SOUTHERN JOURNAL OF SCIENCES

ESTABLISHED IN 1993

Original research paper

THE INFLUENCE OF CLIMATIC FACTORS ON THE CHANGE IN THE ELASTIC-STRENGTH INDICATORS OF EPOXY POLYMERS BINDERS USED IN LIQUID THERMAL INSULATION COATINGS

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Received 20 November 2021; received in revised form 30 November 2021; accepted 14 December 2021

ABSTRACT

Introduction: Thermal insulating coatings are increasingly being introduced into construction practice for internal and external finishing enclosing structures and pipelines. Thermal insulation coatings are usually made based on polymer binder and mineral fillers. The durability and stability of the properties of heat-insulating materials depend on the type of binder. As a rule, polymers are used as a binder: epoxy resin; silicone rubber; urea-formaldehyde resins; aqueous dispersed polymers - styrene-butadiene, polyvinyl acetate, and acrylate (acrylic and styrene-acrylic). The quality indicator of binders can be assessed by the influence of the seasonality of climatic impact, and as a result, the best elastic strength characteristics of binders can be established after one month to a year of field tests. **Aim:** To determine the influence of climatic factors on the change in the elastic-strength indicators of epoxy polymers binders used in liquid thermal insulation coatings. **Methods:** A tensile testing machine of the AGS-X series with the TRAPEZIUM X software was used for mechanical tests. The tests were carried out in accordance with GOST 11262-2017 (ISO 527-2: 2012) "Plastics. Tensile test method". **Results and Discussion**: The paper discusses the results of experimental studies of the compositions of polymer binders and their resistance to various climatic factors, which will later be used as a polymer binder for thermal insulation coatings based on fine mineral granular systems. **Conclusions:** When analyzing the changes in the characteristics of polymer samples after exposure to climatic factors, it was found that compositions based on Etal-247 epoxy resin, cured with amine hardeners Etal-1440N, Etal-1460, Etal-1472, and Etal-45M, demonstrate the best elastic strength characteristics after one year of full-scale tests. The high stability of the indicators under consideration allows us to conclude that the use of Etal-247 resin as a base leads to creating of the most climate-resistant epoxy coatings.

Keywords: *Durability, temperature, elongation, tensile strength of samples, modified resin.*

1. INTRODUCTION:

The influence of climatic factors on the durability of polymer coatings was investigated and considered in the works of authors (Kablov, 2010; Kablov *et al.*, 2010; Kablov *et al.*, 2011; Startsev, Krotov and Golub, 1998; Startsev, 2009; Kablov, 2018; Selyaev, 2018; Nizina *et al.*, 2016; Selyaev *et al.*, 2020). Furthermore, based on experimental studies of field observations, the following main influencing factors were established and identified:

- solar radiation, its component in the ultraviolet range;
- the temperature of the ambient air and the temperature of the outer layers of the products;
- the amplitude of daily fluctuations in the temperature of both the air and the surface of the outer layers of the samples;
- relative air humidity and the amplitude of daily fluctuations in air and product humidity;
- average wind speed;

DOI: 10.48141/SJS.v30.n33.2022.07_ORYNBEKOV_pgs_44_53.pdf.

- the duration of exposure to positive and negative temperatures;

- the content of chemically active oxides in the air.

The action of the above environmental factors leads to the degradation of the polymer material, which is accompanied by the accumulation of damage and destruction of products, structures, buildings and structures.

Under the influence of climatic factors, the mechanisms of material degradation can be different: destruction; erosion; corrosion; plasticization; swelling and shrinkage; sorption and desorption; chemical interaction.

Under the influence of these factors, changes in the structure, the shape of the product, stress-strain state occur, internal stresses appear, strength, deformability (embrittlement) decrease. Cracks appear in the coating, it peels off, changes color and geometric parameters.

2. MATERIALS AND METHODS:

An AGS-X series tensile testing machine with TRAPEZIUM X software was used to carry out mechanical tensile testing of polymer composites compositions. The frequency of fixing the values of stresses and strains was 0.01 s. The tests were carried out in accordance with GOST 11262-2017 (ISO 527-2:2012) "Plastics. Tensile test method" at a temperature of 23 ± 2 °C and relative humidity of 50 ± 5% (GOST 11262-2017 (ISO 527-2: 2012), 2018). The spreading speed of the jaws of the tensile testing machine was 2 mm/min. In parallel, at least 6 samples were tested, having the shape of "eights" (type 2 according to GOST 11262).

GOST 11262-2017 (ISO 527-2:2012) - A test specimen is stretched along its main longitudinal axis at a constant speed, during stretching, the specimen withstands the load, and the elongation of the specimen is measured, and the specified indicators are determined. A testing machine capable of measuring the load with an error of less than 1% of the measured value when the specimen is stretched, and a constant rate of expansion of the clamps within limits is required by this standard.

