

Method of quantitative assessment of changes in "critical" levels of elastic-strength parameters of epoxy polymers in the process of natural climatic aging

T. A. Nizina^{*}, *D. R. Nizin*, and *N. S. Kanaeva*

Department of Building Structures, National Research Mordovia State University, 430005 Saransk, Russia

Abstract. The method for quantitative analysis of the kinetics of damage accumulation in the structure of series of polymer samples at stretching is proposed. The proposed approach is to calculate the fractality indices of time series by means of a minimum coverage method, followed by a failure frequency analysis, while increasing the levels of applied stresses and relative deformations. Epoxy polymer based on ED-20 resin hardened by Etal-1460 hardener, was selected as the object of the study. The results of the study of changes in elastic-strength indicators and levels of "critical" stresses and relative elongation in the stretching of epoxy polymer during the natural climate impact are presented.

1 Introduction

Throughout the development of scientific and technical thought, obtaining direct results of research and development was accompanied by a continuous accumulation of various data arrays. However, their further use was complicated by technical and methodological problems – primarily, the lack of necessary computing power. The beginning of the 21st century was marked by the emergence and development of an entire field of science related to the big data acquisition, storage, processing and research.

Active recent implementation of high-precision modern equipment in the practice of scientific research, including for determining the strength characteristics of composite materials of various types and purposes, also leads to obtaining a big amount of experimental values. To better understand the process of composites deformation, the team of authors proposed a method for determining characteristic points of the studied curves based on a fractal analysis of time series using the minimum coverage method [1 – 3]. For each sample, depending on the loading rate and strength characteristics, as a rule, from 1.5 to 150 thousand lines are processed.

A characteristic feature of polymer composite materials is a complex multi-level structure which leads to significant differences in the nature of the destruction of various polymer types. The scientific literature studies the effect of structural heterogeneity of composite

^{*} Corresponding author: nizinata@yandex.ru

materials on their behavior under static and dynamic loads [4 – 8]. It is shown that a high degree of structural heterogeneity reflecting the process of forming the original structure of polymeric materials, is a key factor influencing their physical and mechanical properties.

It is the structural heterogeneity of composite building materials that even at relatively low levels of mechanical stress may lead to loosening of weakened zones, which later cause fracture of composites [9 – 11]. In this case, the fracture process is of a discrete-continuous nature that develops over time and is characterized by the multiple events of origination, development, and aggregation of various kinds of defects until the appearance of macro cracks leading to the sample fracture. Processing the resulting datasets, including through fractal calculus techniques, provides new valuable information on the accumulation of damage when applying loads to samples, as well as allows determining the quantitative values of "critical" stress and deformation levels of sample series. Of additional interest is the assessment of changes in the nature of composite deformation after exposure to a variety of aggressive factors, including climatic ones.

2 Materials and Methods

The paper provides an analysis of the deformation curves of the epoxy polymer exposed under the natural climatic factors in a temperate continental climate for one calendar year. Mechanical tensile tests were in accordance with GOST 11262-2017 (ISO 527-2:2012) Plastics. Tensile Test Method, for samples in the control state, as well as after 45, 90, 180, 270 and 360 days of full-scale exposure. The object of study was the epoxy polymer derived based on ED-20 resin (GOST 10587-84) hardened by Etal-1460 amine hardener produced by ENPTs EPITAL JSC.

The samples were subjected to natural exhibition on the test stands of the environmental and meteorological monitoring laboratory, construction technologies and examinations of the National Research Mordovia State University (Saransk) for one calendar year. The AGS–X series tensile testing machine with TRAPEZIUM X software was used for mechanical tensile testing of epoxy polymer samples. The frequency of registering stress and deformation values was 0.01 sec. The tests were performed at a temperature of 23 ± 2 oC and relative air humidity of $50 \pm 5\%$. The tensile testing machine clamp movement speed was 2 mm/min. At least 6 samples were tested for each composition in parallel (type 2 according to GOST 11262-2017).

The method of determining the coordinates of "critical" points on deformation curves of polymer samples during the loading process is outlined in [3, 12]. To determine fractality index μ when analyzing the section of the deformation curve of polymer composites, we used the sequence m of embedded partitions where $m = 2^n$, where $n = 0, 1, 2, 3, 4$. At the same time, for each point of the deformation curve, the previous time interval was examined, corresponding to 16 (24) experimental points, i.e. 0.16 seconds. For each partition,

$$\omega_m = [a = t_0 < t_1 < \dots < t_m = b]$$

depending on the step δ ($\delta = (b - a)/m$) step (the amplitude variation was calculated $V_f(\delta)$ using equation [13, 14].

