The Effect of Natural Climatic Aging on Damage Accumulation Kinetics in the Structure of Epoxy Polymers Under Tensile Loads

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Abstract. The approach is proposed for assessing the "critical" state of polymer materials under the effect of aggressive media. Changes in kinetics of failure accumulation of three compositions of epoxy polymers based on ED-20, Etal-247 and Etal-370 epoxy resins cured by Etal-1440 in 45, 90, 180, 270 and 360 days of natural climatic exposure were analyzed. We have identified changes in the rate of damage accumulation when the total level of failures exceeds 70÷80% of their maximum corresponding to the achievement of maximum tensile stresses. Damage accumulation kinetics was calculated based on the author's method using methods of fractal analysis of deformation curves for polymer materials samples under tension. This approach involves determining the coordinates of "critical" points of deformation curves for which the fractality index values calculated over the previous short time intervals using the least coverage method, were less than 0.5. High stability of epoxy polymer parameters based on modified Etal-247 resin under the natural climatic factors has been found. After a year of full-scale exposure, for this type of epoxy polymer the "critical" levels of tensile stresses and their corresponding relative elongation are reduced by 11% and 16%. At the same time, for polymers based on ED-20 and Etal-370 epoxy resins, these figures are 1.9 and 2.7 ($\sigma^{70}_{crit.}$) and 2.7 and 5.1 ($\varepsilon^{70}_{crit.}$) times reduced, respectively, which indicates a significant damage accumulation.

Keywords: Epoxy polymers · Deformation curves · Damage accumulation · Stress increase · Fractal analysis · Minimal coverage method

1 Introduction

One of the most effective ways to increase durability of building products and structures under the effect of aggressive factors is the use of protective and decorative coatings based on polymer binders. The use of polymer coatings for the protection of reinforced concrete structures both reliably isolates the concrete and reinforcement from the aggressive environment, and increases crack resistance and load-bearing capacity, reduces shrinkage, creep, deformability, etc. [1–4]. Polymer coatings also act

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as a kind of regulator of the base material structural formation, caused by a decrease in the total volume of macro- and micro-defects on the surface and in the body of reinforced concrete structures, as well as changes in the nature of porosity due to the transfer of open pores to closed ones. In connection with the high complex of strength and adhesion characteristics, compositions based on epoxy binders [5–8] are the most widespread from a wide enough range of protective and decorative coatings of building products and structures.

As a rule, the standard mode of operation of polymer-based protective and decorative coatings implies cyclic effect of both aggressive factors and mechanical loads. It is in connection with the cyclic nature, a number of coefficients are introduced when designing them, taking into account possible multi-directional deviation of operating loads from the calculated values. As a result, the material strength limit at maximum load never corresponds to the actual value of the operating load. However, the designing polymer-based structures operated under the climatic factors practically does not take into account the decrease in performance characteristics of polymer materials due to natural aging. In addition, when calculating the maximum allowable performance characteristics of protective and decorative polymer coatings, they do not take into account the reversibility and irreversibility of the resulting changes in properties [9, 10].

The paper assessed the effect of the natural climatic aging duration on changes in kinetics of damage accumulation in the structure of polymer materials samples under tensile loads. Quantitative values are determined on the basis of the author's method, which allows determining the coordinates of critical points of deformation curves built by methods of fractal analysis [11, 12]. It was shown that the environmental exposure leads to changes both in performance characteristics and the rate of accumulation of reversible and irreversible changes in the polymer material structure.

2 Methods and Materials

The objects of study were samples of three compositions of epoxy polymers based on ED-20, Etal-247 and Etal-370 resins cured by Etal-1440 amine hardener (production of ENPC EPITAL JSC). It is designed for curing epoxy resins and compounds based on them at temperatures from +10 °C. Mixtures based on Etal-1440 hardener have a long life of 4–5 h at +20 °C, which is important in the development of compounds for protective and decorative coatings of building structures.

ED-20 epoxy resin is a liquid reactive oligomeric product based on diglicidyl ether of biphenylolpropane and corresponds to GOST R 56211-2014. Mass fraction of epoxy groups is 20÷22.5%; dynamic viscosity at 20 20 °C is 12÷25 Pa · s.

Etal-247 (TU 2257-247-18826195-07) and Etal-370 (TU 2257-370-18826195-99) epoxy resins are low-viscosity modified resins with viscosity 20÷22 and 4.5÷5.0 times lower than that of ED-20, respectively. Mass fraction of epoxy groups for Etal-247 and Etal-370 is at least 21.4÷22.8 and 21.5%, respectively.

