The study of a consistent pattern of heat and mass transfer at drying fiber-forming polymers

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Abstract. In this article, the consistent pattern of mass transfer in the process of drying granular polyethylene terephthalate (PET), polycaproamide (PCA), and polyamide 66 (PA 66) were studied. A modified quasi-stationary method was used to analyze the data. The characteristic time and the hydrodynamic intensity index were obtained based on experimental data. Some features of water sorption and desorption by fiber-forming polymers were studied.

1. Introduction
To select the drying process modes for any material, including polymer, it is necessary to determine its relation to water, and also to characterize the material as an object of drying.

There are several classification criteria for determining the hydrophobicity or hydrophilicity of polymers. These properties include the amount of absorbed moisture at a temperature of 20°C and relative humidity $\phi = 100\%$; the presence of polar groups in the polymer, high electrical resistance, and contact angle.

A significant number of review articles, collections, and monographs are devoted to the problems of the relationship between polymer material and water. We discussed this issue earlier in [1]. Based on the literature data, the material can be analyzed according to several classifications.

1. First, the ability of the material to absorb moisture from the air at 20°C and relative air humidity $\phi = 100\%$ are determined. The same ability determines the mechanism and rate of diffusion. According to this classification, groups of hydrophobic polymers are distinguished that absorb up to 2 wt.% of water, weakly swellable (from 2 to 10%), and hydrophilic (from 10 or more wt.%).

2. Secondly, the determination of the hydrophobicity of polymers can be due to the small number of polar groups. In this case, the polymer has low water and electrolyte sorption, high electrical resistance, and low dielectric constant.

3. Third, the contact angle, which exceeds 90° in the case of hydrophobicity of the polymer.

Even though some of the considered polymers have polar groups and the contact angle is slightly less by 90°, their properties correspond to hydrophobic polymers.
Let us consider PET, PA-66, and PKA polymers from the standpoint of their ability to absorb moisture from the air. According to this classification, polyethylene terephthalate (PET) belongs to hydrophobic polymers, and polyamides 6 and 66 are weakly swellable. Separately, it should be noted that the considered polymers can contain not only the surface but also internal moisture.

The need for drying the considered polymers is because they are subject to hydrolytic degradation, that is, the presence of moisture impairs the properties of the finished product. Characterization of the sorption properties of a polymer is not always sufficient to determine the material as an object for drying. Polyamides -6, -66, -610, -12 and polyethylene terephthalate, dried from water, according to the classification of S. Rudobashta are classified as non-porous materials, that is, the drying process obeys Fick's law of molecular diffusion [2].

According to the classification of B.S. Sazhin [3], these polymers are also combined into one group of materials with an ultramicroporous structure.

Table 1 shows the classification features of the considered polymers from the standpoint of their interaction with water, as well as their classification as an object of drying.

| Polymer | Equilibrium humidity in the air at 293 K and $\phi= 60\%$ | Water absorption, % (mass) | Material structure (by classification) | Class (subclass), characteristic, critical pore radius | Drying time, min |
|---------|----------------------------------------------------------|-----------------------------|---------------------------------------|-----------------------------------------------------|-----------------|
| PET     | 0.4-0.5                                                  | 0.5-0.8                     | non-porous                           | 4.3.0. granular materials                           | >60             |
| PA 66   | 3.5-4.5                                                  | 12-14                       | non-porous                           | 4.3.0. granular materials                           | >60             |
| PKA     | 3.5-4.5                                                  | 14-17                       | non-porous                           | 4.3.0. granular materials                           | >60             |

The classification of wet materials is necessary to select the drying mode and also to determine the most suitable method for calculating the process.

In [4], the possibility of classification of wet materials was considered, which was based on the analysis of the interfacial mass transfer of the processes implemented in the drying process. All drying options were divided by the authors into three types of tasks: external, internal, and balance. In this case, the assignment of a task to internal or external is determined by the criterion Bi.

For $Bi \geq 20$, the problem is considered internal, while for $Bi \leq 1$ it is external.

2. The basis for the choice of a mathematical model
When drying polymers, as a rule, internal diffusion predominates at relatively high Bio numbers. Moreover, as experiments show, there is usually no pronounced the first period of the process (a period of constant drying rate).

Considerable difficulties arise in the theoretical analysis of internal heat and mass transfer because there are [5] about fifteen elementary types of transfer of mass and heat, ranging from the simplest transfers, such as diffusion, thermal conductivity, convective transfers of mass of moisture and heat, to more complex filtration flows due to excessive pressures arising during the supply of heat inside porous materials with significant filtration resistance.

