Full factor plan application to polymer composites hardness investigation

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Abstract. Polymer composites have become widespread in many fields of technology. The article considers the creation of a mathematical model for predicting the hardness of dispersed-filled polymer composite materials based on silicone rubbers of synthetic heat resistant low molecular weight rubber A type with fine aluminium hydroxide powder addition. A full factor experiment was chosen as a test method. The main statistical criteria were checked, the reproducibility of the experiments and the adequacy of the obtained model were shown.

1. Introduction
At present, polymer composites are used in almost all fields of engineering, in most industries (aircraft and rocket construction, shipbuilding, microelectronics, etc.) [1]. One type of such composites is dispersed-filled polymer composites, which are used as specialized coating materials, sealants, compounds and adhesives. The main quality indicators of dispersed-filled polymer composites include hardness, tensile strength and elongation, specific volume resistance [2]. Hardness is one of the most important characteristics among physical and mechanical characteristics of materials [3].

Levels of hardness values, as well as other listed material quality indicators, depend on a variety of factors (polymer and filler grade, component ratio, filler pretreatment mode, mixing time, availability of additional modifiers). Objectively, they can be evaluated only on the basis of measurements made on specially prepared samples. An alternative option is to use a mathematical model to predict hardness values levels for different combinations of influencing factors. This method saves resources and increases efficiency in the development of new polymer composites structures.

The aim of the research is to define a mathematical model allowing to predict the hardness of dispersed-filled polymer composites with high accuracy. The main objectives are to select the modelling method, to plan and implement the experimental research, to evaluate regression coefficients and to verify the main statistical criteria.

2. Materials and methods
Polymer composites samples based on silicone rubbers of the synthetic heat resistant low molecular weight rubber A type with fine aluminium hydroxide powder addition is the object of this research. Shore hardness [1] is chosen as the studied characteristic. Hardness measurement was carried out using a portable hardness meter NOVOTEST TSh-A. A full factor experiment was chosen as a test method.

The impact on the response function of the investigated process not only of each factor considered in the experiment alone, but also of their interactions is generally taken into account when considering
the full factor experiment [4]. The impact effect of the change in values of one or more factors on the nature of the change in response function Y from the change in another factor is meant by factor interaction.

Main stages of the full factor experiment [5-7]:

- Select factors and define variation levels
- Model selection
- Planning matrix creation

The planning matrix must meet the conditions of orthogonality, normality, symmetry relatively to the center of the extremum, rotatability.

- Experiment conduction
- Polynom coefficients calculation
- Statistical testing of hypotheses about the properties of the experiment [8]
  - assessment of experiments reproducibility;
  - evaluation of regression coefficients significance;
  - model adequacy assessment

Let us consider the controlled factors in this research. Mass fraction of filler (Al(OH)₃, %) in the mixture is selected as the first controlled factor, since on average there is an increase in strength as the content of filler in the mixture increases for most polymeric composites variants.

Mechanical-chemical processing also refers to filler - it is application of filler particles on the surface during their grinding (disintegration) of a thin layer of auxiliary substances (in this case - vinylsilane). The last controlled factor is the addition of polymethylsiloxane (PMS-50) to the composite composition.

A summary list of controlled factors with variation levels is presented below:

- Filler ratio, % by weight - 2 levels (30 and 50);
- Mechanical-chemical processing – 2 levels (no processing/vinylsilane);
- Presence of polymethylsiloxane (PMS-50), % by weight - 2 levels (0 and 5).

In case when the three factors vary on two levels, the number of experiments will be N=2³=8, and the planning matrix of the full factor plan will be as shown in table 1.

| Table 1. Planning matrix of the full factor plan. |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| X0   | X1   | X2   | X3   | X1X2 | X2X3 | X1X3 | X1X2X3 |
|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| 1    | +    | –    | –    | –    | +    | +    | –    |
| 2    | +    | +    | –    | –    | –    | +    | –    |
| 3    | +    | –    | +    | –    | –    | –    | +    |
| 4    | +    | +    | +    | –    | +    | –    | –    |
| 5    | +    | –    | –    | +    | +    | –    | –    |
| 6    | +    | +    | –    | +    | –    | –    | +    |
| 7    | +    | –    | +    | +    | –    | +    | –    |
| 8    | +    | +    | +    | +    | +    | +    | +    |

A graphical interpretation of the location of conditional factor levels relative to the plan center is shown in figure 1.
Figure 1. Experimental points location in case of full factor plan.

Table 2 lists the effect levels of the factors X1, X2, X3 interaction effect.

| Level | Filler fraction, % X1 | Mechanical-chemical processing X2 | Presence of polymethylsiloxane (PMS-50) X3 |
|-------|-----------------------|----------------------------------|------------------------------------------|
| 1     | 30                    | no                               | no                                       |
| 2     | 50                    | vinyl silane                     | yes                                      |

Based on the full factor plan, it is necessary to draw up a matrix of sample compositions for their manufacture and subsequent hardness measurement. The resulting matrix is shown in table 3.