2.1. Experimental studies of the influence of climatic factors on the change in the elastic-strength indicators of binders

Joint analysis of changes in strength characteristics and weight gain of epoxy polymers Etal-247 + Etal-45M specimens at the initial stage of exposure allows us to put forward several hypotheses regarding the physical-chemical processes occurring in the structure of the polymer matrix (Figure 1) (Kablov, 2010; Kablov *et al.*, 2010; Kablov *et al.*, 2011; Startsev, Krotov and Golub, 1998; Startsev, 2009; Kablov, 2010; Kablov *et al.*, 2010; Kablov *et al.*, 2011; Startsev, Krotov and Golub, 1998; Startsev, 2009; Selyaev *et al.*, 2020). Analysis of the data presented in Figure 1*a*, indicates that the relative humidity of samples at the age of 3 months is practically independent of the time of the beginning of the exposure. In this case, the change in the strength indicators of the samples for each of the series of samples is different (Figure 1*b*), which indicates the absence of a direct relationship between the weight gain and the ultimate tensile strength.

The discrepancy in strength indicators depending on the moment of the beginning of exposure can be described based on the main acting environmental factors (Kablov *et al.*, 2010; Kablov *et al.*, 2011; Startsev, Krotov and Golub, 1998). In particular, although the solar radiation levels in the spring and autumn periods are almost identical, in the first case, there is a slight increase, and in the second, a decrease in strength indicators.

The reason for this is probably the difference in the surface temperature of polymeric materials and the duration of its exposure. Since, among the spring months, only May is characterized by high "activity", as opposed to three months of the summer period, it can be assumed that mainly relaxation processes of the initial structural disequilibrium take place in the first case. At the same time, high levels of solar radiation, combined with temperatures above the glass transition temperature of the polymer binder, during the summer period, could lead to partial surface degradation of the polymer matrix.

The invariability of strength indicators at the end of the autumn period may indicate the equilibrium of the processes of hydrolysis of active, unreacted groups and desorption of low molecular weight reaction products as a result of several successive cycles of moistening and drying (Kablov, 2018; Selyaev, 2018; Nizina *et al.*, 2016). Since the winter months are characterized mainly by negative temperatures in combination with the minimum values of solar radiation, plasticization of the structure of the polymer matrix with atmospheric moisture should be considered as the main reason for the

decrease in strength indicators at this stage.

Analyzing the change in the strength characteristics of specimens of the composition Etal-247 + Etal-45M of various series relative to the common time axis (Figure 2), it should be noted that, despite the same external effect, the change in the properties of specimens of this composition is multidirectional in almost all areas. Taking into account the fact that under prolonged exposure to load, temperature, and moisture, a certain limiting state of the epoxy polymer is reached, characterized by a constant value of strength, it can be argued that the stabilization of properties for the series of samples exposed from March 1 and June 1 was never achieved. The maximum reduction in strength for specimens of these series was 30%. For epoxy polymers exhibited from September 1, the decrease in strength did not exceed 10%; from January 1 - the maximum decrease in strength (about 20%) was recorded in the first three months of aging, while no significant changes were recorded in the remaining time interval. Probably, the stabilization of properties in volume for samples of the "autumn" series occurred at the early stages of exposure, which led to the preservation of properties throughout the experimental study. Since the final seasons of exposure for this series of samples are "spring, summer, and autumn", with a high degree of confidence, one can assume a strong destructive effect of solar radiation on the properties of the epoxy polymer. Nevertheless, due to a large amount of atmospheric precipitation in the spring-autumn time interval of 2021 in combination with the equally high level of solar radiation “summer”, it is likely that at this stage, there is also a balance of hydrolytic and desorption processes. The greatest decrease in strength (6%) was recorded for the spring period, which can be explained by the destruction of the surface layer of polymer samples. The change in the properties of the "winter" series samples is inherently close to the course of climatic aging of samples exposed in natural conditions since 2021. The saturation of the samples of this series with moisture at the initial stage, in the absence of a significant effect of solar radiation, despite further drying during the spring season, led to a significant decrease in the strength properties. Apparently, the prevailing role of drying the prevailing role of drying made it possible to compensate for the negative effect of thermal and moisture aging and prevent a further decrease in strength.

Summarizing the data obtained, it can be argued with a high degree of confidence that for the first incomplete 10 months of exposure, the samples of the compositions under consideration did not transition to the ultimate stable state, characterized by an almost unchanged value of strength indicators. The absence of sharp changes in the strength indicators of epoxy polymers Etal-247 + Etal-45M for less than 10 months of exposure may indicate sufficient stability of the material properties over time.

