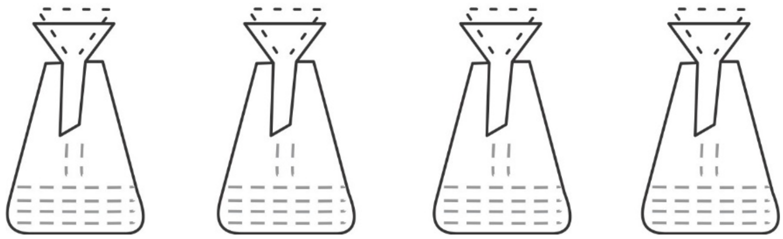

Fig.2. Laboratory installations for studying the permeability of a polymer film: 1. δ = 0.5mm, 2. δ = 1mm, 3. δ = 1.5mm, 4. δ = 2.5mm.

Obtained results are shown in the table below. The permeability of polymers according to the degree of polymerization and thickness.

Name of polymers	Degree of polymerization	The permeability of capsule-forming polymers in various thicknesses, min.			
		Capsule-forming film thickness, mm.			
		0.5	1.0	1.5	2.5
K-KMS	65	210	345	440	720
	70	125	260	330	540
	75	70	173	220	360
	85	60	115	180	240

NH_4-KMS	65 70 75 85	150 112 75 50	300 225 150 100	450 310 225 150	600 450 300 200
Ca-$(KMS)_2$	65 70 75 85	360 270 180 120	690 520 345 230	1080 760 540 360	1440 1030 720 480
Na-KMS	65 70 75 85	205 120 75 55	330 255 170 110	410 320 200 170	700 520 350 230

From the analysis presented in the table, it can be seen that the permeability of polymer coatings changes depending on the degree of polymerization and the thickness of the polymer film, because in polymers (NH4, K, Na) CMC, reducing the degree of polymer by up to 65% reduces the permeability of the capsule-forming polymer by 3%. Changing the degree of polymerization to 65-85% increases permeability, which is associated with an increase in carboxymethyl groups in the macro chain of the polymer. The thickness of the capsule-forming coating also affects permeability reduction. Thus, with an increase in the thickness of the capsule-forming film, its permeability decreases proportionally. However, increasing the thickness of the polymer capsule-forming agents is ineffective. This leads to an increase in the consumption of polymeric material and a decrease in economic efficiency. Therefore, to solve this issue, when choosing the thickness of a capsule-forming film, it is necessary to take into account the vegetative period of plants. For example, for cotton, corn, grain, the thickness of a capsule-forming film in the range of 0.5–1.0 mm is reasonable. From the data in the above table, it also turns out that permeability in samples made of Ca- (CMC) 2 has a permeability 4 times lower (360-1400 min).

However, when using Ca (CMC) 2 in the soil, the amount of Ca^{+2} ion increases, therefore the coating of the superphosphate granules with these capsule-forming agents is impractical, since retrogradation occurs in the soil (the conversion of digestible phosphate to an insoluble form), and can be used to cover the granules (NH_2) 2CO, NH_4NO_3, etc. The use of a capsule-forming film (NH_4, K, Na,) CMC enriches the soil with nutrients, so using them as a film-forming coating is more appropriate. One of the main indicators characterizing the material of the capsule-forming film is the duration of dissolution. To study the duration of dissolution, we chose 100 grams- granules of superphosphate with a diameter of 2mm. They were covered with a 15% solution of the above polymer (journal Scientific News, t.15. No. 3, p.73-76, SGU), having a degree of polymerization of 65, 70, 75, 85%. The diameter of the capsule-forming film was kept in the range of 0.5; 1.0; 1.5; 2.5 mm respectively. Then from each sample chose 3 pcs. and placed in a glass with 100 ml. water to determine the duration of dissolution on the degree of polymerization. The results obtained are graphically shown in Fig. 3, 4, 5, 6.

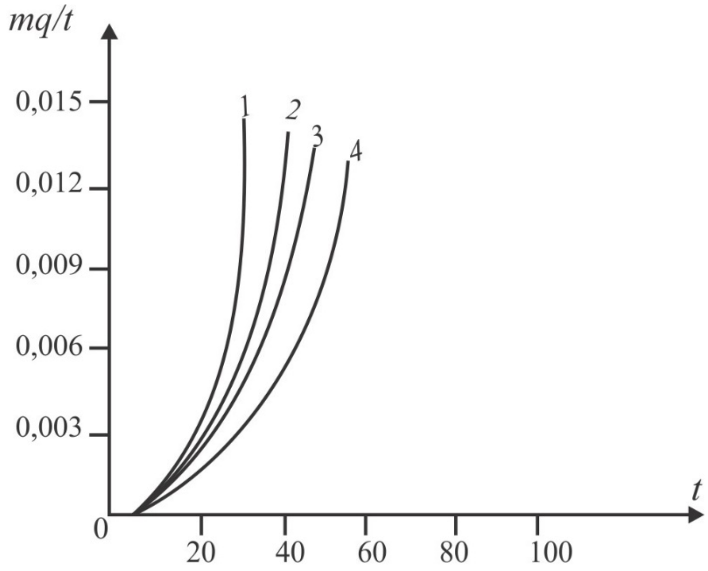

Figure 3. Polymerization degree 65%, thickness 0.5mm.
1-NH_4-KMS; 2-K-KMS; 3-Na-KMS; 4- Ca $(KMS)_2$.

