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RESISTANCE TO AGING RESEARCH IN SEA WATER COMPOSITES WITH THE POLYESTER-GLASS RECYCLATE

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Abstract

Composites are materials used for various types of constructions in the automotive industry, aviation, and shipbuilding. Due to the wide use of these materials, there is a problem with their recycling. Such material requires appropriate processing technology, which has been developed to obtain a recyclate with a specific granulation. The use of hand laminating technology made composites with the addition of polyester and glass recyclate with granulation of 1.2, as well as content: 0%, 20%, 30%. These types of materials are exposed to various types of atmospheric factors that affect their durability. Aging is defined as changes in the composite when exposed to atmospheric conditions, such as sunlight, temperature, thermal cycles, water in various forms and wind. This article uses recycled polyester and glass composites to investigate the effect of aging in seawater on their strength properties. These tests can be used to pre-assess the applicability of newly developed materials as construction or protective coatings. They were carried out on a specially prepared station for accelerated tests, with elevated temperature (35ºCC), as well as brine spray imitating sea atmosphere. The method is used to accelerate the aging processes occurring in composite materials. Samples were subjected to cycles of 5, 30 and 60 days respectively. Samples were weighed and measured before and after each cycle. In order to investigate the effect of aging on strength properties, the composites underwent a static tensile test in accordance with the standard for plastics. Studies have shown that as a result of the aging process, the strength properties decrease slightly, which affects the favourable assessment of these materials as constructional.

Keywords: *recycling, polyester-glass recyclate, aging of composites, tensile test*

1. Introduction

Polymer composites are used in both general-purpose constructions (pipes, tanks, ship hulls), vehicle components, panels in construction, as well as for more technologically complex structures, such as aerospace, military or biomedical constructions. The increasing use of these materials results from their unique properties, which are not available in materials such as steel or aluminum. This applies, for example, to a high ratio of strength and stiffness to mass as well as resistance to corrosion and fatigue. Considering the low cost of manufacturing them, as well as the possibility of relatively easy execution of complicated shapes of finished construction elements, with a reduced number of technological operations, it makes composites an excellent construction material [3, 6].

In available literature, corrosion in composites is termed – aging. This is mainly due to the lack of observed and described chemical and electro-chemical reactions occurring between the composite material and the corrosive environment in which it is found. Therefore, aging is general any changes taking place in the composite during the operation of various factors, mainly atmospheric factors (physical factors prevail). The most important of them are wind, temperature, water (including seawater) and sunlight [1, 10].

Aging can be divided into natural, artificial and climatic. The changes in composite materials can be permanent or reversible. Persistent changes include chemical changes occurring as a result of polymerization, depolymerisation, cross-linking and oxidation, as well as those transformations classified as caused by thermodynamic factors, i.e. crystallization, ordering of macromolecules. The boundary between reversible and irreversible changes is not strict and often not practical [1, 10].

Degradation of the polymer laminate under the influence of atmospheric conditions, such as water in various forms, is a process with many stages leading to changes in the material structure. This mainly affects physical and mechanical properties. Composites do not belong to water-soluble materials, but have the ability to absorb them in various amounts. It depends on the composition of the composite, the proportion of the matrix, its chemical structure, strength of the matrix and fibre adhesion, structural quality [4, 6].

Phenomena related to water absorption (sorption) can be divided into adsorption processes on the surface of polymer and fibres as well as absorption, in which water penetrates into the polymer structure and the surface layer of fibres causing various chemical changes. The penetration of water into the material occurs through mechanisms:

- diffusion – directly to the matrix,
- capillary flow – to the fibre / warp boundary layer,
- transport of water molecules by micro cracks.

These mechanisms become particularly active after damage to the composite, e.g. due to an impact or formation of the crack network caused by prolonged diffusion of water. These internal discontinuities cause further penetration of water, causing self-degrading degradation of the material [7, 9].

The penetration of water molecules into the polymer is nothing but the physical aging of the material. Water penetrates into micro fissures as well as empty spots left after the resin has been washed out and thus reduces the properties of the composite. These factors cause, among others delamination along the fibres, as well as lowering crack resistance. Laminates lose their properties only after a few months of immersion in water. Short-term exposure to water does not reduce their properties [10].

