The Effect of Moisture State on Kinetics of Damage Accumulation in the Structure of Epoxy Polymer Samples Under Tensile Stresses

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Abstract. The paper studies the influence of the moisture state on the elastic-strength parameters and kinetics of damage accumulation in the structure of epoxy polymer samples based on Etal-247 resin and Etal-45TZ2 hardener. Damage accumulation process is quantitatively described based on the author's technique determining the position of critical points on deformation curves of polymer materials using fractal analysis methods. To assess critical fraction of cumulative failures of the polymer matrix structural elements, we used the parameter defined as the ratio of the number of points with a fractality index less than 0.5 to the total number of points on deformation curves (until reaching the "critical" level of tensile stresses). It has been established that an increase in the moisture content of a polymer material makes it possible to achieve, under tensile loads, formation of a pronounced stage of forced highly elastic deformations. We have revealed a decrease in the ultimate tensile strength and an increase in the relative elongation at break for moisture-saturated specimens compared to the polymer in the equilibrium-moisture state, by 6.0 and 6.7 times, respectively. It was found that at the ultimate moisture saturation, the rate of failure accumulation accelerates with an increase in the level of applied stress at strain compared to the samples in the equilibrium-moisture state, by 4.3–5.5 times.

Keywords: Epoxy polymers · Deformation curves · Moisture content · Fractal analysis · Fractality index · Failure accumulation

1 Introduction

At present, the objective of ensuring reliable operation of building materials, products and structures exposed to natural climatic effects is becoming more and more urgent. Along with the temperature and intensity of actinometric factors, the most significant climatic factors influencing the properties of polymeric building composites during operation are humidity and precipitation [1–3]. Moisture absorbed by polymer composites activates the processes of structural relaxation, has a partially reversible plasticizing effect, and also participates in hydrolysis and afterhardening reactions [4].

Studies [5–7] have shown that moisture absorption of polymeric materials and the associated loss of strength are determined by structure and type of polymer matrix,

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binder composition, hardening degree, thickness and porosity of samples, as well as the state of the interfacial layer at the matrix/filler interface. Chemical interaction of moisture with polymer composites causes the hydrolysis of macromolecules and subsequent material destruction reactions [7]. However, the effect of moisture manifests itself not only in chemical interaction. Water fills in various microdefects, causing matrix microcracking in residual stress concentration zones. In addition, moisture absorbed by the polymer matrix can act as a plasticizer, weakening the absorption interactions between macromolecules (or their links) of the polymer and the strength of adsorption interaction at the interface [8, 9]. Penetrating between the polymer matrix molecules, water causes relaxation of internal stresses, increases mobility of macromolecules, decreases the cross-linking level.

Under natural climatic operation conditions, maximum moisture saturation of the polymer material is virtually not achieved due to relatively low moisture sorption rate and the competing desorption process due to surface heating and cooling, changes in the environmental humidity, and atmospheric pressure, etc. However, the need to take into account the polymer moisture content effect, including in ultimate equilibrium-moisture states (dry and moisture-saturated), is extremely important for understanding the operation of polymers under natural climatic conditions. Quantitative assessment of kinetics of damage accumulation in polymer sample structure under mechanical loads is of additional interest.

2 Methods and Materials

The objects of the study were epoxy polymer samples based on Etal-247 resin and Etal-45TZ2 hardener by ENPTs EPITAL JSC. Etal-247 epoxy resin (TU 2257-247-18826195-07) is a low-viscosity modified resin with Brookfield viscosity of 650 ÷ 750 cP at 25 °C. Mass fraction of epoxy groups for Etal-247 and is at least 21.4 ÷ 22.8%.

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 10 samples were tested for each composition in parallel (type 2 according to GOST 11262-2017). Strength and deformation characteristics of the test polymer samples were determined in three different moisture states - equilibrium-moisture, dry, and moisture-saturated. Samples were dried at a temperature of 60 °C, and moistened in desiccators over water until reaching constant weight values according to GOST R 56762-2015 Polymer Composites. Method for Determining Moisture Absorption and Equilibrium State.

This work assesses the effect of epoxy polymer moisture state on the change in its strength and deformation characteristics, as well as kinetics of failure accumulation in the sample structure under tensile loads. Quantitative values of accumulated failures are determined on the basis of the author's technique, which allows determining the coordinates of critical points of deformation curves built by methods of fractal analysis [10–13]. The proposed technique 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. Time intervals of 0.16 s were studied with analyzed area shifted with a step of 0.01 s.

To estimate the level of accumulated failures leading to the destruction of samples under tensile loads, we used 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 on deformation curves (until reaching the level of "critical" tensile stresses). An algorithm for assessing failure accumulation is described in [12]. At the same time, to assess the behavior of polymer composites in different moisture conditions under mechanical loads, the data of all samples of the studied series was processed.

3 Results and Discussion

Analysis of the results showed that sample deformation curves (in equilibrium-moisture and dry states) have both ascending and descending branches, which makes it possible to determine strength and deformation characteristics of the epoxy polymer under tension and at break (Fig. 1). The arithmetic mean values of the tensile strength and elongation at the maximum load of a series of samples in an equilibrium-moisture state, respectively, are equal to 53.5 MPa and 7.98%, in a dry state – 48.18 MPa and 7.79%; ultimate strength and elongation at break in the equilibrium-moisture state – 47.06 MPa and 8.74%, in dry state – 36.67 MPa and 12.54%.

