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DISTRIBUTION DESIGN OF PLASTICIZER USED FOR NITROCELLULOSE GRANULES SATURATION

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Abstract. The results of research of concentration distribution of plasticizer on the radius of cellulose nitrate granules are presented in the article. A smooth handing down profile of this distribution is confirmed for the cellulose nitrate granules obtained with the varnish method on the example of camphor and dibutyl phthalate. The mathematical description of this distribution, the basic parameter of which is determined with the plasticizer content in granules, is offered.

Keywords: plasticizer, granules, cellulose nitrates, saturation, distribution profile.

1. Introduction

Operational efficiency of many products from polymeric materials increases at saturation of their surface with low-molecular substances. In particular, saturation with plasticizing substance of blankets of the granules made from cellulose nitrates allows providing demanded characteristics of power-saturated materials [1, 2]. Saturation of such materials, along with the general content of the plasticizer, is also characterized by its distribution in the granules. Thus in many cases the operating parameters of the indicated materials depend exactly on distribution of plasticizer [1].

It is considered [2] that in the examined case the most efficient distribution of plasticizing substances approaches rectangular profile, *i.e.* with the constant concentration in the layers adjacent to the surface of granules (saturation zone). Such distribution simplifies calculations as allows entering the unambiguous characteristic of a saturation zone – its thickness. However, researchers have not reached consensus on the plasticizer content changes in granules of nitrocellulose and what factors the nature of its distribution depends on.

B. Brodman *et al.* [3, 4] determined the concentration of dibutyl phthalate in spherical cellulose nitrate granules with the method of isotope-tracers and came to the conclusion that the concentration of its plasticizer does not change by the thickness of the saturation zone. At the same time dependences obtained based on solution of the differential diffusion equation show that the distribution of low-molecular weight substances in a polymer cannot be even [5]. It is confirmed with the experimental data on the extraction of deterrent from spherical gunpowder [6], as well as concentration measurements of different plasticizers in cellulose nitrate granules with an interferential method of electron probe microanalysis [7].

The objective of this research is to evaluate the nature of the distribution of the plasticizer at its saturation of cellulose nitrate granules and to establish its dependence on technological parameters of saturation process based on the proposed model.

2. Experimental

2.1. The Characteristic of Raw Materials

The cellulose nitrates with nitrogen content no less than 13.0 % granulated with the varnish method were used at the experimental estimation of the nature of the distribution of plasticizer. The oriented fibrillar structure is absent in the granules received in such a way that influences their diffusive descriptions. For experimental researches cellulose nitrate granules with actual density 1300 kg/m^3 were used, that allowed to obtain a stable saturation zone.

Granules having a form near to spherical one (Fig. 1) and factious composition $0.315\cdot10^{-3}$–$0.4\cdot10^{-3}$ m – 25 %; $0.4\cdot10^{-3}$–$0.63\cdot10^{-3}$ m – 75 %, were saturated with a camphor or dibutyl phthalate. Dibutyl phthalate with qualification clean (state standard 8728-88) and synthetic camphor of brand A (state standard 1123-79250) were used.

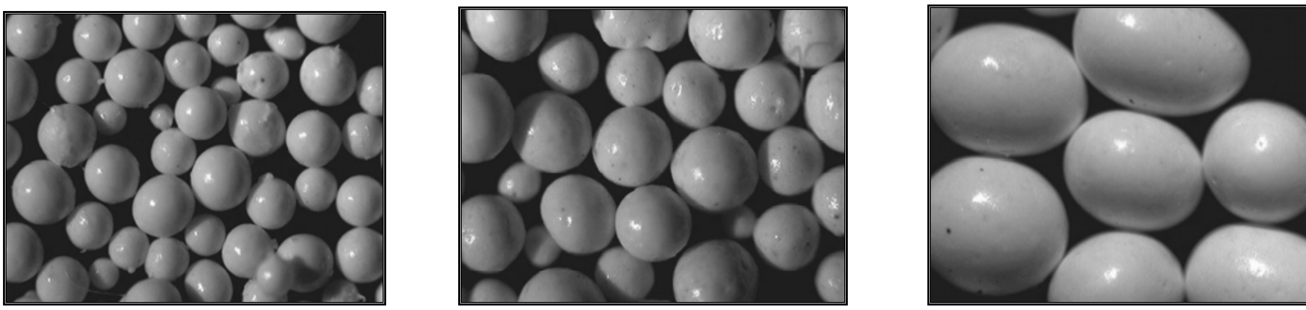

Fig. 1. The forms of granules obtained *via* varnish method

2.2. The Research Method

Granules were placed in plasticizer alcohol solution of the set concentration for saturation and maintained for a set time and then separated from the solution and dried at the temperature of 328–333 K. In the dried up granules we determined the general maintenance of plasticizer according to the change of its concentration in alcohol solution, which was measured with the gas chromatograph LHM-8MD, and the change of the plasticizer concentration according to the radius of granules using the methodology described below.