The mechanism of destroying the surface layers of polymer composites during exposure in water is bubbling. Research on this phenomenon has been carried out for a long time. It is particularly noticeable in the case of laminates immersed all the time in reins, e.g. yachts [6].

There is extensive literature on corrosion testing of materials. Rawe, for example, proved that the increase in water temperature accelerates the aging process. Cooking for two hours gives comparable results every three months immersion at room temperature. Other authors have conducted tests in seawater at 30ºC on polymer laminates reinforced with glass fibre [2]. Most of the tests use elevated relative humidity, temperature and brine spray. Such a method gives about 100-fold acceleration of corrosive processes and shortens the duration of a corrosion test many times [11].

The main objective of the study was to determine the effect of the recyclate content and the corrosive environment on the mechanical properties of the composite.

For this purpose, composites with different recycled content were made. The tests were carried out on the samples subjecting them to a corrosive environment (3% of the year in. NaCl). After an adequate residence time of the samples in the salt mist, they were subjected to a static tensile test. The results of mechanical properties were the parameters determining the resistance of the composite to the corrosive environment.

2. The course of research and methodology

The research material was a polyester-glass layered composite with the addition of recyclate. The polyester-glass recyclate was obtained from a fragment of the hull of a sea-going ship [5]. The basis on which the results of the tested composites based on recyclate were derived was a composite without recyclate. The composite was a kind of base material. The tests were carried out on samples made of composite without recyclate and with 20% and 30% recyclate content with a pellet size of ≤ 1.2 mm. Samples for static tensile tests were prepared in accordance with the PN-EN ISO 527-4_2000P standard. The shape and dimensions of the samples are shown in Fig. 1

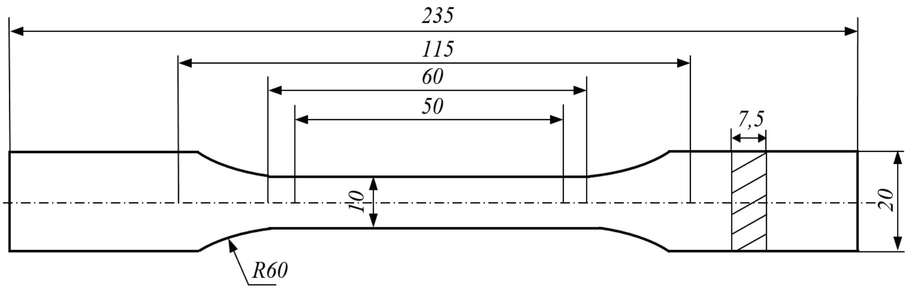

Fig.1. The shape and dimensions of samples for static tensile tests

Samples prepared in this way::
- composite without recyclate (assumed the designation K0),
- composite with 20% recyclate content and granulate size 1.2 mm (denoted K20.1.2),
- composite with 30% recyclate content and 1.2 mm granulate size (marked K30.1.2),

subjected to a static tensile test. Average values of mechanical properties of the tested materials were presented in Tab. 1.

Tab. 1. Mechanical properties of the tested composite materials obtained from a static tensile test

Material	R_m [MPa]	ε [%]
K0	108	2.00
K20.1.2	40	1.44
K30.1.2	25	0.85

Then samples were made of composite materials designed for corrosion tests. Corrosion tests were divided into 3 cycles:

I – exposure time – 120 hours,
II – exposure time – 720 hours,
III – exposure time – 1440 hours.

A corresponding batch of samples from the tested materials K0, K20.1.2 and K30.1.2 was prepared for each cycle. The side surfaces of corrosion test samples were not protected against penetration of the NaCl solution inside them, thus simulating the case of damage to the marine structure and exposure of the surface to the penetration of the salt solution. The samples for corrosion tests were placed on a stand in two layers in such a way that the NaCl condensate from the upper layer of the samples did not fall on the tested surface of the lower layer samples (Fig. 2).