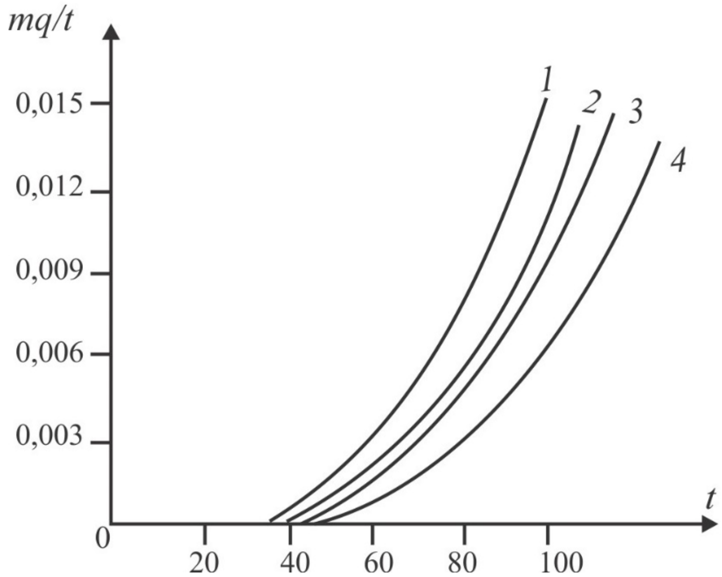

Figure 4. Polymerization degree 70%, thickness 1.0 mm.
1-NH_4-KMS; 2-K-KMS; 3-Na-KMS; 4- Ca $(KMS)_2$.

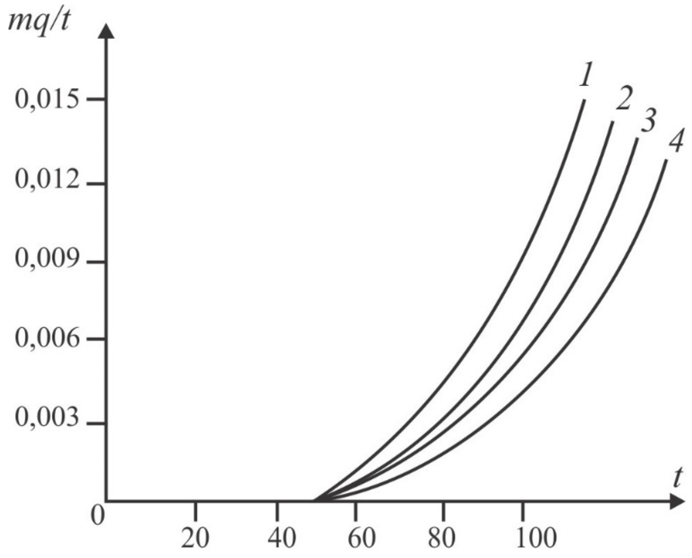

Figure 5. Polymerization degree 75%, thickness 1.5 mm.
1-NH_4-KMS; 2-K-KMS; 3-Na-KMS; 4- Ca $(KMS)_2$.

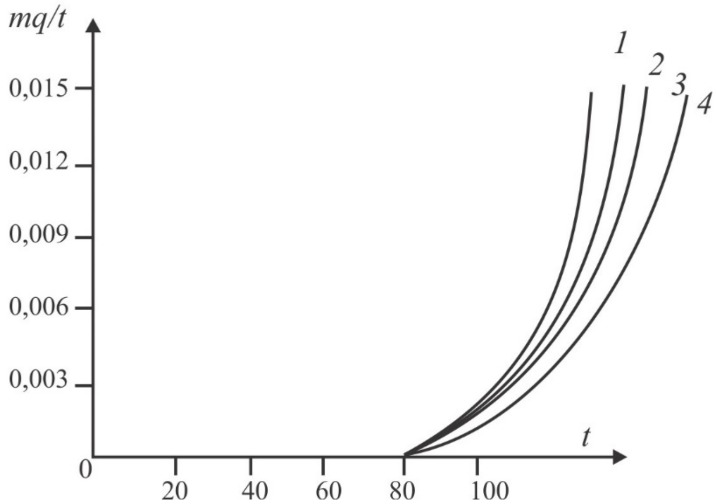

Figure 6. Polymerization degree 85%, thickness 2.5 mm.
1-NH_4-KMS; 2-K-KMS; 3-Na-KMS; 4- Ca $(KMS)_2$