The methodology of determination of change of plasticizer concentration on the radius of granules is based on the layer-by-layer etching of granules with saponification of cellulose nitrate with alkaline solution. From the standard set of granules saturated with the plasticizer we took a sample with mass $M_1 = 5\cdot10^{-3}$ kg and made a selection of 20 granules from it. We determined the middle granule size for this selection under a microscope, expected mass of one granule and number of granules in the sample. Then the sample of granules was exposed to etch with 30 % potassium hydroxide solution at the temperature of 293 K during set time τ_1. After expiration of this time, granules were separated from the solution, washed with a saturated solution of boric acid, water and dried. We also took a selection in 20 granules from the dried up granules, determined the middle radius of granules after etching under a microscope and calculated the volume of the etched layer ΔV_1.

We measured the volume of alkaline solution obtained as a result of granules etching. Then we extracted this solution with a hexamethylene. The extract was analyzed on a gas chromatograph. The value of the plasticizer concentration in the extract was calculated on the volume-mass concentration (kg/m^3) in alkaline solution and mass of plasticizer was determined in it. This mass corresponds to its mass in the etched layer of granules.

The plasticizer concentration in the etched layer of granules a_1 was determined as

$$a_1 = \frac{M_1}{N \cdot \Delta V_1}, \text{ kg/m}^3$$

where N is determined number of granules in a sample.

Further we took a new sample of granules, etched a layer at etching time of $\tau_2 > \tau_1$ with measuring of grain size before and after etching and determined the concentration in the second layer by the difference of the masses of plasticizer in alkaline solutions after the second and the first etching. The same way we determined the concentration in the subsequent layers of granules. An index corresponding to the number of layer 1, 2, 3…n was appropriated to every obtained size.

We built the distribution curves of plasticizer according to the radius of the "averaged" sample of granules based on the obtained values concentrations. Thus amount of experimental points on which we built the distribution curves was determined by the choice of time of etching $\tau_1, \tau_2 \ldots \tau_n$.

3. Results and Discussion

The experimental concentration distributions of camphor and dibutyl phthalate in cellulose nitrate granules are shown in Fig. 2 (the beginning of coordinates is combined with the center of granule), built for the certain parameters of saturation process (to the initial concentration of solution C_i, solution temperature t, saturation time τ).

The analysis of these data shows that on the radius of granules the plasticizer concentration is unevenly distributed in the form of smooth dropping of curves to the abscissa axis. A rather sharp falling of concentration takes place near the surface of granules; concentration curves are gradually approaching the abscissa axis while moving away from the surface, which is typical of diffusion processes. The gradual change of concentration while moving away from the surface leads to uncertainty at the estimation of the thickness of the saturation zone, because the clear concentration border of this area is absent. In this case, as a thickness of the saturation zone we accepted the distance from the surface of granule to point-on-wave in which a plasticizer concentration is 1 % from its value on a surface (Fig. 3).

It is possible to use the previously proposed [9] approximation dependence for description of concentration distribution of plasticizer on the radius of granules

$$\frac{a - a_i}{a_0 - a_i} = 1 - \left[1 - \left(\frac{r}{R}\right)^m\right]^2 \qquad (1)$$

where a, a_i, and a_0 are local plasticizer concentrations: current value, in a center of granule, and on its surface, respectively.