Let us analyze the climatic resistance of compositions containing the aliphatic diluent Etal-1 (Figure 3). The data obtained for the unmodified composition ED-20 + Etal-45M confirm the previously put forward hypothesis about seasonal differences in the course of structural relaxation processes and the elimination of the initial disequilibrium. So, for compositions, the initial period of exposure of which fell on the seasons with a high level of solar radiation "spring and summer", a sharp drop in strength (more than two times) was recorded after three months. At the same time, the decrease in the strength indicators of the series of samples corresponding to the other two seasons, "winter and spring" occurred more evenly - by 15÷25% per season. Despite the differences in the rate of change in tensile strength, after 10 months of exposure, the strength of all series of samples, without exception, decreased by 60–65% from the initial value. Moreover, if for the epoxy polymers compositions of the "spring" and "summer" series this level was achieved after 6 months of exposure, for the "winter" series - after 9 months, then for the "autumn" series - only by the end of the experimental study, which also suggests the key role of solar radiation in the aging process of the epoxy composition ED-20 + Etal-45M.

The change in the strength of samples of epoxy composition modified with 10% Etal-1 for the "spring" and "summer" series practically does not differ from the control composition. A similar decrease in the absolute value of strength to the level of 20–25 MPa was recorded already after 3 months from the beginning of the exposure. In the future, there are only minor deviations from the obtained values - no more than 6% of the initial value.

For the compositions of other series, changes at the initial stage occur by analogy with the composition Etal-247 + Etal-45M. So, for samples of the "winter" series, there is a decrease in strength caused by the plasticization of intermolecular bonds. However, in the future, due to the effect of solar radiation, there is first a restoration of strength indicators, which is not

typical for an unmodified composition, and then their decrease. Consequently, the introduction of Etal-1 into the composition of ED-20 + Etal-45M leads to a change in the structure of the polymer matrix, in particular, to an increase in the degree of influence of atmospheric moisture on the properties of the epoxy polymer (Startsev, 2009; Kablov, 2018; Selyaev, 2018). Specimens of the "autumn" series, on the other hand, do not undergo significant changes in strength at the initial stage. Nevertheless, by analogy with the composition of ED-20 + Etal-45M, the main decrease in strength takes place precisely during the spring and summer seasons.

The composition (75% ED-20 + 25% Etal-1) + Etal-45M deserves special attention. By analogy with other compositions, at the initial stage, depending on the season of exposure, both an increase and a decrease in strength indicators are observed. At the same time, unlike other modified compositions, a drop in strength over the first 3 months of exposure was recorded only for samples of the "summer" series; in other cases, there is a slight change in properties. It should be noted that regardless of the start of exposure, a sharp drop in strength indicators is observed exclusively in the summer months, which is confirmed by the graphs in Figure 3. As in the case with the samples of the composition (90% ED-20 + 10% Etal-1) + Etal-45M, the recovery of the strength parameters of the epoxy polymers was recorded mainly during the autumn months.

A likely reason for this may be the high proportion of hydroxyl bonds in the composition of the polymer matrix and, accordingly, their increased contribution to the resulting strength value. Consequently, at elevated levels of solar radiation, a number of hydroxyl bonds are destroyed, and the subsequent desorption of low molecular weight components of the polymer matrix takes place, Consequently, at elevated levels of solar radiation, a number of hydroxyl bonds are destroyed, and the subsequent desorption of low molecular weight components of the polymer matrix takes place, leading to a decrease in strength indicators. The increased level of precipitation, in turn, activates the interaction between reactive bonds, leading to additional cross-linking of macromolecules. In total, this change in indicators makes it possible to characterize the properties of the composition under consideration as unstable. Nevertheless, it was found that the greatest change is observed during the relaxation of the initial disequilibrium, that is, hydrolysis of the residues of uncured binder components and the subsequent desorption of low molecular weight reaction products upon drying. As the number of cycles increases, the change in properties slows down.

2.1.1. Change in elastic-strength and sorption characteristics of polymers during natural climatic aging

It is known that the properties of polymers and their durability during exposure are largely determined by the type of curing system, which makes it extremely important to assess the climatic resistance of polymeric materials with the identification of the most effective resins and hardeners.

The beginning of full-scale exposure at the test site - from December 1, 2020, to September 2021, samples of epoxy polymers were exposed, the compositions of which are shown in Table 1 (except for compositions No. 3, 11, 13, and 14). The change in the elastic-strength parameters of epoxy polymers was recorded after 45, 90, 180, 270, and 300 days of climatic exposure.

According to the results of the tests carried out, it was found that the greatest, almost monotonic, decrease in properties over 180 and 270 days is observed for polymers based on ED-20 epoxy resin, cured, respectively, by Etal-1460 and Etal-45M amine hardeners (Figure 4a). After one year of full-scale exposure, the decrease in strength indicators for the composition cured by Etal-45M reaches 60%, Etal-1460 - 69%. After 10 months of climatic action in a temperate continental climate, the highest stability of properties was recorded for a polymer cured by Etal-1440N. The decrease in tensile strength, in this case, did not exceed 34%. Exposure of this composition for 45 days led to an increase in strength indicators by 13%.