The system of differential equations [5] describing the process can be solved only numerically, and the solution of this system is often complicated by the instability of the solution.
To avoid laborious numerical calculations and find a large number of kinetic transfer coefficients, it was proposed [5] to use a simplified empirical model to describe the internal heat and mass transfer – a modified quasi-stationary method (MQS) obtained based on the diffusion and heat and mass transfer equations, which makes it possible to find refining coefficients based on the minimum experimental data.

The MQS method not only simplifies the calculations of the process but also makes it possible to reveal the limiting cases of the internal problem of kinetics. The MQS model is described by the following power-law dependence for dimensionless moisture content:

$$MR = \frac{1}{1 + (\tau / \sigma)^n}$$  \hspace{1cm} (1)

where MR is the dimensionless moisture content:

$$MR = \frac{w - w^*}{w_0 - w^*}$$  \hspace{1cm} (2)

$n$ is the exponent (index of hydrodynamic activity); $\sigma$ is the characteristic process time, which depends on temperature and material properties, $w$ is present, $w_0$ is the initial moisture content, and $w^*$ is the equilibrium moisture content.

The index of hydrodynamic activity depends on the medium movement velocity relative to the processed material, and also takes into account the heating period of the material.

It should also be noted that expression (1) is a dimensionless and generalizing equation for the kinetics of the internal drying problem.

To determine and obtain kinetic curves, experimental data are required, which are presented in Table 2. As mentioned earlier, the amount of experimental data can be minimal.

**Table 2. Typical points of the drying process (according to experiment)**

| Polymer | Initial moisture content, $w_0$, wt.% | Final moisture content, $w_e$, wt.% | Drying time, min |
|---------|---------------------------------------|-------------------------------------|------------------|
| PET     | 0.3                                   | 0.05                                | 390              |
| PA 66   | 9                                     | 0.4                                 | 21               |
| PKA     | 12.3                                  | 0.13                                | 33               |

Experimental data on the drying of three fiber-forming polymers – PCA, PET, and PA 66 were generalized using the MQS method.

For each experiment, the kinetic parameters $\sigma$ and $n$ were obtained. The values of the kinetic parameters are given in Table 3.

Also, Table 3 shows the final equilibrium moisture content that is required for a quality molding process for these polymers.

**Table 3.**

| Polymer | Characteristic time of the drying process, $\sigma$ | Hydrodynamic activity index, $n$ | Final equilibrium moisture content, $w^*$ |
|---------|--------------------------------------------------|----------------------------------|------------------------------------------|
| PET     | 93                                               | 2.16                             | 0.005                                    |
| PA 66   | 1530                                             | 1.3                              | 0.01                                     |
| PKA     | 4                                                | 1.4                              | 0.01                                     |

A generalization of the experimental data is presented graphically in Fig.1.
As is seen, when using the MQS model, it is enough to know two experimental points to estimate the kinetics of the drying process at any time.

Good agreement between the calculation and experimental data was obtained. The correlation coefficient was 97%.

The linearization of the generalizing dependence (1) was also performed employing the logarithmic coordinates. The agreement of the calculation with the experimental data is also good (Fig. 2).

![Generalization of data according to the MQS model. Test points designation: + - PKA, • •PET and ○- Polyamide PA 66.](image1)

**Figure 1.** Generalization of data according to the MQS model. Test points designation: + - PKA, • •PET and ○- Polyamide PA 66.

![Generalizing dependency linearization. Test points designation: + - PKA, • •PET and ○- Polyamide PA 66.](image2)

**Figure 2.** Generalizing dependency linearization. Test points designation: + - PKA, • •PET and ○- Polyamide PA 66.
3. Conclusion
A modified quasi-stationary method is considered for describing the internal heat and mass transfer of several polymers. These materials sorb water in different ways, the drying process has a different duration. Nevertheless, when describing the drying process from the standpoint of heat and mass transfer using MQS method, this model is obviously confirmed.

To find the kinetic regularities of these polymers, a numerical solution of the system of modified nonlinear equations of internal and external heat and mass transfer was carried out by the Galerkin method [6]. The obtained kinetic curves practically coincide with the curve shown in Fig. 1 obtained by the MQS method.

The linearization of the generalizing dependence (1) is carried out using the logarithmic coordinates.

This method makes it possible to predict the course of the drying process. To describe the process using the MQS method, it is necessary to know the kinetic coefficients n and s. If they are unknown, the coefficients can be determined with a minimum amount of experimental data.

The study was sponsored by RFBR in the framework of research project No. 19-08-00704.

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