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

where $K_i(\delta)$ was defined as the difference between the maximum and minimum increase in tensile stress in the time interval $[t_{i-1}, t_i]$. In this case, point "a" characterizes the beginning of the study area 0.16 sec. long, point "b" characterizes its ending.

Coefficient β of regression equation $\log(V_f(\delta)) = \alpha_0 + \beta \times \log(\delta)$ determined using the least squares method, was used to determine the fractality index and the minimum coverage dimension for each section studied:

$$\mu = -\beta; D_{\mu} = 1 + \mu \tag{2}$$

In order to distinguish between the integral fractality indices μ and fractal dimensions D_{μ} , defined for the entire deformation curve under study (up to the level of reaching maximum stresses), and this type of fractal indicators, estimated by preceding time intervals of 0.16 sec., we will introduce the designation $\mu(\sigma, \varepsilon)$ and $D_{\mu}(\sigma, \varepsilon)$.

The fractality indices of the deformation curves were calculated using the author's software product in Python.

3 Results and discussion

A typical type of graphical dependencies of change in the fractality index of the deformation curve of an epoxy polymer sample in the control state (before climatic exposure), resulting from the proposed author's method, is shown in Figure 1, a. "Critical" points corresponding to the smallest values of fractality indices are marked with red (No. 1, 2) and yellow (No. 3-20). To visualize the results, "critical" points were applied to the deformation curve (Figure 1, b) The area of the analyzed values was limited to a point on the deformation curve corresponding to the level of achieving maximum tensile stresses by the sample.

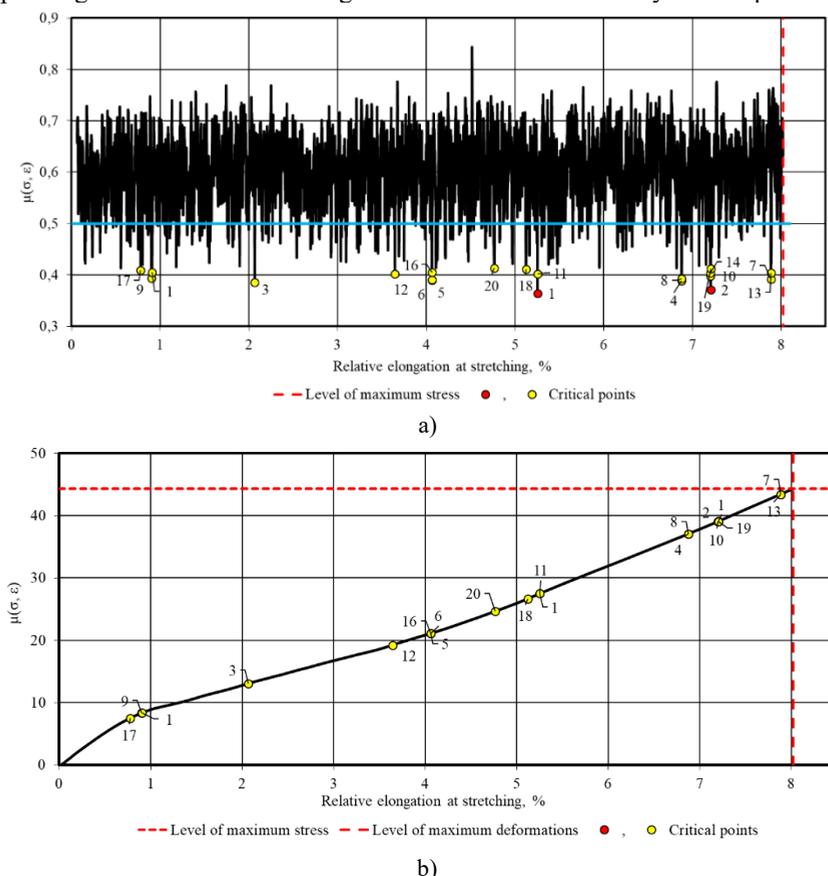


Fig. 1. Change of the deformation curve fractality index (a) for ED-20+Etal-1460 epoxy polymer sample (b) at stretching depending on the relative elongation at stretching with applied "critical" points determined by the fractal analysis method.