Natural exposure of polymers based on ED-20 epoxy resin is accompanied by a significant decrease in deformative characteristics, which is primarily associated with the embrittlement of the compositions (Figure 4b). The greatest decrease in the relative elongation of polymers is observed up to 180 - 270 days with the stabilization of indicators in the subsequent time interval. For polymers cured, Etal-1460 and Etal-45M, the elongation at maximum load decreases by 7.7 and 3.6 times. For samples cured with Etal-1440N amine hardener, the maximum reduction in tensile deformability does not exceed 2.4 times.

3. RESULTS AND DISCUSSION:

3.1. Results

Analysis of the sorption parameters of epoxy polymers based on ED-20 showed (Figure 5a) that under the influence of climatic factors, accompanied by moistening and drying of the samples, it can occur as a monotonic increase in the mass of the samples (composition 1 - ED-20 + Etal-1440N) and its cyclical change (compositions 2, 4). The greatest cyclicity of mass change is observed for the composition ED-20 + Etal-45M. For polymers based on ED-20 epoxy resin, cured by Etal-1460 and Etal-1440N (Figure 5b), after 3 months of full-scale exposure, an increase in the elastic modulus in tension by 17-22% is observed, which is obviously also associated with embrittlement of samples. Further exposure has practically no effect on this indicator for the composition ED-20 + Etal-1460. An increase in the duration of natural exposure to more than 180 days leads to a decrease in the elastic modulus for the ED-20 + Etal-1440N composition, which does not exceed 10%. Long-term climatic exposure does not significantly affect the change in the elastic modulus of the ED-20 + Etal-45M epoxy polymer. After 10 months of full-scale exposure, the decrease in this characteristic is no more than 10% (Figure 5 b).

Analysis of the results of full-scale exposure of epoxy polymer based on low-viscosity resin Etal-370 (compositions 9, 10, 12) indicates (Figure 6a) about a higher climatic resistance in a time interval of up to 180 days in comparison with compositions No. 1, 2, 4 on based on ED-20 (Figure 4). For the compositions Etal-370 + Etal-1460 and Etal-370 + Etal-45M, an increase in tensile strength was recorded, reaching 42 and 31%, respectively, compared with the control values. However, further exposure of the compositions under natural conditions leads to a sharp decrease in properties - the relative tensile strength for these polymers by 300 days is 49÷52% of the initial indicator.

The greatest decrease in deformative indicators also occurs in the time interval from 180 to 300 days (Figure 6b). After a year of full-scale exposure, the reduction in tensile elongation varies depending on the brand of hardener in the range from 3.3 to 4 times. The nature of the change in the mass of the epoxy polymer based on the modified Etal-370 resin (Figrky 7a) indicates the highest sorption moisture absorption during the winter (time interval 0 - 90 days) and autumn (270 - 300 days) periods, which, first of all, , is associated with a combination of low temperature and high ambient humidity.

Natural exposure of polymers of this group is accompanied by an increase in the modulus of elasticity in tension, depending on the hardener, up to 10–32% compared to the control samples (Figure 7b).

3.2. Discussions

Compositions based on modified epoxy resin Etal-247 (Figure 8a) have the highest climatic resistance, according to the results of field tests. The maximum decrease in tensile strength after 10 months of full-scale exposure does not exceed 20% for the composition cured by Etal-45M. For polymers cured Etal-1440N and Etal-1460, the residual tensile strength after 300 days of testing is 98 and 84% of the control values, respectively. The impact of climatic factors on the composition of Etal-247 + Etal-1472 practically does not lead to a change in properties over the entire investigated time interval. Polymers based on Etal-247 epoxy resin are also characterized by the highest, compared with other studied polymers, stability of deformation characteristics (Figure 8b). In this case, the maximum decrease 101 in tensile elongation over the entire time interval does not exceed 37%, which is significantly less than for compositions obtained based on ED-20 and Etal-370 epoxy resins (Figures 4, 6).

The nature of the curves describing the change in the mass of epoxy polymers based on Etal-247 resin (Figure 9) is similar to the above graphical dependencies shown in Figures 5a and 3a. In addition, the most noticeable variation in weight depending on the duration of full-scale exposure is also observed for the polymer cured by Etal-45M.

4. CONCLUSIONS:

When analyzing the changes in the characteristics of polymer samples after exposure to climatic factors, it was found that compositions based on Etal-247 epoxy resin, cured with amine hardeners Etal-1440N, Etal-1460, Etal-1472 and Etal-45M, demonstrate the best elastic strength characteristics after one year of full-scale tests. Furthermore, the high stability of the indicators under consideration allows us to conclude that the use of Etal-247 resin as a base leads to creating of the most climate-resistant epoxy

coatings.

5. DECLARATIONS

5.1. Study Limitations

No limitations were known at the time of the study.

5.2. Acknowledgements

The authors are grateful to the leadership of the Satbayev University and the Science Committee of the ME&S RK for creating the conditions for carrying out this work.

5.3. Funding source

This research is funded by the Science Committee of the Ministry of Education and Science of the Republic of Kazakhstan and was done as part of the project AP08855714 “Thermal insulation coatings based on finely dispersed mineral granular systems” in the framework of "Grant funding for scientific and (or) scientific and technical projects for 2020-2022 with an implementation period of 27 months”.