Table 3. Sample composition matrix for the experiment.

| Sample № | Synthetic heat resistant low molecular weight rubber A, weight % (x1) | Al(OH)₃, weight % (x2) | Mechanical-chemical processing (x3) | Presence of polymethylsiloxane (PMS-50), weight % (x3) |
|-----------|---------------------------------------------------------------------|------------------------|------------------------------------|-------------------------------------------------|
| 1         | 70                                                                  | 30                     | -                                  | 0                                               |
| 2         | 50                                                                  | 50                     | -                                  | 0                                               |
| 3         | 70                                                                  | 30 vinyl silane        | -                                  | 0                                               |
| 4         | 50                                                                  | 50 vinyl silane        | -                                  | 0                                               |
| 5         | 65                                                                  | 30                     | -                                  | 5                                               |
| 6         | 45                                                                  | 50                     | -                                  | 5                                               |
| 7         | 65                                                                  | 30 vinyl silane        | -                                  | 5                                               |
| 8         | 45                                                                  | 50 vinyl silane        | -                                  | 5                                               |

3. Results and discussion

According to the matrix given in table 3, polymer composites samples were prepared for subsequent hardness measurement. The results of the Shore hardness measurements of the samples are recorded in table 4.

Table 4. Hardness measurements results.

| № | Measured values of Shore hardness, units | Yav, units |
|---|-----------------------------------------|------------|
|   | y1                                      | y2         | y3         | y4         | y5         |
Calculation of regression coefficients \((b_i)\) of full factor experiment is performed by standard equation (1), in which conditional levels of the current factor are substituted.

\[
b_i = \frac{1}{N} \sum_{j=1}^{N} x_i y_i
\]  

(1)

The resulting regression coefficient values are recorded in table 5.

**Table 5.** Regression coefficients calculation results.

| N   | X0  | X1  | X2  | X3  | X1X2 | X2X3 | X1X3 | X1X2X3 |
|-----|-----|-----|-----|-----|------|------|------|--------|
|     | b_i |     |     |     |      |      |      |        |
| 1   | 35  | 36  | 37  | 35  | 35   | 35.6 |      |        |
| 2   | 42  | 43  | 41  | 42  | 41   | 41.8 |      |        |
| 3   | 29  | 30  | 31  | 30  | 31   | 30.2 |      |        |
| 4   | 37  | 39  | 39  | 38  | 40   | 38.6 |      |        |
| 5   | 33  | 34  | 33  | 31  | 33   | 32.8 |      |        |
| 6   | 40  | 39  | 41  | 40  | 38   | 39.6 |      |        |
| 7   | 27  | 28  | 26  | 25  | 28   | 26.8 |      |        |
| 8   | 35  | 33  | 34  | 32  | 33   | 33.4 |      |        |

The results of the test of the main statistical criteria are presented below.

The hypothesis of statistical significance (difference from zero) of regression coefficients is tested according to Student's criterion. Data for calculations are taken from tables 5-6, obtained results of Student's criterion values are given in table 7. Calculation of \(t_{\text{calc}}\) is performed as per formula:

\[
t_{\text{calc}} = \frac{|b_i|}{\sqrt{S_y^2/N}}
\]  

(2)

Calculation of reproducibility dispersion is performed by formula:

\[
S_y^2 = \frac{1}{(N-1)} \sum_{i=1}^{N} (y_i - y_{av})^2
\]  

(3)

**Table 6.** Results of experiment reproducibility dispersion calculations.

| \(Y_{av}\) | 35.6 | 41.8 | 30.2 | 38.6 | 32.8 | 39.6 | 26.8 | 33.4 |
|-----------|------|------|------|------|------|------|------|------|
| \(S_{yi}^2\) | 0.8  | 0.7  | 0.7  | 1.3  | 1.2  | 1.3  | 1.7  | 1.3  |
| \(S_{y}^2\) |      |      |      |      |      |      |      | 1.125|

**Table 7.** Student’s criterion values results.

| \(t_{\text{calc}}\) | 92.93 | 9.33 | 6.93 | 4.53 | 0.67 | 1.2  | 0.4  | 0.8  |
|----------------------|-------|------|------|------|------|------|------|------|

Critical value of criterion \(t_{cr}\) is found from table of Student’s distribution by number of degrees of freedom \(f = N (K-1)\) and level of significance \(q\).

