Application of mathematical planning in production of filled emulsion rubbers

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Abstract. The applicability of mathematical planning of experiment in the field of chemistry and chemical engineering, in particular in the industrial production of synthetic rubbers, is considered in the article. Possibility of using secondary material resources, which are waste products of light industry, in the production of elastomeric compositions is studied. The method of obtaining a powdered cellulose additive from wastes containing cellulose fiber is described. The best way of introducing the obtained additive into elastomeric compositions based on the emulsion rubber is established. Optimal conditions for obtaining filled emulsion rubber with the help of a powdered cellulose additive were established basing on the mathematical planning of experiment.

1. Introduction

Nowadays a scientific and technological progress is developing rapidly. One of the factors driving this development is a widespread application of mathematical methods for carrying out the experiments at an industrial site aimed at processing the experimental data and constructing mathematical models of processes for finding optimal conditions of a technological process, which ultimately leads to an increase in technological and economic efficiency of the designed and operating facilities of various industries. The number of experiments for adequate model development can be minimized if one applies the methods of optimal design of the experiment. Besides, both time and material costs allocated for studying simulated processes can be significantly reduced. In a number of cases, the application of methods of regression and correlation analysis to study the industrial facilities makes it possible to obtain recommendations for optimizing their operation on the basis of statistical processing of the experimental data by the observational studies made at the site in the conditions of its normal operation. An additional advantage of this method is the possibility to identify and exclude mutual influence of the factors studied; to identify influence of certain factors on the output characteristic of the system under study, which makes it possible to describe practical recommendations on the technological process management being studied [1].

Today the industrial potential growth goes in line with the formation and accumulation of a significant amount of waste. About 1/3 of the consumed raw materials are spent on the production of industrial products, 2/3 are waste and by-products. Taking into account the fact that raw materials are not unlimited and are getting depleted, and a search for new deposits is associated with large costs, great attention is paid to the recycling and use of both polymeric waste products and old polymeric products. These include light industry enterprises that have raw materials available to produce fiber...
additives. A large number of fibers and fibrous materials are formed as waste in the textile enterprises, sewing workshops and others. Therefore, a search for the most promising fields of their application is an important and urgent task [2].

Fibrous additives are widely used in composite compositions involved in the production of rubber products. In industry, the main way to introduce fibrous additives into rubber compounds is carried out on the rollers during the rubber compound preparation. The presence of fiber additives in the compositions makes it possible to obtain products with a number of positive properties. However, the introduction on the rollers does not allow achieving their uniform distribution in the volume of a rubber compound, which in turn is reflected in both physical and mechanical parameters of vulcanized rubber.

In works [3, 4] that were published it was noted that in rubbers obtained by the emulsion method fiber additives should be introduced with an acidifying agent from latex at the separation stage. However, using such method, a small amount of fiber additive (up to 1% wt.) can be introduced into the rubber. At present, introduction of higher dosage of additives into the rubber at the production stage is very topical. In this connection it is of great interest to convert a fiber additive into a powdered state, which should allow preparation of a rubber composite with a high additive content. In addition, the conversion of the fiber additive into a powdery state should have a different effect on the properties of the resulting composites rather than a fibrous component. At the same time, fiber and powder additives are of the same nature.

This article is devoted to the establishment of optimal conditions to create elastomeric compositions in the presence of a powdered additive derived from light industry waste, using mathematical planning of experiment.

2. Materials and methods
A powdered additive, waste containing cellulose fiber and end-of-life products on its basis were used for the production. The cotton fibers, items or wastes were ground and treated with an aqueous solution of sulfuric acid in the process of heating and constant stirring. After that the obtained mushy mass (fiber + sulfuric acid solution) was filtered. Then, the powdered additive was dried after which the powder was further comminuted to a finer-dispersed state (size of the main fraction was 0.5 mm) [5]. The obtained acidic powdered cellulose additive contained sulfuric acid residues, as well as the products of its interaction with cellulose. Next, the acidic powdered cellulose additive was neutralized with alkali and a neutral powdered cellulose additive (NPC) was obtained.

