Comparative analysis of thermofluctuation constants of polyvinyl chloride plates obtained in various ways

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Abstract. To reliably predict efficiency of solids, it is necessary to know the values of their thermofluctuation constants, which are determined by experimentally obtained data using graphical, graphoanalytical, and mathematical methods. Using the same initial data, the thermal fluctuation constants were determined by different methods. The graphical method is presented by calculation using graphs built on graph paper. The graphic-analytical method uses MS Excel. The mathematical method operates directly with equations instead of a graphical representation. It is shown that the chosen method of obtaining the constants has a significant effect on the final result. It is recommended to use a mathematical method when determining the thermal fluctuation constants.

1. Introduction

One of the key stages in the development of physical concepts of strength is to take into account the influence of the thermal motion of atoms on the destruction process [1-4]. The need to explain the presence of the temperature-time dependence of the process of destruction and deformation led to the formation of the postulate that the decisive factors in the destruction of a solid are the thermal motion of atoms [1,5,6]. This postulate formed the basis of the thermofluctuation concept of fracture and deformation of a solid. Thus the durability of the body depends on operating conditions (under ideal conditions, temperature and load) and the so-called thermofluctuation constants: \( \tau_m, U_0, \gamma, T_m \), and is determined by the formula [7-9]:

\[
\tau = \tau_m \cdot \exp \left[ \frac{U_0 - \gamma \cdot \sigma}{R} \cdot \left( \frac{1}{T} - \frac{1}{T_m} \right) \right],
\]

where, \( \tau \) – the durability of the material or the time until reaching one of the limiting conditions, \( c \); \( R \) – universal gas constant, kJ/mol*K; \( \sigma \) – stress, MPa; \( T \) – temperature, K; \( \tau_m, U_0, \gamma, T_m \) are thermofluctuation constants.

To determine the thermofluctuation constants of the generalized Zhurkov equation, we use a technique based on the reconstruction based on the experimental data of a graph of the dependence of the logarithm of durability on voltage into a graph of the dependence of the logarithm of durability on the inverse temperature, from which two of the four constants are determined. The remaining two constants can be determined from the dependence of the activation energy from the tension. Although the methodology is uniform, there are three possible scenarios for its implementation: the graphical
method, graphoanalytical and mathematical. The determination algorithm for all methods is the same, however, the reliability of the results will be different, which will be shown below.

2. Research methodology

Based on the experimental data obtained, a graph is constructed in the coordinates \( \log \tau - \sigma \) (Figure 1, a), in which the three created lines are straight lines of temperatures. These lines can form a family of fan-shaped lines that converge at a point. The next step in determining the constants is to rebuild the resulting graph (Figure 1, a) into a graph in the coordinates \( \log \tau - \frac{1000}{T} \) (Figure 1, b), in which the straight lines are the lines of stresses. To implement such a rearrangement, three tensions which must intersect the temperature lines (Figure 1) in the first positive quarter are selected arbitrarily. The intersections of the selected stresses with temperature lines give the coordinates of the points of tension lines in the coordinate system \( \log \tau - \frac{1000}{T} \). Thus, the coordinates of the graph points in the coordinate system \( \log \tau - \frac{1000}{T} \) along the abscissa axis are the inverse of the direct temperature times 1000 and the point of intersection with the line of the corresponding temperature along the ordinate.

![Figure 1](image_url)

**Figure 1.** The scheme for determining the thermofluctuation constants of the generalized Zhurkov equation: 

- a – a graph in the coordinates \( \log \tau - \sigma \) with selected stresses \( \sigma \) crossing the temperature lines;
- b – a graph in \( \log \tau - \frac{1000}{T} \) coordinates with determination of two constants based on the pole point;
- c – a graph in coordinates \( U - \sigma \) with determination of the remaining thermofluctuation constants.

In the case of the forward and backward beams in the \( \log \tau - \frac{1000}{T} \) coordinates, we also obtain a family of fan-shaped straight lines that converge at a point called the pole. The coordinates of the pole point allow us to determine two constants of the generalized Zhurkov equation: \( \log \tau_0 \) and \( T_m \), where \( \log \tau_0 \) is directly the coordinate of the point, and \( T_m \) is found from the ratio \( \frac{1000}{T_m} \).