Mechanical tensile testing of the samples of compositions under study was made using an AGS-X series tensile testing machine with TRAPEZIUM X software. Test temperature was 23 ± 2 °C and relative air humidity was 50 ± 5%. The tensile testing

machine clamp movement speed was 2 mm/min. The readings were registered at 0.01 s. At least 6 samples were tested for each composition in parallel (type 2 according to GOST 11262-2017).

The samples were subjected to natural exhibition on the test stands of the environmental and meteorological monitoring laboratory, construction technologies and examinations of the Ogarev National Research Mordovia State University (Saransk). Physical and mechanical performance was determined after 45, 90, 180, 270 and 360 days of full-scale exposure.

The kinetics of damage accumulation was assessed on the basis of data obtained using the author's methodology. Its algorithm is given in [11, 12]. The proposed approach involves determining the coordinates of "critical" points of the deformation curves for which the fractality index values calculated over the previous short time intervals using the least coverage method, are less than 0.5. Typical curves of the fractality index change depending on the tensile elongation are given in [12]. This study also analyzed time intervals with a duration of 0.16 s which corresponded to the analysis of 16 previous experimental points with a displacement of the analyzed area with a step of 0.01 s.

3 Results and Discussion

In [12], the team of authors proposed to estimate the level of accumulated failures leading to the destruction of samples under tensile loads, to use a parameter defined as the ratio of the number of points with a fractality index less than 0.5 to the total number of points of deformation curves (until reaching the level of maximum voltages). It was shown that in order to obtain a reliable assessment of the polymer composite behavior under the mechanical loads, the data of the entire series under study, not individual samples, should be processed.

In this work, we studied the change in the elastic-strength performance and kinetics of failure accumulation in epoxy polymers under tensile loads in the control state and after full-scale climatic exposure for 45, 90, 180, 270, and 360 days. The results of changes in elastic-strength performance in the process of climatic aging in absolute and relative values are given in Table 1. It was found that for the control samples, the highest strength and deformation performance was registered for polymers based on ED-20 and Etal-370 epoxy resins. Tensile strength and elongation at maximum load for the ED-20 + Etal-1440 sample is 52.9 MPa and 9.8%, for Etal-370 + Etal-1440 it is 54.7 MPa and 11.1%. Epoxy polymer samples based on modified Etal-247 resin are characterized by tensile strength of 40.8 MPa and relative elongation of 8.6%, which, respectively, is 23–25% and 12–22% lower than those of other compositions.

The field test results have shown that the climatic effect within one calendar year leads to a significant decrease in the elastic-strength perf of polymers based on ED-20 and Etal-370 epoxy resins. In particular, the loss of strength and deformation characteristics of ED-20 + Etal-1440 is 34 and 49%, Etal-370 + Etal-1440-48 and 73%. At the same time, the polymer based on the modified epoxy resin Etal-247 has shown significantly greater stability both in assessing the tensile strength (8% lower than the initial value) and the relative elongation (23% lower).

Table 1. Elastic-strength performance of epoxy polymers cured by Etal-1440 during natural climatic aging.

Epoxy resin	Natural exposure duration, days					
	0	45	90	180	270	360
Ultimate tensile strength, MPa Relative tensile strength, rel. units						
ED-20	52.9 1.00	59.7 1.13	46.6 0.88	38.9 0.74	36.5 0.69	34.7 0.66
Etal-247	40.8 1.00	41.4 1.02	38.7 0.95	39.4 0.97	36.9 0.90	37.3 0.92
Etal-370	54.7 1.00	53.3 0.97	47.2 0.86	56.1 1.03	45.7 0.84	28.7 0.52
Relative elongation at maximum load, % Relative tensile elongation, rel. units						
ED-20	9.8 1.00	8.9 0.91	5.9 0.60	5.0 0.52	4.1 0.42	4.9 0.51
Etal-247	8.6 1.00	7.7 0.90	7.0 0.81	7.7 0.90	6.9 0.80	6.7 0.77
Etal-370	11.1 1.00	7.0 0.64	6.3 0.57	8.3 0.75	5.8 0.53	2.9 0.27

Failure accumulation curves for the samples of epoxy polymers cured by Etal-1440, depending on the level of applied tensions and relative tensile elongation are shown in Fig. 1. In this case, 100% means the maximum number of failures leading to the achievement of the maximum levels of tensile stresses. For the series of the compositions under study, this parameter, depending on the duration of full-scale exposure, varies from 4.36 to 8.19%.