5.4. Competing Interests

The authors declare that no potential conflict of interest exists in this publication.

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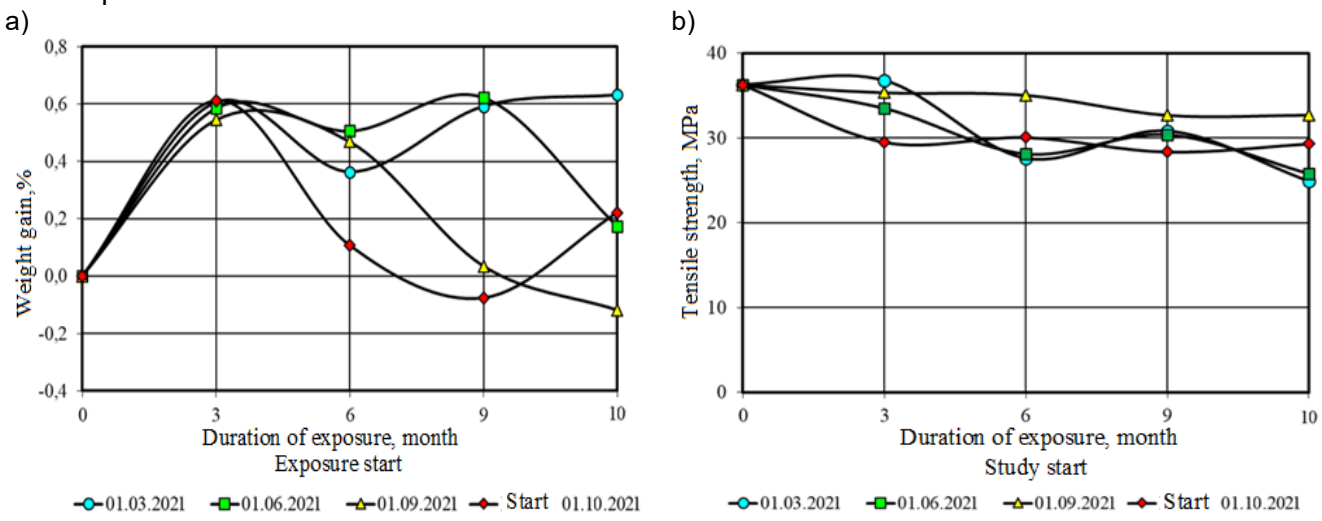

Figure 1. *Change in mass (a) and tensile strength (b) samples of composition Etal-247 + Etal-45M, depending on the season of the beginning of exposure*

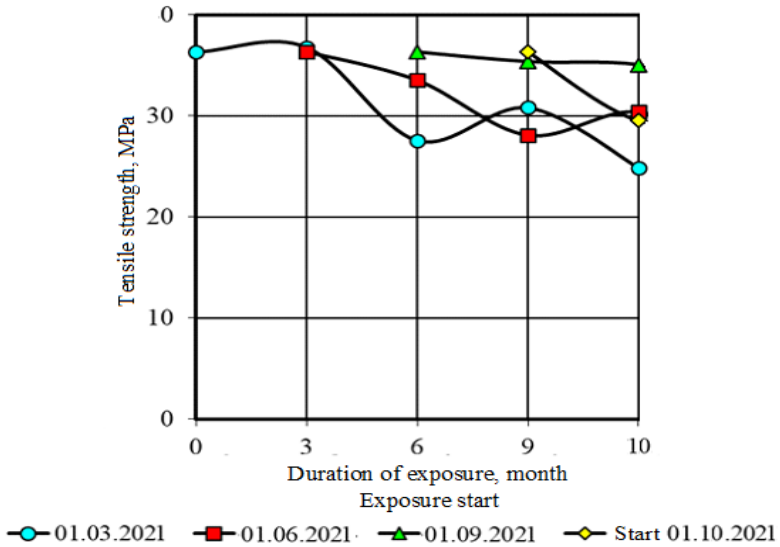

Figure 2. *Change in tensile strength of specimens of composition Etal-247 + Etal-45M under tension relative to the common time axis*