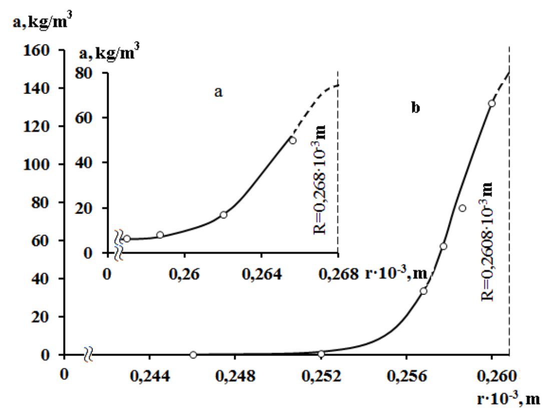

Fig. 2. The experimental concentration distributions of plasticizers on the radius of cellulose nitrate granules: dibutyl phthalate, $C_i = 1$ %, $t = 323$ K, $\tau = 300$ s (a) and camphor, $C_i = 10$ %, $t = 323$ K, $\tau = 3600$ s (b)

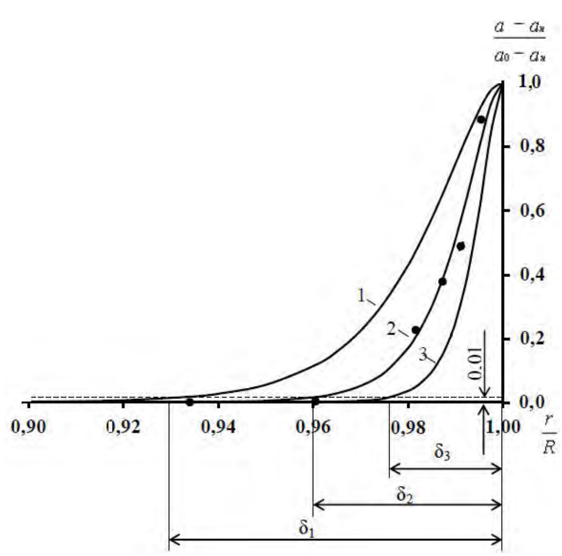

Fig. 3. The comparison of calculation and experimental types of concentration distribution of camphor: $m = 70$, $\delta_1 = 17.6\cdot10^{-6}$ m (1); $m = 120$, $\delta_2 = 10.4\cdot10^{-6}$ m (2) and $m = 200$, $\delta_3 = 7.2\cdot10^{-6}$ m (3). $C_i = 10$ %; $t = 323$ K; $\tau = 3600$ s

The index of degree m (distribution parameter) in dependence (1) characterizes the form of distribution profile and thickness of zone saturation. Its value for concrete terms is set experimentally.

In Fig. 3 points represent the experimental curves of concentration distribution at the saturation of cellulose nitrate granules with camphor ($C_i = 10$ %, $t = 323$ K; $\tau = 3600$ s) and lines represent the distribution curves calculated by the dependence (1) at the different values of deterrent parameter $m = 70$; 120; 200. From this comparison it follows that at the corresponding selection of value of parameter m, in this case m is equal to 120, the experimental distribution profile is well described with the dependence (1). The presented data show also that profiles of concentration distribution become more flat and thickness of the saturation zone increases with the reduction of parameter m.

In view of the complexity of obtaining the experimental curves of the concentration distribution of the plasticizer by the radius of granules and selection of distribution parameter m based on it, it is offered to determine this profile by the general average integral amount of plasticizer passing to the granules, based on the pattern offered in model [10].

Plasticizer is occluded according to this model on the surface of granules from the surrounding solution. Taking into account poor superficial porosity of cellulose nitrate granules received with the varnish method we ignore its saturation with capillary impregnation, considering that the adsorption surface coincides with the geometrical surface of granule. Adsorbed with the surface of granules plasticizer molecules penetrate into granules due to the diffusion, forming saturation zone in it [11]. At sufficient plasticizer content in the solution this zone broadens and its border moves up to the center of granule.

Formula relating mass of plasticizer received to the granule in the saturation process with the parameter m was obtained from the balance of the saturation zone on a plasticizer with the expression of local concentration from dependence (1)

$$\overline{G} = \frac{9a_0(1+m)}{(3+m)\cdot(3+2m)r_g} \qquad (2)$$

where $\overline{G} = G/M$ is relative mass of plasticizer received in granules; M is mass of granules, processed with plasticizer solution; r_g is density of powder granules used for saturation.

Formula (2) allows to define the parameter m at known (from experiment or calculation) value of relative mass of plasticizer in granules and its concentration on the surface of granules a_0 and respectively to calculate concentration distribution of plasticizer on the radius of granules by dependence (1).

Such a calculation was performed using the experimental data obtained at saturation of cellulose nitrate granules with camphor of alcoholic solutions, offered in work [11]. Its purpose was research of influence of regime parameters of saturation process on character of distribution of camphor on the radius of granules. The concentration of camphor on the surface of granules, corresponding to these parameters, was determined by dependence

$$a_0 = KC_i$$

where C_i is an initial concentration of camphor in alcoholic solution; K is a sorption coefficient, equal to 6.5 at the density of the saturated granules $\rho_g = 1300$ kg/m³.