To determine the remaining two constants \( U_0 \) and \( \gamma \) for each tension line by the formula (2), the activation energy value should be calculated [7].

Then, according to the data obtained, a graph is constructed in the coordinates \( U - \sigma \) (Figure 1, c). By extrapolating the resulting straight line to the ordinate axis (Figure 1, c), the constant \( U_0 \) can be found. The slope of this straight line for the direct beam corresponds to the structural-mechanical constant \( \gamma \).

The thermofluctuation constants of the generalized Zhurkov equation were determined in three different ways (graphical, graphoanalytic, and mathematical) based on experimentally obtained data on the dependence of durability on temperature of polyvinyl chloride plates [10-12] under transverse bending [13].

When implementing the graphical method, the following constant values were obtained: \( \tau_m = 0.18 \) s; \( U_0 = 370 \) kJ/mol; \( \gamma = 58 \) kJ/(mol•MPa); \( T_m = 390 \) K.
When implementing graphoanalytical method using «Microsoft Excel» program by plotting, the following values of constants were obtained [14]:

\[ \tau_m = -0.011 \text{ s}; \]
\[ U_0 = -327 \text{ kJ/mol}; \]
\[ \gamma = -48 \text{ kJ/(mol\cdot MPa)}; \]
\[ T_m = 431 \text{ K}. \]

Taking into account the fact that graphs are only a way of displaying any facts, but not their essence, the thermofluctuation constants of the generalized Zhurkov equation can be found directly using mathematical analysis (mathematical method).

When constructing a family of lines from a set of initial points, it is reasonable to apply the least squares method. The method is based on minimizing the sum of squared deviations of some functions from the desired variables [15-18]. It can be used to “solve” overdetermined systems of equations (when the number of equations exceeds the number of unknowns), to find a solution in the case of ordinary (not redefined) nonlinear systems of equations, to approximate the point values of some function. OLS is one of the basic regression analysis methods for estimating unknown parameters of regression models from sample data [19,20]. In this case, based on experience, we can assume that the dependence of the decimal logarithm of durability at a given temperature on tension is linear. Thus, we are faced with the problem of linear approximation. It is necessary to find an equation that describes the line of this very dependence. According to the method, the equation must satisfy the condition under which the function of two variables \( F(a,b) = \sum (y_i - (a \cdot x_i + b))^2 \) takes the smallest value. Or in other words, the sum of the squares of the deviations of the sample points from this line will be minimal. This ensures high accuracy of the approximation over the entire length of the function.

For this case, it is necessary to solve a system of equations with two unknowns. Since it is necessary to find the minima of the functions, the equations will describe the extrema of these functions, i.e. the point where the partial derivatives are equal to zero.

\[
\begin{align*}
\frac{\Delta F(a,b)}{\Delta a} = 0 & \iff -2\sum_{i=1}^{n} (y_i - (a \cdot x_i - b)) \cdot x_i = 0 \\
\frac{\Delta F(a,b)}{\Delta b} = 0 & \iff -2\sum_{i=1}^{n} (y_i - (a \cdot x_i - b)) = 0 \\
\sum_{i=1}^{n} x_i^2 + b \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} x_i y_i & \iff a \sum_{i=1}^{n} x_i^2 + b \sum_{i=1}^{n} x_i = \sum_{i=1}^{n} y_i \\
\sum_{i=1}^{n} x_i + nb = \sum_{i=1}^{n} y_i & \iff a \sum_{i=1}^{n} x_i + nb = \sum_{i=1}^{n} y_i \\
\end{align*}
\]

here, \( x, y \) are the coordinates of the points from the sample; \( n \) is the number of points in the sample.

Using this method, the following direct temperature equations are obtained:

\[ T = 15 \text{ °C} \implies \lg \tau(\sigma) = -2.484 \cdot x + 15.766; \]
\[ T = 30 \text{ °C} \implies \lg \tau(\sigma) = -1.822 \cdot x + 11.366; \]
\[ T = 45 \text{ °C} \implies \lg \tau(\sigma) = -2.247 \cdot x + 13.381. \]

To determine the pole, it is necessary to determine the intersection points of each function relative to each other.