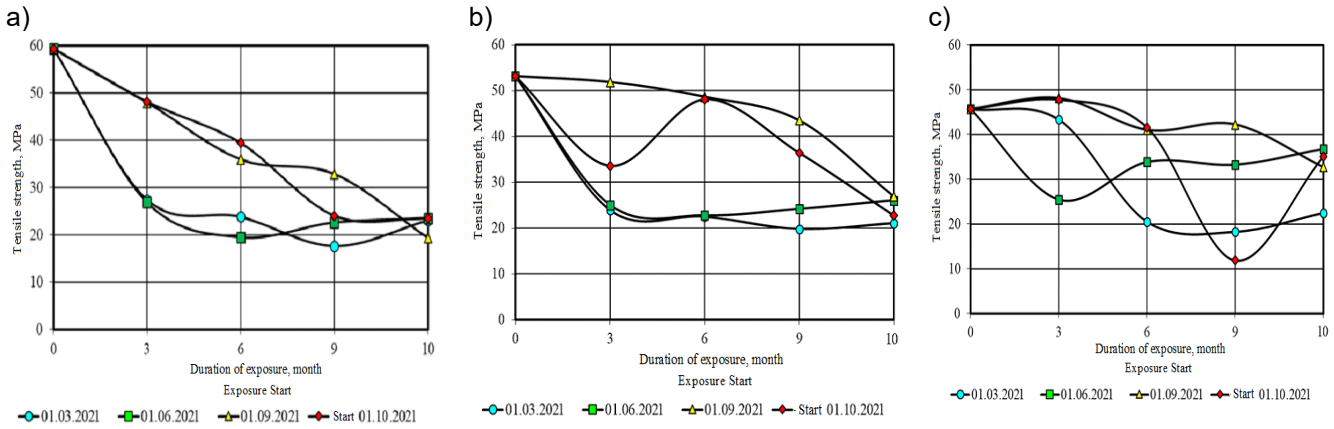

Figure 3. *Change in the ultimate strength of specimens modified by Etal-1, depending on the season of the beginning of exposure (a - ED-20 + Etal-45M; b - (90% ED-20 + 10% Etal-1) + Etal-45M; c - (75% ED-20 + 25% Etal-1) + Etal-45M).*

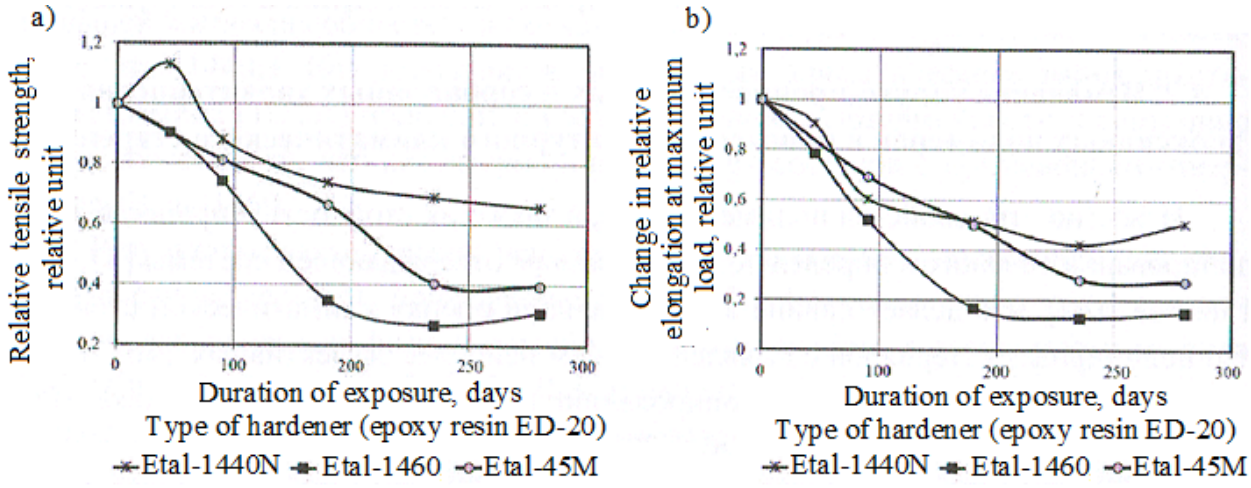

Figure 4. *Change in the relative ultimate strength (a) and relative elongation (b) during stretching of epoxy polymer based on ED-20 resin, depending on the duration of full-scale exposure*