From the technological point of view of obtaining filled emulsion rubbers an important factor would be the selection of the NPC introduction method. The process for the isolation of rubber from latex was studied using the laboratory installation consisting of a vessel equipped with a stirrer and placed in a thermostat to maintain temperature. The coagulator was loaded with latex (dry residue ~ 18% by weight) and thermostated at a set temperature for 10-15 minutes. In the disclosed methods, the NPC was introduced into the resulting rubber crumb at the stage of latex separation, using an aqueous solution of aluminum chloride (10% wt.) and an acidifying agent - an aqueous solution of sulfuric acid (1-2% wt.) as a coagulating agent. The content of the powdered additive varied from 0.5 to 25% wt. for rubber.

The cellulosic additive was introduced in the following ways: in a dry form directly into the latex before applying it for coagulation; in dry form into latex, containing a coagulating agent; in latex together with an aqueous solution of a coagulating agent; with sulfur at the final stage of the release of rubber from latex.

3. Results and clarification
Analysis of the obtained data makes it possible to conclude that it is expedient to introduce the powdered cellulose additive with a coagulating agent. It should be noted that introduction of a powdered cellulose additive in the amount of up to 5.0% for rubber provides its full capture by a formed crumb of rubber. Increasing the dosage of the powdered cellulose additive from 5.0 to 25% wt.
for rubber leads to its partial loss with sulfur and washing water in the amount of 5 to 10%, respectively.

Another task when obtaining elastomeric compositions is the problem of optimization, i.e. finding such combination of influencing independent variables at which the chosen optimality index takes an extreme value. The experiment was planned to be applied to one of the most important technological stages of the process of obtaining elastomeric compositions - the coagulation stage of latex emulsion rubbers. To determine the factors that have the greatest impact on the process of obtaining filled emulsion rubbers, a study of the coagulation process in the presence of NPC was carried out with the help of a full factor experiment. For this purpose an experimental design was developed with the help of full factor experiment $2^3$ for the coagulation of emulsion rubber latex in the presence of a neutral powdered cellulosic additive, using aluminum chloride as a coagulant. The matrix of planning full factorial experiment $2^3$ is shown in Table 1.

The regression equation with the coefficients of two-way and three-way interactions is as follows:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{123}x_1x_2x_3.$$  

The third order regression members can be neglected because of their insignificant influence on the output regression value. Then the regression equation is presented as follows:

$$Y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_4 + b_{12}x_1x_2 + b_{13}x_1x_3.$$  

According to compiled matrix N = $2^3 = 8$, experiments were conducted at the upper and lower levels of the variable factors. To calculate the variance of reproducibility, which characterizes the experimental error, each experiment was duplicated twice (n = 2) and the line-by-line variances of these experiments were calculated. The results of the calculation are presented in Table 2. The values of the variable factors are given in Table 3.

### Table 1. Matrix of planning full factorial experiment $2^3$

| No. of experiment | $x_0$ | $x_1$ | $x_2$ | $x_3$ | $x_1x_2$ | $x_1x_3$ | $x_2x_3$ | $y$  |
|-------------------|------|------|------|------|---------|---------|---------|-----|
| 1                 | -1   | -1   | -1   | -1   | 1       | 1       | 1       | 44.30 |
| 2                 | -1   | 1    | -1   | -1   | 1       | 1       | -1      | 93.50 |
| 3                 | 1    | -1   | -1   | -1   | -1      | 1       | -1      | 46.20 |
| 4                 | 1    | 1    | -1   | -1   | 1       | -1      | -1      | 92.50 |
| 5                 | 1    | -1   | -1   | -1   | -1      | -1      | -1      | 55.10 |
| 6                 | 1    | 1    | -1   | -1   | 1       | -1      | -1      | 98.10 |
| 7                 | 1    | -1   | 1    | -1   | -1      | 1       | -1      | 56.10 |
| 8                 | 1    | 1    | 1    | 1    | 1       | 1       | 1       | 98.60 |

