Fractal analysis of tensile deformation curves of epoxy polymers based on modified epoxy binders

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Abstract. The paper proposes an approach to study the mechanism of deformation of epoxy polymers based on the methods of fractal calculations. The advantages of the method for determining the fractality index of the deformation curves of polymer samples using the minimum coverage method are shown. An algorithm for the quantitative determination of the location of the "critical" points of the deformation curves of polymer samples under tension is proposed. It is shown that the use of the developed methodology for the fractal analysis of time series on the basis of a set of points of deformation curves of epoxy polymer samples under tension, provides valuable information about the processes occurring in the structure of composite materials affected by mechanical loads and various aggressive factors.

1. Introduction

Analysis of the mechanisms of deformation and destruction of composite building materials is an important task of building materials science, its relevance related to the development of new types of composite materials based on polymeric binders is growing year by year. It is known that destruction of composite building materials is a process of multiple origin, development, and aggregation of various types of defects and microcracks up to the appearance of macrocracks [1]. Heterogenous structure of building materials leads to formation of weakened zones, subsequently causing loosening and destruction of composites.

When a microcrack reaches an inclusion (pore or filler), it results in the discharge of the critical energy density at the crack mouth and the system transition to an unstable state (bifurcation point). Branching, a change in the mechanism and direction of the destruction crack development is possible at the bifurcation point. At the same time, the destruction is of a probabilistic nature, and the process of damage accumulation is self-similar which makes it promising to use the fractal analysis methods for its analysis [2–4].

2. Formulation of the problem

The scientific papers provide various methods for determining the fractal dimension of the structure of real composite materials based on cement and polymeric binders [1, 4–10]. In [6, 8], it is shown that using fractal analysis to quantify the structural heterogeneity of polymeric materials and the pore structure of cement composites, we can find a compact way of describing such objects.

In [9, 11, 12], the authors' team proposed a method for determining the fractal dimension of deformation curves based on the minimum coverage method, providing an integral quantitative estimate of
the process of building composite destruction under compression, and enabling to determine the position of parametric points of the destruction curve. The proposed method is based on the use of data read using advanced test equipment making it possible to record changes in stresses and strains during the application of high-frequency mechanical loads to a sample. In particular, the WilleGeotechnik® software and hardware complex used in [9, 11] provides readings in increments of a split second.

3. Problem solution

The study object was a polymer based on the modified epoxy resin Etal-247 (Specifications (TU) 2257-247-18826195-07) cured by the hardener Etal-1440N (Specifications (TU) 2257-3570-18826195-03). Technical characteristics of Etal-247 resin: mass fraction of epoxy groups – not less than 21.4-22.8%; Brookfield viscosity at 25 °C – 650-750 centipoise. Compounds hardened by Etal-1440N, have a long viability of 4-5 hours at +20 °C, provide Martens heat resistance of cured compositions up to 140 °C.

The AGS–X series tensile testing machine with TRAPEZIUM X software was used for mechanical tests of polymer composites under tension. The values of stresses and strains were recorded at a frequency of 0.01 sec. We performed tests in accordance with GOST 11262-2017 (ISO 527-2:2012) "Plastics. Tensile Test Method" at a temperature of 23±2 °C and a relative air humidity of 50±5%. The clamps of the tensile testing machine moved at 2 mm/min. At least six 8-shaped samples were tested simultaneously (type 2 according to GOST 11262-2017).

4. Results and discussion

4.1. Analysis of the increase in stresses of polymer composites under tension depending on the step of fixing the readings

Analysis of the results showed that the deformation curve for samples of this composition is characterized by both ascending and descending branches, so we can determine the strength and deformation characteristics of epoxy polymer both at tension and at break (Figure 1, a). The tensile strength and relative elongation at maximum load are 41.05 MPa and 8.53%, respectively; the tensile strength and elongation at break (destruction) are 38.47 MPa and 10.14%. Detailing of the deformation (stress-strain) curve (Figure 1, b), built using the advanced test equipment with a high frequency of readings, shows that the loading process (Figure 1, a) is accompanied by discrete acts of increase and decrease in stress (Figure 1, b). We analyze the change in stress growth in epoxy polymers upon application of tensile forces depending on the reading step increment (from 0.01 to 0.16 s). The analysis of the time dependences built (Figure 2) shows that with an ever greater structuring of the curve is observed when increasing the step. In particular, if at a reading step of 0.01 s (Figure 2, a), the voltage increase variation more resembles noise without a certain tendency (except for the segment corresponding to the maximum destructive loads), then at a step of 0.16 s (Figure 2 b) it is possible to visually trace the formation of three zones with different patterns of change in the values designated by straight lines (red) with different slope angles. The time interval from the beginning of deformation to 40 seconds of loading is characterized by a reduction in the average stress increase from 0.10÷0.11 to 0.6÷0.7 MPa per every 0.16 seconds; at the same time, the characteristic under study in this segment varies from 0.03 to 0.14 MPa.