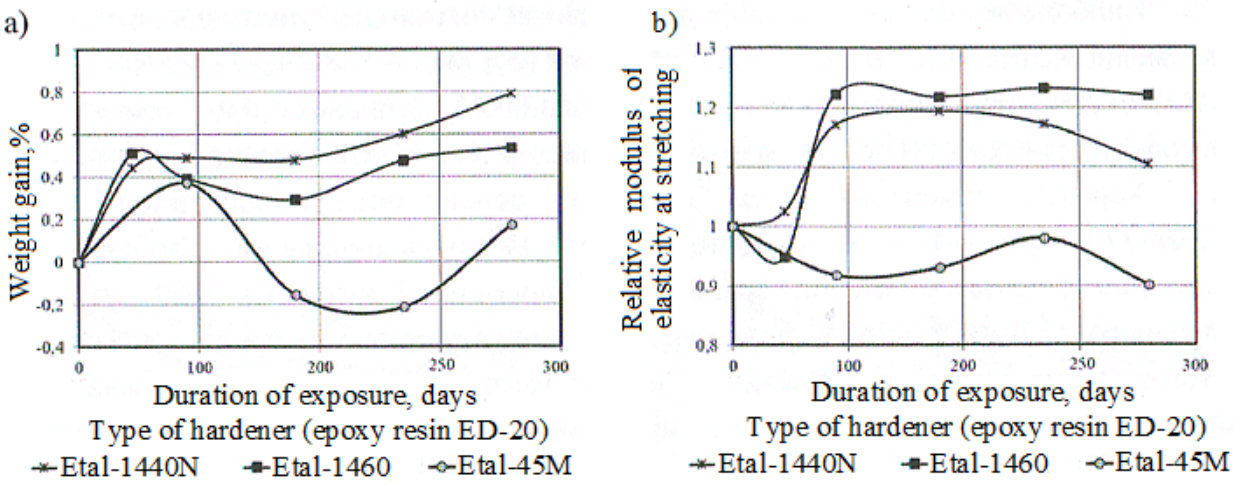

Figure 5. *Change in mass (a) and relative modulus of elasticity in tension (b) of epoxy polymer based on ED-20 resin, depending on the duration of full-scale exposure*

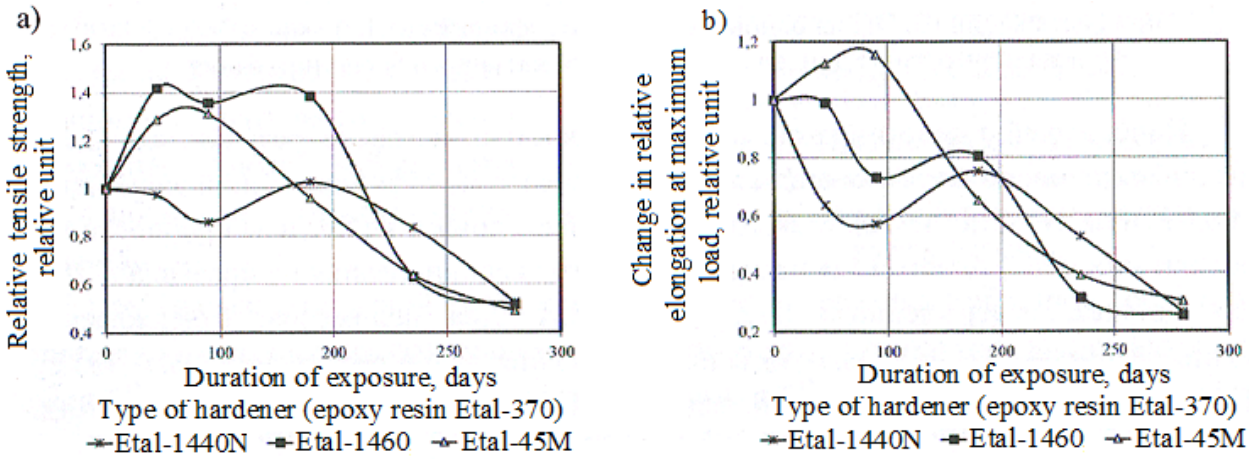

Figure 6. *Change in the relative ultimate strength (a) and relative elongation (b) during stretching of the epoxy polymer based on the modified Etal-370 resin, depending on the duration of full-scale exposure*

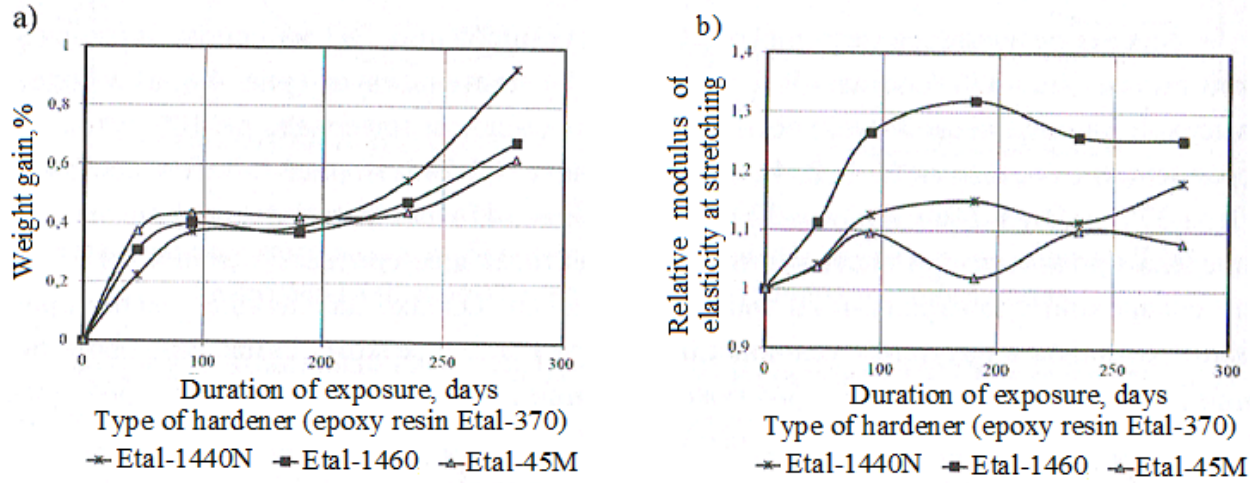

Figure 7. *Change in mass (a) and relative modulus of elasticity in tension (b) of an epoxy polymer based on modified Etal-370 resin depending on the duration of natural exposure*