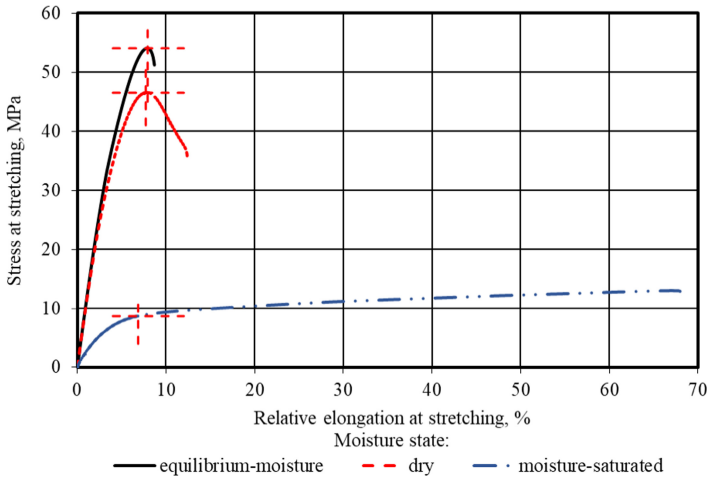

Fig. 1. Deformation curves of epoxy polymer samples under tension in different moisture conditions: equilibrium-moisture, dry and moisture-saturated (red dashed lines show the levels of ultimate tensile strength and the corresponding elongations).

Moisture saturation of samples of control compositions before equilibrium state sets in them leads to a significant decrease in strength and an increase in elongation at break (Fig. 1). Deformation curves of moisture-saturated samples are ascending with two different slope sections which causes certain difficulties in identifying the ultimate

tensile strength. To determine it, we have assessed the change in the increase in tensile stresses registered with a frequency of readings 0.01 s depending on relative elongation (Fig. 2). It was found that at a certain level of tensile deformations, the increase in stresses tends to zero, which manifests itself both for samples in moisture-saturated (Fig. 2a), and in dry (Fig. 2b) and equilibrium-moisture states. It is this level of relative deformations highlighted in Fig. 2 with a red vertical line, was taken in further analysis as the one where the samples achieve "critical" stresses identified as ultimate tensile stress.

In Fig. 1, these "critical" levels of tensile stresses in polymer samples and the corresponding relative elongations are shown by intersecting red dashed lines. The average values of the studied characteristics after statistical processing of a series of samples in different moisture conditions are given in Table 1. The average moisture content of samples in the equilibrium-moisture state was 1.41%, and 4.92% wt. in the moisture-saturated state.

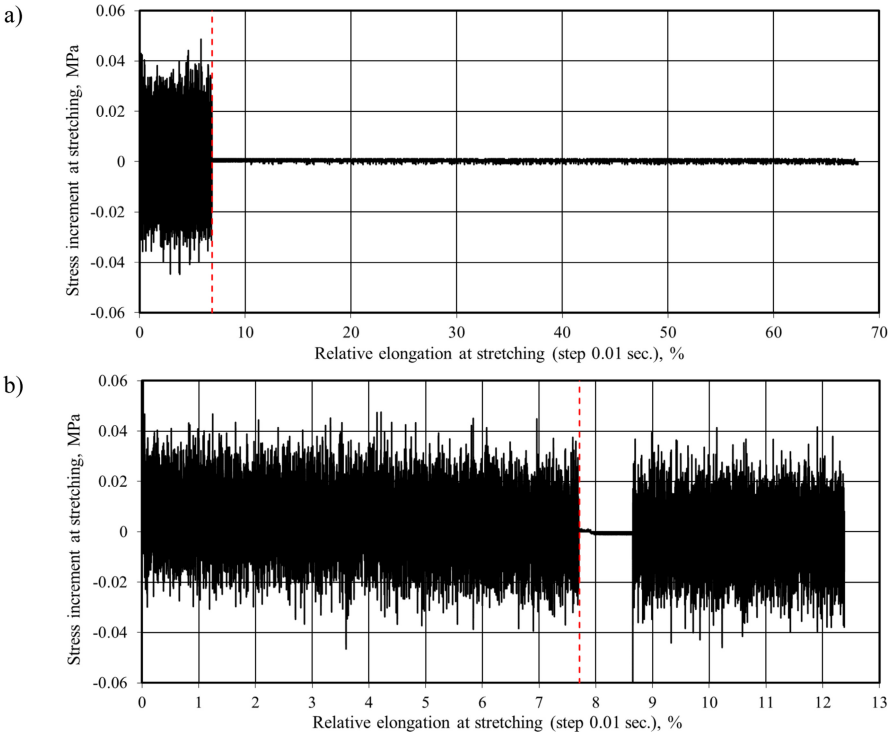

Fig. 2. The change in stress increment (step of readings registration is 0.01 s.) depending on relative elongation during tension of epoxy polymer samples in the moisture-saturated (a) and dry (b) states (red dashed vertical line shows the level of relative elongation corresponding to the "critical" stress at stretching).