\( T = 15 \text{ °C} \) and \( T = 30 \text{ °C} \): Intersection coordinate: \( (6.647; -0.744) \).

\( T = 15 \text{ °C} \) and \( T = 45 \text{ °C} \): Intersection coordinate: \( (10.063; -9.231) \).

\( T = 30 \text{ °C} \) and \( T = 45 \text{ °C} \): Intersection coordinate: \( (4.741; 2.728) \).

Taking into account the inevitability of an error in determining durability (the logarithm of durability), an analysis of the obtained experimental data at a temperature of 45 degrees Celsius (durability at the given tensions is minimal, which determines the difficulty of fixing it accurately) allows us to assume that the approximating direct temperature line obtained by the least squares
method is 45 degrees Celsius inadequately reflects reality. Therefore, the assumption is valid that it can be replaced by another approximating straight line lying within the obtained confidence intervals of points. Thus, the direct temperature of 45 degrees Celsius will have the following form –
\[
\lg (\tau) = 1.68413 \cdot x + 10.4504.
\]
As a result, we have the following family of lines:
\[
T = 15 \degree C - \lg (\sigma) = -2.484 \cdot x + 15.766;
\]
\[
T = 30 \degree C - \lg (\sigma) = -1.822 \cdot x + 11.366;
\]
\[
T = 45 \degree C - \lg (\sigma) = -1.68413 \cdot x + 10.4504.
\]
The resulting lines converge at the (6.647; 0.744) point, which is a sign of a direct beam.

When rebuilding graphs in the coordinates “logarithm of time - temperature”, like the manual method, you need to select several tensions and find the value of the decimal logarithm of time in these tensions. For the sample we will use three values of 5.2 MPa, 5.6 MPa, 6.0 MPa. The calculation results are summarized in table 1.

**Table 1.** Data for rebuilding a graph into a “logarithm of time - temperature” coordinate system.

| Temperature, °C | 5.2 MPa | 5.6 MPa | 6.0 MPa |
|----------------|---------|---------|---------|
| \(\lg (\tau)\) | 2.8492  | 1.8916  | 1.693   |
| 15             | 1.8556  | 1.1628  | 1.019   |
| 30             | 0.862   | 0.434   | 0.3456  |
| 45             |         |         |         |

Having received three points for each voltage value, you can also approximate the \(\lg (1/T) = a \cdot (1/T) + b\) functions. In this case, there is no need to declare temperature values as \(10^1/T\), since now we are dealing not with a physical graph, but directly with the functions that this graph describes. The concept of scale now does not matter. Let’s group the values of the points in table 2.

**Table 2.** The Coordinates for the mathematical "reconstruction" of the graph.

| \(T (x_i)\) | \(\sigma = 5.2\) MPa | \(\sigma = 5.6\) MPa | \(\sigma = 6.0\) MPa |
|------------|-----------------------|-----------------------|-----------------------|
|            | 273                   | 273                   | 273                   |
| \(+15\)    | 273                   | 273                   | 273                   |
| \(+30\)    | 273                   | 273                   | 273                   |
| \(+45\)    | 273                   | 273                   | 273                   |
| \(\lg (y_i)\) | 2.8492               | 1.8916               | 1.693               |
| 15         | 1.8556               | 1.1628               | 1.019               |
| 30         | 0.862             | 0.434               | 0.3456              |
| 45         | 0.3456             |                    |                     |
| Function   | \(\lg (1/T) = 3564,97 \cdot (1/T) - 9.64\) | \(\lg (1/T) = 2579,52 \cdot (1/T) - 7.181\) | \(\lg (1/T) = 1592,273 \cdot (1/T) - 4.716\) |