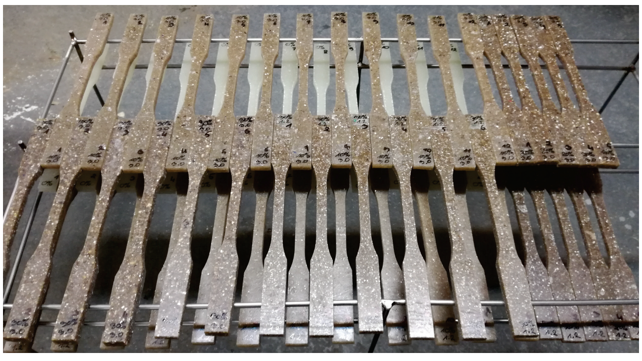

Fig. 2. Samples for testing placed on a stand

The stand with the samples was placed in a specially designed and made test bench for corrosion tests. The rock of the stand includes a sample stand, an injector salt mist generator, an electric heater with temperature control and a thermometer. Depending on the cycle, the samples were exposed to 3% of the NaCI for 3 months, respectively for 120 hours, 720 hours, and 1440 hours. The temperature of the NaCl aqueous solution was 35ºC. During the day the salt fog was generated for 8 hours at the closed chamber, for 16 hours the salt spray was suspended, the lid was opened and the samples were vented.

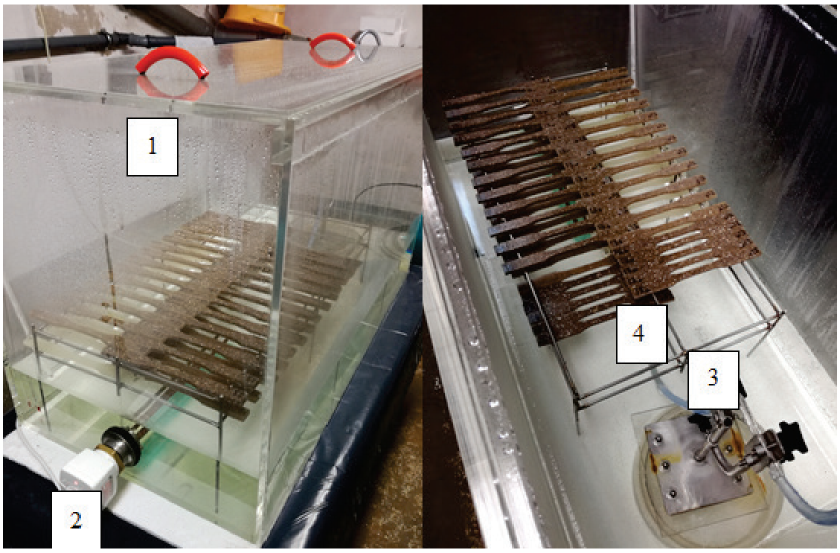

Fig. 3. Tank for corrosion tests with salt spray: 1 – tank, 2 – heater, 3 – injector, 4 – stand with samples

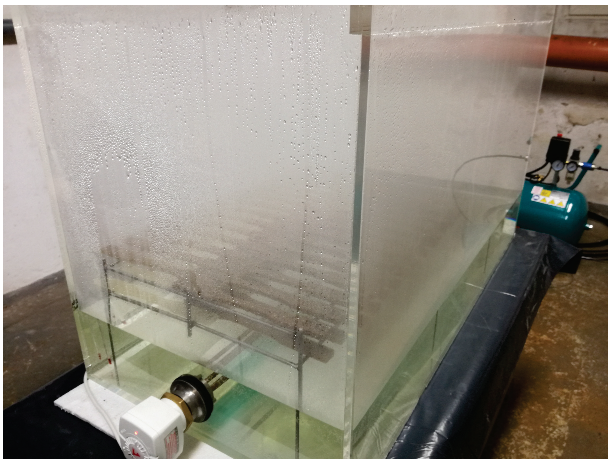

Fig. 4. View of the stand during corrosion tests in salt spray

The arrangement of samples, components of the corrosion station and a view of salt mist are shown in Figs. 3 and 4. Before and after each corrosion exposure cycle, the samples were dried, measured, and weighed. For each cycle after the corrosion test process, the samples were subjected to a static tensile test on a testing machine with a hydraulic drive type MPMD P10B with the TestXpert II software version 3.61. Zwick & Roell together with the use of Epsilon extensometer model 3542 [8]. Fig. 5 shows the scrap of samples of composite materials tested.