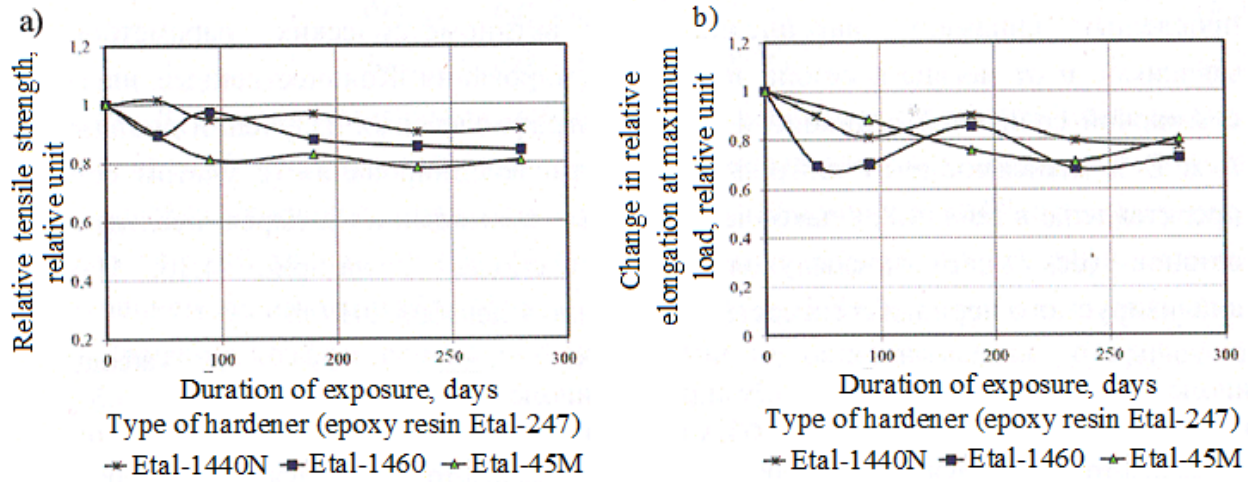

Figure 8. *Change in the relative ultimate strength (a) and relative elongation (b) during stretching of an epoxy polymer based on modified Etal-247 resin, depending on the duration of natural exposure*

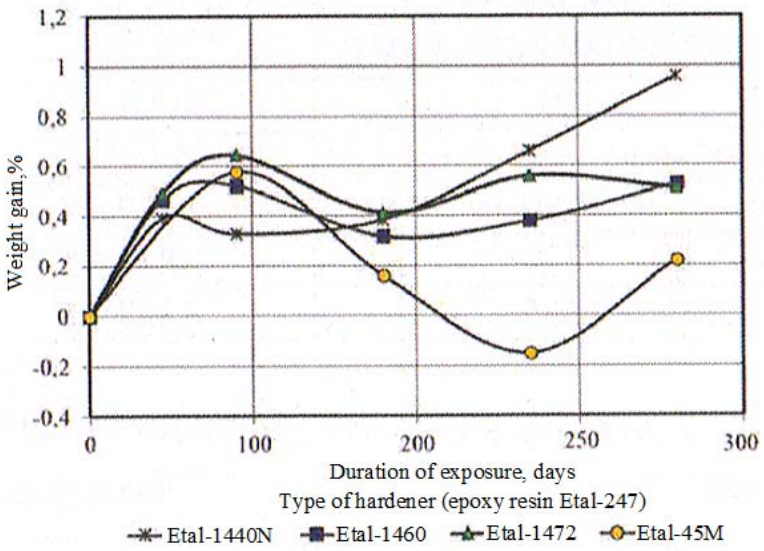

Figure 9. *The weight gain of EP based on modified Etal-247 resin, depending on the duration of full-scale exposure*

Table 1. *Compositions of the studied epoxy polymers*

No. of composition	Epoxy resin mark	Hardener mark	Resin : Hardener ratio
1	ED-20	Etal – 1440H	100÷56
2		Etal л – 1460	100÷39
3		Etal – 1472	100÷25
4		Etal – 45M	100÷50
5	Etal – 247	Etal – 1440H	100÷53.2
6		Etal – 1460	100÷37
7		Etal – 1472	100÷23.75
8		Etal – 45M	100÷47.5
9	Etal – 370	Etal – 1440H	100÷56
10		Etal – 1460	100÷39
11		Etal – 1472	100÷25
12		Etal – 45M	100÷50
13	ED – 20	Polyethylene polyamine	100÷10
14	Etal – 247	Polyethylene polyamine	100÷9.5