The second noticeable time interval (from 40 to 90 s) for the sample under study is characterized by a minimal change in the mean values of the stress increase, which makes 0.045÷0.057 MPa (Figure 2, b). For clarity, this segment on the deformation curve (Figure 1, a) is bounded by vertical lines of green (40 s) and blue (90 s). The analysis of data in Figure 2 (b) shows a significant gradient in the studied parameter (from -0.02 to 0.13 MPa) recorded in the time interval of 49.28÷44.94 s, comparable to the stress reduction when reaching maximum tensile force. For the polymer sample under study (red dashed line in Figure 1), this time interval corresponds to the level of relative deformations of 3.28÷3.29%, which is 38.5÷38.6% of the deformation at maximum load, and a stress of 23.08÷23.10 MPa (56.2÷56.3% of the tensile strength limit). Such an abrupt change in stress growth can presuma-
bly be explained by the appearance of a “critical” state associated with the formation of defects and cracks in the polymer structure at tensile loads.

The third time interval is associated with a decrease in the average level of the stress growth which has negative values at a stage close to the achievement of ultimate loads. At the same time, the general tendency for the decrease in this parameter in the time interval from 90 s and further is described by one linear model (Figure 2, b). The point of formation of the main crack leading to the sample destruction under tensile loads, was registered at 139.56÷139.68 seconds from the beginning of loading and corresponds to a stress of 40.48÷40.52 MPa and a relative deformation of 9.30÷9.31%.

**Figure 1.** General view (a) and fragment (b) of the strain curve of epoxy polymer samples under tension (solid red line in figure “a” shows the level of maximum stresses and the corresponding strains)
The above analysis showed that the study of changes in the growth of stresses built at a small registration step, provides valuable information about the process of deformation of polymer specimens under mechanical loads, but in this case it is extremely important to choose the frequency of the curve building. In addition, certain errors in the analysis can introduce a shift in the beginning and end of the analyzed interval, which requires the search for new analysis techniques, as well as an understanding of which particular stress gradient should be attributed to the “critical” state. At the same time, taking into account that the change in deformations and stresses in the samples under study during mechanical tests was recorded in time with a certain predetermined step (0.01 s), it is feasible to use the theory of fractal analysis of time series to analyze the deformation curves with the identification of characteristic points on it.

Figure 2. Time series of the growth of tensile stresses in the epoxy polymer sample depending on the reading step: a – 0.01, b – 0.16 s

Consider a time series \( y(t) \) defined on a certain segment \( [a, b] \). To calculate the fractal dimension, we use the minimum coverage method, which is more accurate than the cell dimension method. Its
main aspects are described in [11, 13–15]. The essence of the method consists in uniform breaking down of the segment

$$\omega_m = [\alpha = t_0 < t_1 < \cdots < t_m = b]$$

to $m$ parts and calculating function $y = f(t)$ in the class of coverages consisting of rectangles with base $\delta = \frac{b-a}{m}$ (Figure 3) [15]. Then the height of the rectangle in segment $[t_{i-1}, t_i]$ will be equal to the difference between the maximum and minimum value of function $f(t)$ on this segment – $K_i(\delta)$. By introducing the magnitude of the amplitude variation of function $f(t)$ corresponding to the breakdown scale $\delta$ in segment $[a, b]$

$$V_f(\delta) = \sum_{i=1}^{m} K_i(\delta),$$

we obtain the dependence to determine the total coverage area:

$$S_\mu(\delta) = V_f(\delta) \times \delta.$$  \hspace{1cm} (2)

![Figure 3. Fragment of cellular (square) and minimal (rectangular) coatings the graph of the fractal function on a segment $[t_{i-1}, t_i]$](image)

Then, according to [2, 15], fractality index $\mu$ can be determined from the linearization of dependence

$$V_f(\delta) \sim \delta^{-\mu} \text{ at } \delta \to 0.$$  \hspace{1cm} (3)

At the same time, the fractal dimension is related to the fractality index determined by the minimum coverage method, as

$$D_\mu = \mu + 1.$$  \hspace{1cm} (4)

To determine fractality index $\mu$, in this work we used sequence $m$ of nested breakdowns, where $m = 2^n$, $n = 0, 1, 2, 3, 4$. Each breakdown consisted of $2^n$ intervals containing $2^{4-n}$ experimental points. For each breakdown $\omega_m$, amplitude variation $V_f(\delta)$ was calculated using (1), where $K_i(\delta)$ was determined as the difference between the maximum and minimum tensile strain in time interval $[t_{i-1}, t_i]$. Coefficient $\beta$ of regression equation $\log \left( V_f(\delta) \right) = \alpha_0 + \beta \times \log(\delta)$ determined with the least squares method, was used to determine the fractality index and the dimension of the minimum coverage:

$$\mu = -\beta; \ D_\mu = 1 + \mu.$$
4.2. Discussion

Analysis of data reflecting the change in the fractality index depending on the loading duration determined with the shift of the analyzed segment with a step of \(2^4 = 16\) points, showed (Figure 4) that the destruction process (to the right of the red line) is characterized by an abrupt decrease in this parameter varying at loading in the interval from \(0.33\)÷\(0.82\) to zero. At the same time, it is known from the analysis of time series [9, 11, 15] that the higher value \(\mu\), the more stable the series. If \(\mu < 0.5\), then the series is interpreted as a “trend” (a period of sharp upward or downward movement, indicating, as a rule, a “critical” state in the system under study); if \(\mu > 0.5\), then the series is interpreted as “flat” (a period of relative calm). At \(\mu \approx 0.5\), we can say about the conformity of the changes to the Brownian movement.