3. Results of the research

Test results of static tensile test of sample material samples composite after appropriate corrosion cycles are shown in Fig. 6-8.

Fig. 5. Samples after static tensile testing

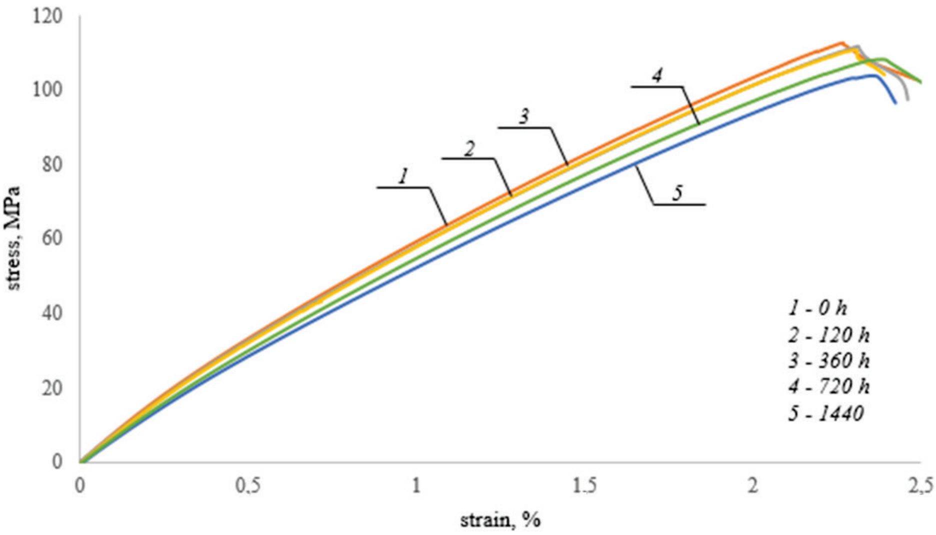

Fig. 6. Tensile test diagram of K0 composite samples after corrosive exposure

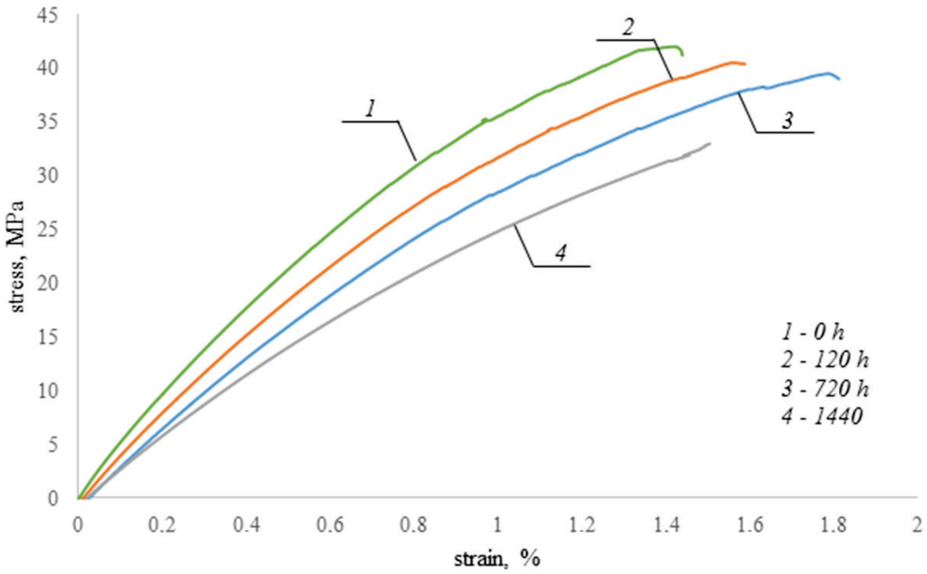

Fig. 7. Tensile test diagram of K20.1.2 composite samples after corrosive exposure