For the experiment in question \(q = 0.05\) and \(f = 32\), thus the tabular value of the Student's criterion \(t_{cr} = 1.694\).
Since the condition of the criterion is $t_{calc} > t_{cr}$, then all the coefficients of the linear factors are significant, and the interactions are insignificant. A mathematical model containing only significant coefficients is as follows (4):

$$y = 34.85x_0 + 3.5x_1 - 2.6x_2 - 1.7x_3$$  \hspace{1cm} (4)

The uniformity (equality) of the dispersions hypothesis characterizing the reproducibility of the experiments conducted in the experiment was tested by the Cochran criterion. The statistics of the criterion are the following ratio:

$$G_{calc} = \frac{\max s_i^2}{\sum s_{yi}^2}$$  \hspace{1cm} (5)

For the obtained value estimates $S_2yi$ from table 6, we have:

$$G_{calc} = \frac{1.7}{0.8+0.7+0.7+1.3+1.2+1.3+1.7+1.3} = 0.189.$$  \hspace{1cm} (6)

Critical value $G_{cr}$ is found from table of Cochran distribution by number of degrees of freedom of numerator $f_1 = K - 1$, denominator $f_2 = N$ and significance level $q$. For the experiment in question, $f_1 = 4$, $f_2 = 8$, $P = 0.95$, thus the table value of the Cochran criterion $G_{cr}$ is 0.391.

Since $G_{calc} < G_{cr}$, the dispersion uniformity hypothesis is correct, the experiments are reproducible. The adequacy of the obtained mathematical model is checked against Fisher’s $F$ criterion. Its calculated value is found to be quotient from dividing the inadequacy variance estimate by the single observation variance estimate.

$$F_{calc} = \frac{S^2_{a}}{S^2_{y}}$$  \hspace{1cm} (7)

where $S_a > S_y$.

If this inequality is not fulfilled, the dispersions must be reversed.

$$S^2_{a} = \frac{1}{(N-L)} \sum_{i=1}^{N} (y_{j'} - y_{jav})^2,$$  \hspace{1cm} (8)

where $L$ is the number of significant coefficients of the regression equation under research, including $b_0$.

Table 8 shows the intermediate values for calculating non-uniformity dispersion values.

| y1 | y2 | y3 | y4 | y5 | $Y_{exp}$ | $Y_{calc}$ | $(Y_{calc} - Y_{exp})^2$ |
|----|----|----|----|----|-----------|------------|-------------------|
| 1  | 35 | 36 | 37 | 35 | 35       | 35.65      | 0.0025           |
| 2  | 42 | 43 | 41 | 42 | 41       | 42.65      | 0.7225           |
| 3  | 29 | 30 | 31 | 30 | 31       | 30.45      | 0.0625           |
| 4  | 37 | 39 | 38 | 40 | 38.6     | 37.45      | 1.3225           |
| 5  | 33 | 34 | 33 | 31 | 33       | 32.25      | 0.3025           |
| 6  | 40 | 39 | 41 | 40 | 39.6     | 39.25      | 0.1225           |
| 7  | 27 | 28 | 26 | 25 | 28       | 27.05      | 0.0625           |
| 8  | 35 | 33 | 34 | 32 | 33.4     | 34.05      | 0.4225           |

The $S^2_{2ad lin}$ inadequacy dispersion value is 0.755.

Critical value $F_{cr}$ is found from Fisher distribution table by number of degrees of freedom of numerator $f_2 = (N-L)$, denominator $f_1 = N \ (K-1)$ and significance level $q$. If $F_{calc} > F_{cr}$ the adequacy hypothesis is rejected.
Using the data in table 8, the linear models (4) can be checked for adequacy. By substituting the values of the two dispersions in expression (7), we obtain

\[ F_{\text{calc}} = 1.49 \quad (9) \]

The degrees of freedom of the numerator and denominator of fraction (6) \( f_1 = 32, f_2 = 4 \), so the table value of the Fisher criterion is 5.74. Since \( F_{\text{calc}} < F_{\text{cr}} \), the linear model is adequate. It follows that the full factor experiment method confirmed the importance of the influence of each of the three considered factors on the strength level of the composites.

4. Conclusion

From the results of carrying out and processing the results of full factor experiment \( 2^3 \), a linear model of the dependence of the Shore hardness of polymer composites based on silicone rubber with aluminium hydroxide (\( \text{Al(OH)}_3 \)) on three influencing factors: the weight fraction of filler, the nature of filler processing and the content of polymethylsiloxane (PMS-50) was obtained. A review of the main statistical criteria showed that the experiments were reproducible and the model was adequate. Thus, the full factor experiment technique can be successfully used to study Shore hardness of the dispersed polymer composites of discussed type. Further studies will be aimed at assessing the applicability of full factor experiment for modeling other polymer composites quality indicators and the accuracy of the forecast of resulting models.

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