Figure 4. A change in the fractality index of the strain curves of the epoxy composite under tension, depending on the duration of loading

Figure 4 shows that in the process of loading, until the sample achieves maximum tensile stresses after 127.83 seconds from the beginning of the test, there is a systematic abrupt decrease in the fractality index below \(\mu = 0.5\), which, in our opinion, is due to the transition of the system to an unstable state associated with the formation of microdamages in the polymer composite structure under tensile loads. In this case, until the composite reaches the state of destruction, the working capacity of the sample is provided mainly by transferring the load to zones without microdefects, expressed on the graph as an increase in \(\mu\) above 0.5. Therefore, from the analysis of Figure 4, we can identify the "critical" loading points where the fractality index will have the lowest values. In this case, for the analyzed polymer sample, such temporal coordinates corresponding to the bifurcation points were (at \(\mu < 0.4\)) in: 11.63; 41.02; 53.57; 59.77; 63.79; 78.80; 91.12; 101.71, and 103.14÷103.18 seconds from the beginning of loading (see the points in Figure 4). The lowest values of the fractality index corresponding to \(\mu \approx 0.32\) are recorded in 81.17 and 103.15÷103.16 s (highlighted with red dots in Figure 3). Considering that for all the studied points in the interval of 103.14÷103.18 seconds, a significant decrease in the fractality index is observed without its “restoring” to values of 0.5 or more, all of them were combined at number 10. Such a consistent drop in \(\mu\) in a series of neighboring points indicates the emergence of the growing "difficulties" in the perception of tensile stresses by the sample and the beginning of the process of the structure decompaction, the emergence of foci of local destruction, subsequently leading to its destruction. The numerical values of stress levels and relative deformations...
in the above “critical” points in absolute and relative values (relative to the point of reaching the maximum tensile stresses) are given in Table 1.

A more detailed analysis of the segments preceding the emergence of “critical” points on the graph of the change in the fractality index versus the loading duration showed that their emergence is observed with a considerable cyclical nature of the change in stresses in the mechanical loading process (Figure 5, a, b). In this case, the emergence of "critical" areas is preceded by the presence of a segment with a small growth of stresses (Figure 5, c, d), which indicates the damage of part of the structure elements and the load transfer to other elements.

Figure 5. Fragments of the deformation curve of epoxy polymers under tension in the vicinity of "critical" points (the numbers of the points correspond to the values given in Table 1)
Table 1. The coordinates of the "critical" points of the epoxy resin deformation curve under the tensile loads

| "Critical" point number | Fractality index μ | \( t_{крит, s} \) | \( \sigma_{крит, MPa} \) | \( \varepsilon_{крит, %} \) | \( t_{раст, s} \) | \( \sigma_{раст, MPa} \) | \( \varepsilon_{раст, %} \) |
|-------------------------|-------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1                       | 0.382             | 11.63           | 6.970           | 0.773           | 9.10            | 16.98           | 9.06            |
| 2                       | 0.401             | 41.02           | 20.345          | 2.732           | 32.09           | 49.56           | 32.03           |
| 3                       | 0.401             | 53.57           | 24.428          | 3.569           | 41.91           | 59.51           | 41.84           |
| 4                       | 0.391             | 59.77           | 26.423          | 3.982           | 46.76           | 64.37           | 46.68           |
| 5                       | 0.397             | 63.79           | 27.672          | 4.251           | 49.90           | 67.41           | 49.83           |
| 6                       | 0.393             | 78.8            | 32.223          | 5.251           | 61.64           | 78.50           | 61.56           |
| 7                       | **0.324**         | **81.17**       | **32.899**      | **5.409**       | **63.50**       | **80.14**       | **63.41**       |
| 8                       | 0.404             | 91.12           | 35.575          | 6.072           | 71.28           | 86.66           | 71.18           |
| 9                       | 0.374             | 101.71          | 37.96           | 6.778           | 79.57           | 92.47           | 79.46           |
| 10                      | **0.317**         | **103.16**      | **38.292**      | **6.875**       | **80.70**       | **93.28**       | **80.60**       |

5. Conclusions
The proposed approach for the study of the mechanism of deformation of composite materials under tension, carried out on the basis of the method of fractal analysis of the deformation curves recorded using modern testing equipment with a high frequency, provides valuable information about the process of accumulation in its structure of micro- and macrodefects resulting in the destruction of composites. In our opinion, carrying out such studies on samples of polymer composites of different compositions, as well as after aging under the influence of various aggressive factors, including climatic factors, will provide valuable information about the processes occurring in the structure of composite materials when tensile loads are applied.

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