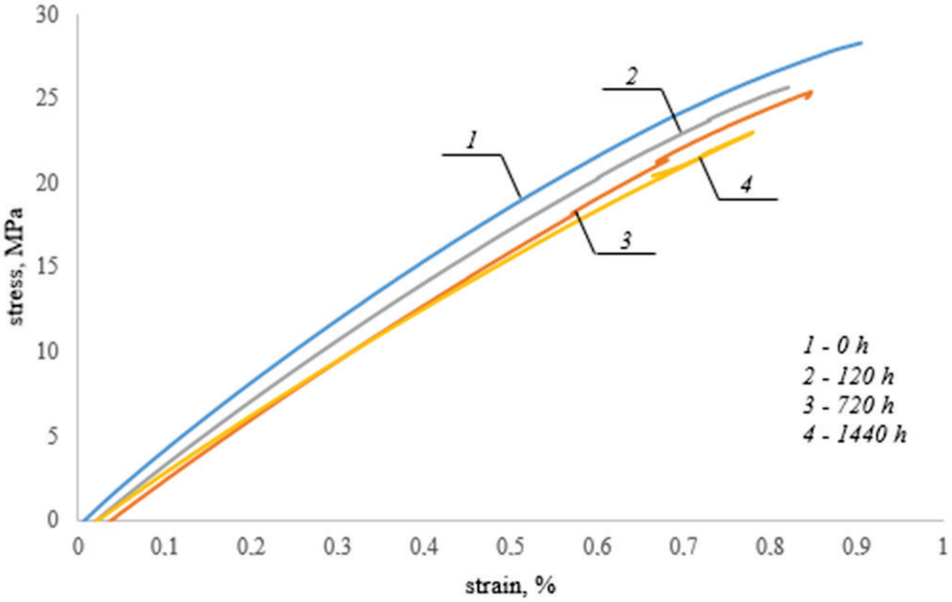

Fig. 8. Tensile test diagram of K30.1.2 composite samples after corrosive exposure

Figure 6 presents the stretching characteristics of K0 composite samples after corrosive exposure. The characteristics show that the corrosive environment of 3% NaCl caused a slight decrease in the strength properties of the composite K0 in relation to the composite not exposed to the corrosive environment. In particular, there has been a reduction in strength (R_m) accordingly:

– after 120 hours of staying in a corrosive environment – by 4%, 360 h – by 6%, 720 h – by 8% and after 1440 h – by 13%.

Figure 7 shows the stretching characteristics of K20.1.2 composite after corrosive exposure. The characteristics show that the recycled content with a longer period of exposure to the corrosive environment causes a reduction in the strength properties of the K20.1.2 composite. In particular, there has been a reduction in strength (R_m):

– after 120 hours of staying in a corrosive environment – by 4%, 720 hours – by 15% and after 1440 hours – by 18%.

Figure 8 shows the stretching characteristics of the K30.1.2 composite after corrosive exposure. A further increase in the recycled content (up to 30%) in the composite under the same corrosive conditions as the samples from the K0 and 20.1.2 materials causes further deterioration of the strength properties. There has been a reduction in strength (R_m) in relation to material not exposed to corrosion:

– after 120 hours of staying in a corrosive environment – by 9%, 720 hours – by 11% and after 1440 hours – by 18%.

With the decrease in strength properties (), a significant decrease in plasticity () occurred. A material with a high content of recycled material exhibits properties of brittle materials.

4. Conclusions

1. The content of polyester-glass recyclate in a polyester-glass sandwich composite reduces its strength and plastic properties.
2. Composite with recyclate in the seawater environment is highly susceptible to further reduction of mechanical properties. Recycled content in the composite above 30% is a material that is completely resistant to the marine environment.
3. The conducted research has shown that recyclate is a waste that clutters and pollutes the environment, processing this “scrap” and using it, as an ingredient for the production of new products not necessarily resistant to corrosion or durable is a very valuable achievement.

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