The analysis of curves in Fig. 1 showed that in the process of natural climatic aging, both the elastic strength characteristics of polymer materials and the accumulation rate of reversible and irreversible changes in their structure change. Thus, if for ED-20 + Etal-1440 samples at the age of 0÷90 days, the share of accumulated failures under tensile load of 20 MPa is in the range of 25÷35% of the maximum value, then for the samples at the age of 270÷360 days, it in the range of 50÷70% Such growth of damage accumulation rate in the polymer matrix structure can be caused by high complexity of processes describing the mechanism of interaction between environment and polymer material. Hydrolysis, plasticizing effect of moisture, destruction of surface layers under the UV radiation and solar radiation, relaxation of initial structural heterogeneity, photodestruction – all this is accompanied by both reversible and irreversible changes in the macromolecular structure of the polymer materials under study.

Besides, the analysis of results showed that excess of the level of accumulated failures above 70÷80% leads to curve distortion, which indicates a change in the rate of failure accumulation associated with the transition of structural elements from a functional state to a defective one. At the same time, the level of tensile stresses and corresponding deformations at which an explicit change in the rate of damage

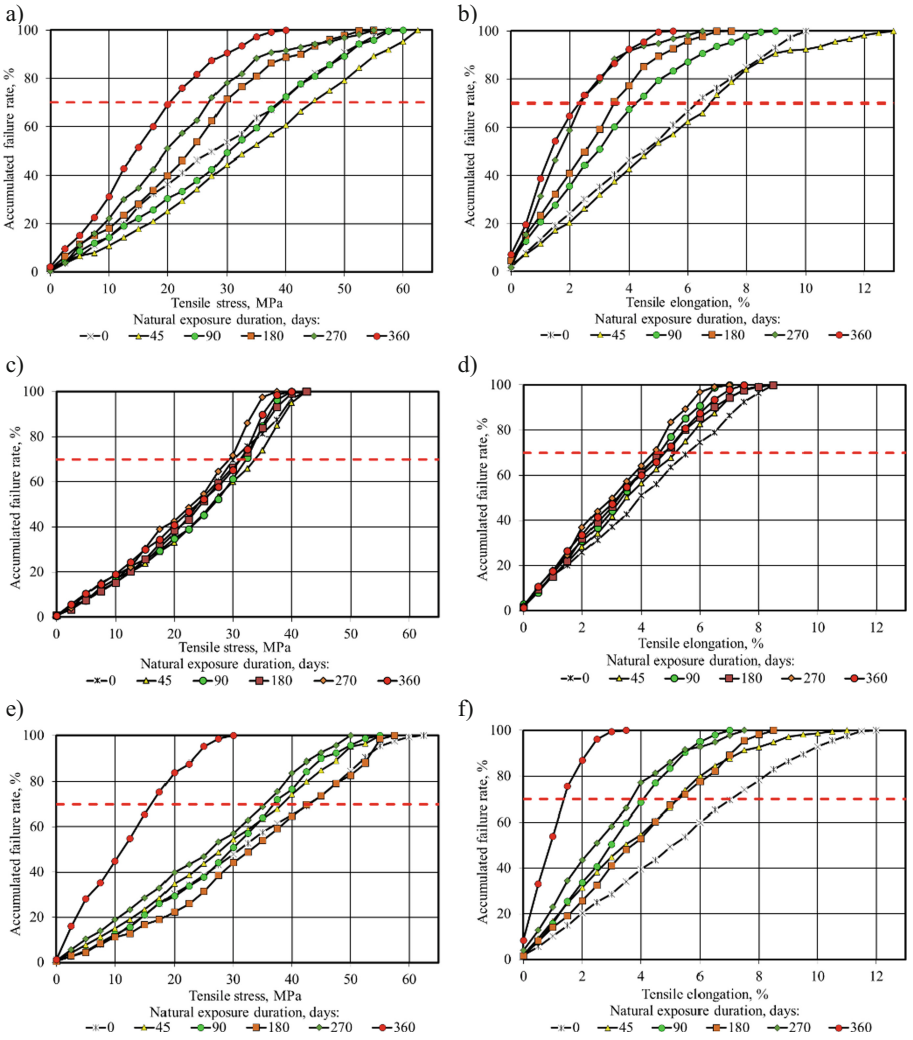

Fig. 1. Curves of failure accumulation in a series of samples of compositions based on epoxy resins: ED-20 (a), Etal-247 (b) and Etal-370 (c) cured by Etal-1440, depending on the level of applied stresses (a, c, f) and relative tensile elongations (b, d, g).

accumulation occurs can be characterized as a maximum level. Its achievement indicates formation of a significant number of defects and cracks in the polymer structure.