In work [15] it is suggested to determine quantitative values of generalized fractal indices for a series of parallel studied samples based on the analysis of 15-20 "critical" points with the lowest fractality index values. However, it should be noted that the picture of "critical" points distribution on the deformation curve may vary significantly both depending on the polymer material under study, and within a single series of samples. Therefore, it is expedient to analyze the full dataset on changing the fractality index of a series of samples and their correlation to the levels of tensile stresses and relative deformations.

In this paper, we analyzed all values of fractality indices μ less than 0.5, interpreted in fractal studies of time series as a "trend", i.e. a period of sharp upward or downward movement, which, as a rule, testifies to the appearance of "critical" state in the system under study [13, 14]. The analysis of change in the failure frequency, including accumulated one, depending on the level of stresses and relative elongation at stretching of a series of samples (ED-20 + Etal-1460) has shown, that the core mass of "critical" points (Figure 2) corresponds to intervals of stress $7\div 31$ MPa and relative elongation at stretching of $0,5\div 7\%$. In this case, the number of failures was determined for the whole array of points of deformation curves parallel to tested samples of epoxy polymer under the condition $\mu(\sigma, \epsilon) < 0.5$. Dashed lines in Figure 2 show the levels of tensile strength of a series of ED-20 + Etal-1460 polymer samples under study in the control state and at average relative elongation upon achievement of maximum tensile loads.

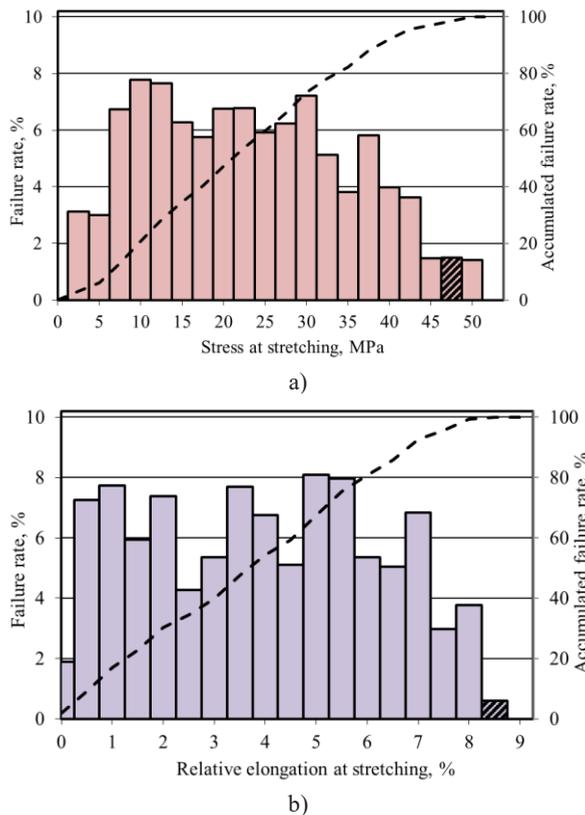


Fig. 2. Changes in frequency and accumulated failure rate ($\mu(\sigma, \epsilon) < 0.5$) depending on stress level (a) and relative elongation at stretching (b) of a series of ED-20+Etal-1460 samples.

Building such graphical dependencies for fractality indices less than 0.48, 0.46, 0.44, 0.42 and 0.4 allows to reveal quantitative levels of stresses and relative deformations at stretching characterized by the highest frequency of failure accumulation, whereas their achievement

indicates the transition of samples to the "critical" state (Figure 3). It should be noted that, in general, peak levels of achieving maximum failure rate are detected at the same levels of stresses and relative deformations, practically independent of the minimum level under analysis μ_{min} . At the same time, with decreasing the level [01], μ_{min} there is an increasing structuring of distribution curves with revealing the most "critical" levels of stresses and deformations. In particular, for control samples of the composition under study, the maximum levels of failures accumulation correspond to tensile stresses 37.5 ± 1.25 MPa and relative elongation 7.0 ± 0.25 % (Figure 3). Also, surges of failure accumulation rates are observed at the levels of tensile stresses of 22.5 ± 1.25 and 27.5 ± 1.25 MPa and relative deformations of $2.0 \pm 0.25\%$ and $4.0 \pm 0.25\%$. The results of changes in the elastic strength indices and levels of "critical" stresses and relative deformations under the natural climatic factors at the stretching of epoxy polymers are given in table 1.