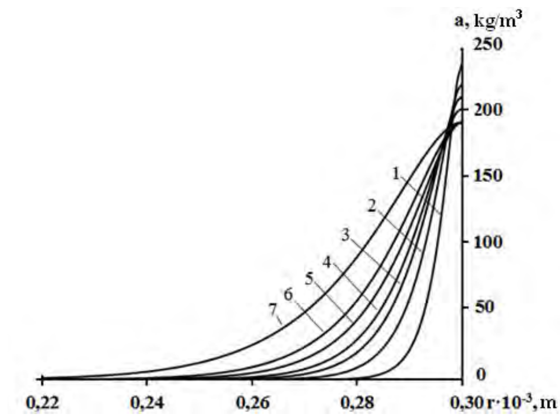

Fig. 4. The influence of saturation time τ on concentration distribution of camphor in the granules (s): 300 (1); 600 (2); 900 (3); 1200 (4); 2400 (5); 3600 (6) and 7200 (7). C_i = 5 wt%, t = 323 K

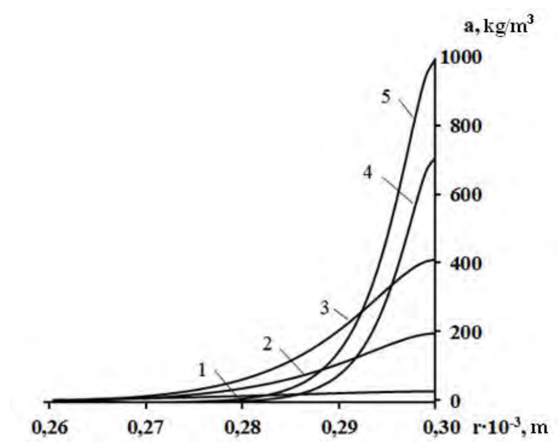

Fig. 5. The influence of solution concentration C_i on distribution of camphor in granules (wt %): 1 (1); 5 (2); 10 (3); 15 (4) and 20 (5)

The results of calculation showed that character of plasticizer distribution in cellulose nitrate granules depends on saturation time. The distribution curves of camphor on the radius of the granules, received at different saturation time from the solution, having the concentration of camphor C_i = 5 wt % and temperature of 323 K are given in Fig. 4.

It ensues from these data that with the increase of saturation time the distribution curves become more declivous and the saturation zone takes the greater volume of granule. Similar results were obtained at research of influence of solution temperature on distribution of camphor in granules at constant other parameters of process.

The research of influence of initial concentration of solution (t = 323 K; τ = 1800 s) showed that at its large values distribution is characterized by a sharp drop of the concentration of camphor on the radius of granules, at small values – the distribution is more smooth, with declivous location of curves (Fig. 5).

The concentration of solution renders most influence on the character of plasticizer distributions in cellulose nitrate granules from the considered parameters.

4. Conclusions

The character of concentration distribution of plasticizer on the radius of cellulose nitrate granules obtained with the varnish method is experimentally set on the example of camphor and dibutyl phthalate. Distributions are represented as smooth falling profiles with the maximum value of concentration on a surface of granules and the gradual decrease, approaching zero value, at moving away from the surface. Possibility of approximating of distributions by the previously proposed mathematical dependence is shown, where the parameter of distribution, included in this dependence, can be determined based on the developed model of saturation of granules on general content of plasticizer in them.

Such design of the distribution of plasticizer granules of cellulose nitrates, using camphor as an example, allowed establishing the influence of the parameters of the saturation process on the distribution of plasticizer on the radius of granules.

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МОДЕЛЮВАННЯ РОЗПОДІЛУ ПЛАСТИФІКАТОРА ПРИ НАСИЧЕННІ НИМ НІТРАТЦЕЛЮЛОЗНИХ ГРАНУЛ

Анотація. *В статті приведені результати дослідження розподілу концентрації пластифікатора за радіусом нітратцелюлозних гранул. На прикладі камфори та дибутилфталата підтверджений плавний спадаючий профіль цього розподілу для нітратцелюлозних гранул, одержаних лаковим способом. Запропоновано математичний опис цього розподілу, основний параметр якого визначається за середнім вмістом пластифікатора в гранулах.*

Ключові слова: *пластифікатор, гранули, нітрати целюлози, насичення, профіль розподілу.*