As it is seen from the figure when dissolved, the capsule-forming polymer is first wetted, then it swells and the solvent (water) through the capillaries formed between the swollen fibers enters the granules coated with a polymer and begins to dissolve it. At the same time, osmosis pressure forms inside the capsule. The resulting pressure of osmosis, squeezing the fertilizer solution, causes it to gradually go out. Over time, the diameter of the capillaries increases and the rate of dissolution increases. This is even more found in granules coated with a 0.5 mm thick capsule-forming film. With an increase in the thickness of the capsule-forming film, the dissolution rate at first slowly, and then proportionally decreases and gradually increases. When the thickness of the capsule-forming film reaches 2.5 mm, a decrease in the dissolution rate is observed very strongly. This can be seen from the slope of the change in the curves in the direction of the xaxis. Therefore, when choosing the thickness of the capsule-forming film, it is necessary to take into account the vegetation period of the plants.

It is also seen from the curves that with a coating thickness of 0.5; 1.0; 1.5 mm swelling time is, respectively, 20, 40, 60 minutes. Also, with a diameter of 2.5 mm - 100 minutes. This is due to the difficulty of permeability of the solvent inside the encapsulated granules. At the time of swelling of the polymer also affects the degree of increase in the thickness of polymerization. Thus, with an increase in the degree of polymerization, the swelling time decreases, and with a decrease, it increases. This can be explained by the number of carboxymethyl groups of the macro chain of the capsule-forming polymer coatings. With a lower degree of polymerization in the macro chain, the number of carboxymethyl groups has a longer duration of dissolution, and in polymers having a higher degree of polymerization, the length of dissolution of such polymers is less.

Summarizing the above, the dependence of the duration of the dissolution of K_{hm} granules coated with polymer capsule-forming agents with different degrees of polymerization can be described by the following expression:

$$K_{h.m} = \frac{{n_1}/{n} \cdot d_k}{\delta} \qquad (1)$$

Given that

$$\delta = \frac{1}{2}\sqrt[3]{\frac{6m_o}{\pi\rho_o}}\left(\sqrt[3]{\frac{\rho_o}{\rho_{pr(1-\beta)}}}\right) \quad \text{və} \quad {n_1}/{n} = \frac{M_1(M - M_0)\cdot d_k}{M_0(M_2 - M_1)} \cdot d_k$$

Then *(4)*

$$K_{hm} = \frac{M_1(M - M_0)}{M_0(M_2 - M_1)} \cdot d_k \,/\, \frac{1}{2}\sqrt[3]{\frac{6m_o}{\pi\rho_o}}\left(\sqrt[3]{\frac{\rho_o}{\rho_{pb(1-\beta)}}}\right) \qquad (2)$$

where n_1 – number of elementary units is substituted by hydrophilic groups, pcs; M_0, M is the average additive molecular weight of an industrial polymer before and after the substitution of elementary units in the chain by hydrophilic groups, M_1 is the molecular weight of elementary units in the polymer chain, M_2 is the molecular weight of elementary units containing hydrophilic groups; δ — thickness of the capsule-forming film, mm; m_0 and m are the masses of the granules before and after encapsulation, kg; ρ_0 - the true density of the polymer granules before encapsulation, kg/m^3 ; ρ_{p} and $\rho_{\text{пр}}$ - the true density of the polymer and the average additive density of the encapsulated granule kg/m^2; β is the mass fraction of the film in the encapsulated granule, m_{p} is the mass flow rate of the polymer solution, kg; C_{p} – the concentration of the polymer solution, kg; $m_{\text{пс}}$ is the mass of a layer of granules, kg; $d_{\text{к}}$- average the additive diameter of capillaries, mm.

From the above graphs in Fig. 3, 4, 5, 6 and from the formula (1), (2) it is possible to determine the dependence of the duration of dissolution of the encapsulated granules with different degrees of the polymer coating.

Findings

Thus, the dependence of the permeability and duration of dissolution of the capsule-forming polymeric materials on the number of hydrophilic groups by the mixed elementary units of the polymer chain was investigated. It was determined that the change in the dependence of the permeability of polymeric coatings on the thickness is first straight and then parabolic. This change is associated with a timely increase in the diameter of the capillaries in the process of swelling. The graphical dependence of the change in permeability and duration of dissolution on the degree of polymerization of the polymer is indicated. To calculate the duration of dissolution proposed equations (1) and (2).

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