According to the results of the studies, it was found (Table 1) that a change in the moisture content of samples from 1.41 to 4.92% leads to a decrease in the tensile strength from 53.30 to 8.95 MPa, which corresponds to a residual strength of only 16.7% from

control values. In this case, deformation characteristics of moisture-saturated samples at break increase 6.7 times, reaching a relative elongation of 67.5%. Such significant changes in elastic-strength parameters are associated with a change in the behavior of moisture-saturated samples under load from glassy to highly elastic.

Removal of free moisture leads to a decrease in the strength characteristics of Etal-247 + Etal-45TZ2 epoxy polymer by 9.9% with virtually unchanged deformation characteristics at stretching (−2.4%). At the same time, it is obvious to assume that diffusion of moisture into the polymer in this case is accompanied by a decrease in the intermolecular interaction forces, which, up to a certain level, may turn out to be "useful" in terms of strength characteristics. However, a further increase in moisture content can have a negative effect on the strength of polymer materials [14], which was clearly manifested for the studied compound.

The next analysis stage included assessing the influence of the moisture state of epoxy polymer samples on kinetics of damage accumulation in their structure under tensile stresses (Fig. 3). This analysis was done for deformation curves until the samples reached the "critical" stress levels. The algorithm for determining the latter was described above. Limit levels of the number of failures for equilibrium-moisture, moisture-saturated and dry states were 5.65, 5.84 and 5.30%, respectively.

Table 1. Elastic-strength and sorption characteristics of Etal-247 + Etal-45TZ2 epoxy polymer in various moisture states.

Moisture state of samples during testing	Average values of the studied characteristics for a series of samples				
	Moisture content of samples, % wt	Tensile strength at stretching, MPa	Relative elongation at stretching, %	Tensile strength at break, MPa	Relative elongation at break, %
Equilibrium-moisture	1.41	53.50	7.98	47.06	8.74
Moisture-saturated	4.92	8.95 (−83.3%)	7.05 (−11.7%)	12.40 (−73.7%)	67.48 (+672%)
Dry	0	48.18 (−9.9%)	7.79 (−2.4%)	36.67 (−22.1%)	12.54 (+43.5%)

The analysis results show (Fig. 3a) that curves of failure rate accumulation depending on the level of applied stress for samples in equilibrium-moisture or dry states are similar. A similar nature of failure accumulation curves was registered for the given series of samples and depending on relative elongation at stretching (Fig. 3a). At the same time, if the failure accumulation rate for moisture-saturated samples just slightly accelerates with an increase in relative elongation at stretching (Fig. 3a), then, depending on the level of tensile stresses, failure accumulation rates accelerate in comparison with samples in equilibrium-moisture state from 4.3 to 5.5 times (Fig. 3a). In particular, 50% of the total number of failures, where achieving this number causes sample destruction, is achieved for moisture-saturated samples already at stresses of about 6.2 MPa. A similar value

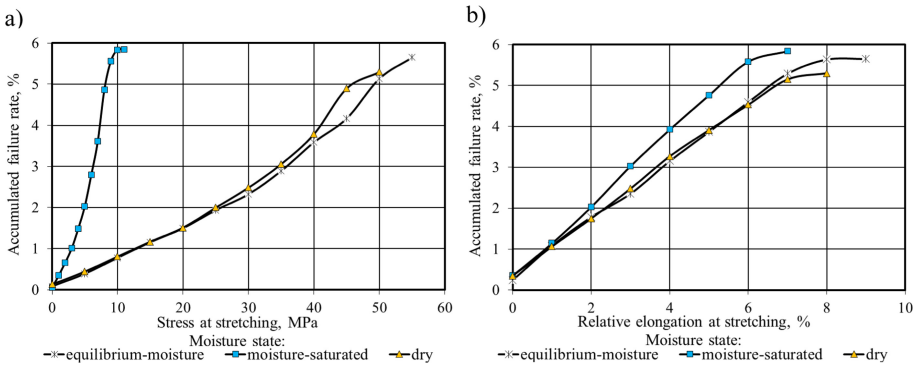

Fig. 3. Failure accumulation curves for a series of samples in different moisture states depending on the level of applied stresses (a) and relative elongations at stretching (b).

for equilibrium-moisture and dry samples is achieved at tensile stress levels of 34.0 and 31.4 MPa, respectively.

4 Conclusion

In the course of the study, a significant effect of the moisture state of samples on the elastic-strength parameters of Etal-247 epoxy resin- and Etal-45TZ2 hardener-based polymer was found. It was found that an increase in the moisture content of a polymer material up to 4.92% is accompanied by formation of a pronounced stage of forced highly elastic deformations with an increase in relative elongation at break and a decrease in tensile strength at stretching, by 6.7 and 6.0 times, respectively. It was found that at the ultimate moisture saturation, failure accumulation rate accelerates with an increase in the level of applied stress at stretching compared to the samples in equilibrium-moisture state, by 4.3–5.5 times.

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