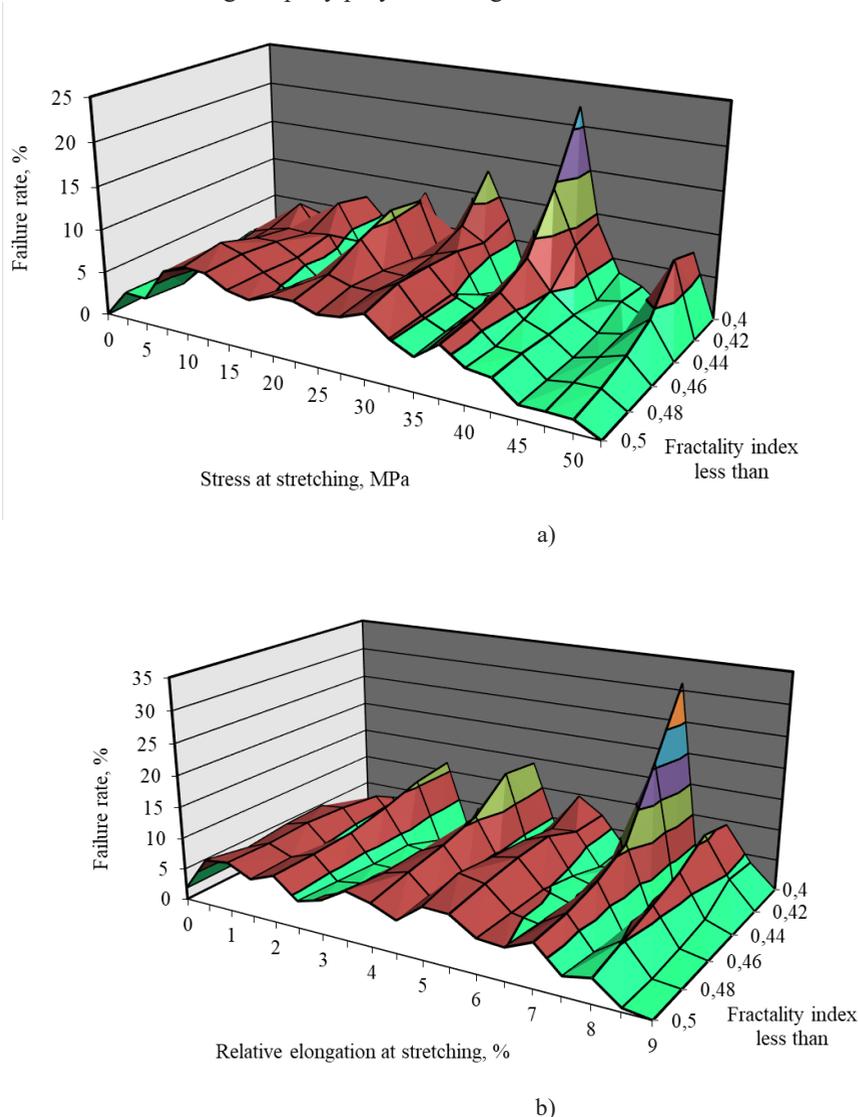


Fig. 3. Change in the failure rate for different levels of fractality index ($\mu(\sigma, \epsilon) < 0.5 \div 0.4$) depending on stress level (a) and relative elongation at stretching (b) of a series of ED-20 + Etal-1460 samples.

Studies have shown that regardless of the duration of full-scale climatic aging, three most pronounced "critical" levels form in the structure of the polymer matrix of epoxy polymer samples under the stretching loads (table 1). At the same time, with the increase in the duration of full-scale exposure, there is a significant acceleration of the accumulation of a significant number of failures determined in accordance with the proposed methodology.

Table 1. Variation of elastic strength characteristics and levels of "critical" stresses and deformations of ED-20 + Etal-1460 epoxy polymer in the process of natural climatic aging under the moderate continental climate.