Based on data in Fig. 1, tensile stress levels and associated relative elongation were calculated, where the accumulated failure rate was 70% (see red dashed line in Fig. 1) – $\sigma_{crit.}^{70}$ and $\varepsilon_{crit.}^{70}$. The results grouped by the type of epoxy resin used and the duration of natural climatic impact, are shown in Fig. 2. It was found out that for polymers based on ED-20 and Etal-370 epoxy resins up to 90 and 270 days of natural exposure, respectively, it is necessary to apply higher levels of tensile stresses for transition of

composites to critical state than for epoxy polymer based on modified Etal-247 resin. At the same time, the increase in the duration of field exposure up to 360 days leads to a significant decrease in the initial critical levels – 1.9 and 2.7 ($\sigma^{70}_{crit.}$) and 2.7 and 5.1 ($\varepsilon^{70}_{crit.}$) times for polymers based on ED-20 and Etal-370 epoxy resins, which indicates a significant damage accumulation.

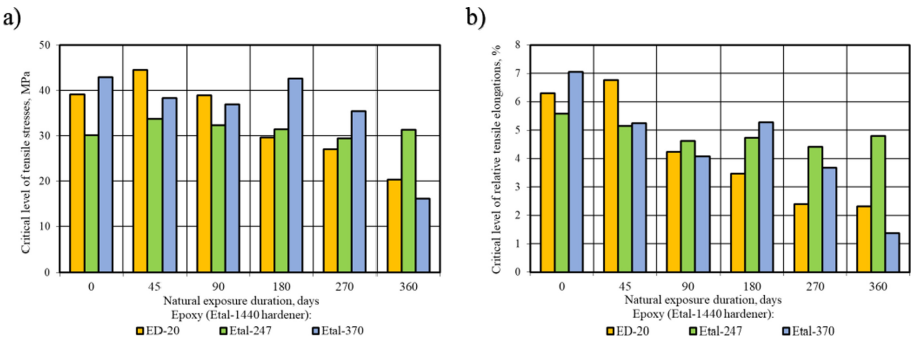

Fig. 2. The change in critical levels of tensile stresses $\sigma^{70}_{crit.}$ and corresponding relative elongation $\varepsilon^{70}_{crit.}$ of epoxy polymers cured by Etal-247 during natural climatic aging.

High stability of epoxy polymer parameters based on modified Etal-247 resin under the natural climatic factors affecting during one calendar year has been confirmed (Fig. 2). Despite lower elastic strength characteristics of control samples of this composition in comparison with the compositions based on ED-20 and Etal-370 resins, the decrease in relative elongation characterizing the embrittlement of polymers after 360 days of natural exposure is not more than 16%. Variation of the critical level of tensile stress depending on the natural exposure duration for polymer Etal-247 + Etal-1440 polymer does not exceed 11%.

In our opinion, it is the indices proposed as criteria of "critical" state, calculated according to failure accumulation curves, that allow us to provide a more representative assessment of climatic resistance of the polymers under study identifying quantitative levels of tensile stresses and relative elongation, where exceeding them is unacceptable for their subsequent normal operation. The use of fractal analysis method for deformation curves registered with a high frequency of readings, results in additional quantitative assessment of climatic resistance and durability of composite materials.

4 Conclusion

The results of the proposed fractal approach in the analysis of deformation curves of polymeric material samples under tensile loads confirmed the possibility to quantitatively analyze kinetics of damage accumulation in the structure of polymers of different compositions effected by a variety of factors (in this case, in-kind climatic effects of different durations). It has been established that the polymer based on the Etal-247

epoxy resin cured by the Etal-1440 amine hardener, has highly stable properties in conditions of exposure to in-kind climatic factors. Thus it can be recommended as a protective and decorative coating of construction products and structures exposed to in-kind climatic impact.

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