Find the vanishing point of the functions. To do this, we define the intersection points of each function relative to each other.
\[
\sigma = 5.2\) MPa and \(\sigma = 5.6\) MPa – \((0.00248021; -0.798)\);
\[
\sigma = 5.2\) MPa and \(\sigma = 6.0\) MPa – \((0.00249608; -0.742)\);
\[
\sigma = 5.6\) MPa and \(\sigma = 6.0\) MPa – \((0.0025121; -0.716)\).
\]

Differences in coordinates could be caused by rounding values in the calculations. For the vanishing point, you can take the \((0.0025; -0.752)\) coordinate. From this coordinate follows:
\[
\tau_0 = 0.177\) s; \(T_m = 400\) K.
\]

When rebuilding the graphs into the coordinates “activation energy - voltage”, like the manual method, you need to calculate the activation energy at a given tension. Given that \(\frac{\Delta \lg \tau}{\Delta (1/T)}\) is nothing
but the angular coefficient $k$ of the $\log_e \left( \frac{1}{T} \right) = k \cdot x + b$ function, we obtain the following equation

$$U(\sigma) = 2.3 \cdot R \cdot k.$$  

Then, for $\sigma = 5.2 \text{ MPa}$  

$$U(\sigma) = 2.3 \cdot 8,314 \cdot 3564.97 = 68170;$$ 

for $\sigma = 5.6 \text{ MPa}$  

$$U(\sigma) = 2.3 \cdot 8,314 \cdot 2579.52 = 49326;$$ 

for $\sigma = 6.0 \text{ MPa}$  

$$U(\sigma) = 2.3 \cdot 8,314 \cdot 1592.273 = 30448.$$ 

When approximating by the least squares method, we obtain the following function:  

$$U(\sigma) = -47152.5 \cdot \sigma + 313368.67.$$ 

From this it follows that $U_0 = 313368.67 \text{ J/mol}$;  

$$\gamma = 47152.5 \text{ J/mol MPa}.$$ 

The thermofluctuation constants of the generalized Zhurkov equation of polyvinyl chloride plates obtained in various ways are summarized in table 3.

| Sample Number | $T_m$, K | $\tau_m$, s | $U_0$, kJ/mol | $\gamma$, kJ/mol·MPa |
|---------------|---------|-------------|--------------|-------------------|
| Mathematical method | 400     | 0.177       | 313.4        | 47.15             |
| Graphoanalytical method | 431     | 0.011       | 327          | 48                |
| Graphical method | 390     | 0.18        | 370          | 58                |

In the process of performing manual graphing to determine the thermofluctuation constants of the generalized Zhurkov equation, it becomes apparent that the human factor plays an important role. Together with a discrete value of the scale and size of the graphs (they cannot be increased without re-drawing), the data approximation method without using a mathematical apparatus can produce significant errors. The mathematical method is devoid of the main disadvantages of the other methods. It has strict rules that do not allow you to make such mistakes. This is due primarily to the fact that we are dealing with primary abstraction, a model. While the plotted — it is, in fact, a model of the model or an abstraction over an abstraction designed to bring the data into a convenient format for perception. Despite this, in the initial mathematical model there is all the information of interest to the researcher, which can be presented in different forms at the choice of the person. It follows the logical conclusion that graphs should be used only for data visualization, after all the thermofluctuation constants of the generalized Zhurkov equation are found, but not as a way to find them.

Regardless of the method used, families of fan-shaped straight lines converging in a direct beam were obtained. From table 3 it is seen that the constants obtained by the graphoanalytic method, with the exception of $\log_e \tau$, occupy an intermediate position relative to the constants obtained by the graphical and mathematical methods, and the values of the constants obtained by the graphical method are higher. Discrepancy of $T_m$ is 15.5 %, $\tau_m$ − 1.7 %, $U_0$ − 17 %, a $\gamma$ − 21 %. It should also be noted that the thermofluctuation constants obtained by the mathematical method give the greatest convergence with the initial data in the verification calculation of the durability of the material. In mathematical calculations, the error is 5 ... 15%; with graphoanalytic reaches 170%; and with graphic – up to 300%.

Thus, it is possible to recommend using the mathematical method when determining thermofluctuation constants, which will improve the reliability of the prediction of its performance.

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