Natural exposure duration, days	Elastic strength characteristics		"Critical" levels	
	Ultimate tensile strength ^a , MPa	Relative elongation at maximum load ^a , %	Stress at stretching, MPa	Relative elongation at stretching, %
0	$\frac{47.16}{1.00}$	$\frac{8.18}{1.00}$	22.5 ± 1.25 27.5 ± 1.25 37.5 ± 1.25	2.0 ± 0.25 4.0 ± 0.25 7.0 ± 0.25
45	$\frac{42.67}{0.90}$	$\frac{6.43}{0.79}$	12.5 ± 1.25 30.0 ± 1.25 37.5 ± 1.25	1.5 ± 0.25 4.0 ± 0.25 5.0 ± 0.25
90	$\frac{34.98}{0.74}$	$\frac{4.23}{0.52}$	5.0 ± 2.50 12.5 ± 1.25 20.0 ± 1.25	0.5 ± 0.25 1.5 ± 0.25 4.0 ± 0.25
180	$\frac{16.37}{0.35}$	$\frac{1.40}{0.17}$	2.5 ± 0.5 7.5 ± 0.5; 12.5 ± 0.5	0.2 ± 0.1 0.8 ± 0.1 1.1 ± 0.2
270	$\frac{12.56}{0.27}$	$\frac{1.07}{0.13}$	4.0 ± 1.5 9.0 ± 0.5 12.0 ± 0.5	0.2 ± 0.1 0.4 ± 0.1 0.8 ± 0.1
360	$\frac{14.52}{0.31}$	$\frac{1.22}{0.15}$	4.0 ± 0.5 8.0 ± 1.0 13.0 ± 0.5	0.4 ± 0.1 0.6 ± 0.1 1.0 ± 0.1

The numerator contains absolute values and the denominator contains relative values.

Implementation of the author's approach allowed a quantitative analysis of changes in the kinetics of damage accumulation in the structure of ED-20 + Etal-1460 epoxy polymer samples under the natural climatic factors. "Critical" levels of stresses and relative deformations have been identified, and their achievement leads to the load redistribution from the failed structural elements to the workable ones. In this case, analyzing not one, the most "typical" sample, but a series of parallel samples studied, allows a more reasonable approach to identifying the "critical" levels of the polymers studied.

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References

1. T. A. Nizina, V. P. Selyaev, D. R. Nizin, A. S. Balykov, D. I. Korovkin, N. S. Kanaeva, IOP Conf. Ser.: Mater. Sci. Eng. **456**, 012058 (2018)
2. T. A. Nizina, D. R. Nizin, N. S. Kanaeva, N. M. Kuznetsov, D. A. Artamonov, Key Eng. Mater. **799**, 217–23 (2019)
3. T. A. Nizina, V. P. Selyaev, D. R. Nizin, N. S. Kanaeva, Constr. Reconstr. **2**, 77–89 (2020)

4. A. A. Askadsky, Yu. I. Matveev, *Chemical Structure and Physical Properties of Polymers* (Chemistry, Moscow, 1983)
5. E. N. Kablov, O. V. Startsev, A. S. Krotov, V. N. Kirillov, *Deform. Destr.* **12**, 40–46 (2010)
6. A. A. Askadsky, M. N. Popova, V. I. Kondrashenko, *Physical Chemistry of Polymer Materials and Methods of their Research* (ASV, Moscow, 2015)
7. V. P. Selyaev, Yu. G. Ivashchenko, T. A. Nizina, *Polymer Concrete: Monograph* (Mordovia State University Press, Saransk, 2016)
8. P. D. Stukhlyak, A. V. Buketov, S. V. Panin, P. O. Marushchak, K. M. Moroz, M. A. Poltaranin, T. Vuherer, L. A. Kornienko, B. A. Lyukshin, *Phys. Mesomech.* **17(2)**, 65–83 (2014)
9. V. S. Ivanova, A. S. Balankin, I. Zh. Bunin, A. A. Oxogoev, *Synergetics and Fractals in Materials Science* (Nauka, 1994)
10. V. I. Travush, V. P. Selyaev, P. V. Selyaev, E. L. Kechutkina, *Ind. Civ. Constr.* **9**, 94–100 (2016)
11. A. I. Makeev, E. M. Chernyshov, *Bull. VSUACE. Ser.: Constr. Architect.* **47(66)**, 111–22 (2017)
12. T. A. Nizina, V. P. Selyaev, D. R. Nizin, D. A. Artamonov, N. S. Kanaeva, *Polymers in Construction* **1(7)**, 48–57 (2019)
13. M. M. Dubovikov, N. S. Starchenko, *Sci. Almanac Gordon* **1**, 1–30 (2003)
14. M. M. Dubovikov, N. S. Starchenko, M. S. Dubovikov, *Phys.* **339**, 591–608 (2004)
15. T. A. Nizina, D. R. Nizin, N. S. Kanaeva, *Lect. Not. Civ. Eng.* **95**, 1–8 (2020)