### Table 2. Processing of results of coagulation tests of latex in the presence of an NPC using aluminum chloride

| No. of experiment | Experiment results | average | dispersion |
|-------------------|--------------------|---------|------------|
| 1                 | 44.5               | 44.1    | 44.3       | 0.08       |
| 2                 | 93.9               | 93.1    | 93.5       | 0.32       |
| 3                 | 46.4               | 46.0    | 46.2       | 0.80       |
| 4                 | 92.8               | 92.2    | 92.5       | 0.18       |
| 5                 | 55.4               | 54.8    | 55.1       | 0.18       |
| 6                 | 98.4               | 97.8    | 98.1       | 0.17       |
| 7                 | 56.3               | 55.9    | 56.1       | 0.08       |
| 8                 | 98.8               | 98.4    | 98.6       | 0.07       |
### Table 3. Values of variable factors

| Optimization parameters | Factor | Factor levels | Variation interval |
|-------------------------|--------|---------------|--------------------|
|                         | notification | real | coded | upper | lower | general |
| Consumption of aluminum chloride, kg/ton of rubber | $V_1$ | $x_1$ | 4 | 0.3 | 2.15 | 1.85 |
| Dosage of NPC, % wt. for rubber | $V_2$ | $x_2$ | 5 | 0.5 | 2.75 | 2.25 |
| Sulfuric acid consumption, kg/ton of rubber | $V_3$ | $x_3$ | 15 | 6 | 10.5 | 4.5 |

The adequacy test was carried out using the variance analysis. Fisher’s criterion is $F = 16655.0$. The obtained value is compared with the table value of the Fisher test $F_{tabl} = 2.8$. The condition of $F_{tabl} < F$, is satisfied and the statistical model found can be considered adequate, i.e. the equation adequately describes the results of experiment.

The coefficient $b_{23}$ is not significant. Then the regression equation is presented as follows:

$$Y = 73.05 + 22.62x_1 + 0.29x_2 + 3.92x_3 - 0.43x_1x_2 - 1.25x_1x_3.$$  

With the natural values of variables introduced, the regression equation is presented as follows:

$$Y = 33.26 + 14.09V_1 + 0.35V_2 + 1.19V_3 - 0.10V_1V_2 - 0.15V_1V_3$$

where $V_1$ is the consumption of aluminum chloride, kg/ton of rubber; $V_2$ is the dosage of NPC, % wt. for rubber; $V_3$ is the sulfuric acid consumption, kg/ton of rubber.

The analysis of coefficients of the regression equations made it possible to visually display the effect of the factors under consideration on the coagulation process estimated from the yield of the formed rubber crumb (Fig. 1).

Fig. 1. The effect of aluminum chloride consumption ($q$, kg/ton of rubber) and the dosage of NPC (d, % wt. for rubber) on the coagulation process

The analysis of coefficient values and signs of the regression equations allows us to state that the main influence on the coagulation process of emulsion rubbers is exerted by the consumption of aluminum chloride and sulfuric acid. It should be noted that the coefficient describing the effect of dosage of NPC on the coagulant consumption is significant. The introduction of NPC together with the coagulating agent leads to a reduction in its consumption twice as much, which contributes to the
reduction of waste water contamination with coagulant residues, and as a consequence, a reduction in the environmental load on the environment.

4. Conclusions
Basing on the results of work, the following conclusions can be made:
- light industry waste can be used to produce a powdered additive for emulsion rubbers;
- powdered additive should be introduce into the emulsion rubbers during the coagulation stage in the process of creating the elastomeric compositions;
- the main factors affecting the process of coagulation of emulsion rubbers are the consumption of both the coagulant and acidifying agent;
- powdered additive introduction together with the coagulant makes it possible to reduce its consumption, as well as to reduce the negative effect on the environment caused by the industrial wastewater.

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