Environmental Factors Affecting the Strength Characteristics of Modified Resin Mortars

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Abstract. Resin concretes are composites in which a cement binder has been completely replaced by a synthetic resin. These materials are a good choice for the construction industry, especially in solutions requiring high strength, fast curing and durability. Polymer mortars are mainly used for the manufacture of industrial floors and prefabricated products such as tanks for aggressive chemicals, sewage pipes, or road and bridge drainage systems, as well as for the repair of damaged concrete structures. In all these applications, the strength and high chemical resistance of the applied material solutions are of key importance. It is particularly crucial to obtain information on how resin composites behave when exposed to aggressive agents over extended periods of time. It is also very important to use waste materials in order to obtain resin composites, as these activities are very well inscribed in the idea of environmental protection and meet the criteria of sustainable construction. The mortars described in this article meet the above principles. The article presents how the compressive strength of glycolyzate-modified epoxy mortars, obtained with the use of poly(ethylene terephthalate), changes after they are immersed in 10% sodium chloride solution. Sodium chloride solution was chosen due to the prospective applicability of the tested composites as repair materials used for e.g. bridges or overpasses that are exposed to this salt solution in wintertime. Changes in the properties of the composite samples were monitored over the period of one year. Statistical analysis of the test results was carried out with the use of Statistica programme. The module available in the mentioned program called Nonparametric Statistics - Comparing multiple independent samples made it possible to check the monitoring times during which the compressive strength values differed significantly. The obtained results allowed for determining the equation of the function approximating the course of changes in mortar properties. The designated parameters of regression equations can be used to project the properties of composites.

1. Introduction
Recent years have seen an increase in the use of polymer composites. This group of materials includes concretes and resin mortars, the binding agent of which is a synthetic resin. Replacing cement with resin binders allows to obtain a material with not only high strength parameters, but also durable and resistant to many chemical agents [1]. The favorable properties of resin composites are confirmed by numerous scientific studies, mainly those focused on the optimization of their composition, the reduction of costs and improvement of mechanical properties. Information on the resistance of polymer composites to aggressive chemicals can be found in literature [2-21]. However, these studies are worth pursuing in a wider context, i.e. by monitoring changes in the properties of composites.
exposed to corrosive substances over extended periods of time. This article describes the test results of changes in compressive strength of epoxy mortar samples monitored over the period of 12 months. The mortar was modified with glycolyzate obtained from poly(ethylene terephthalate) (PET) waste. The modification consisted in partial substitution of resin by a PET waste glycolyzate. It made the obtained materials fit in with the idea of environmental protection and meet the requirements of sustainable construction, while also have very good physical and mechanical parameters. The obtained results allowed to determine the equation of a function approximating the course of changes in mortar properties during its exposure to aggressive medium such as 10% sodium chloride solution. The theory of experiment planning was used again as a part of the research plan. Like in the experiments described by Dębska and Lichołai [21], a composition central plan with a repetition of the experiment at the central point was chosen.

2. Experimental programme

2.1. Materials

Epidian 5 epoxy resin was used to produce resin mortars. Z-1 hardener (triethylenetetraamine) in the amount of 10% by weight in relation to resin was used to harden it. Some selected properties of the resin are shown in Table 1. The aggregate was quartz sand with a 0-2 mm grain size according to the PN-EN196-1 specification. Based on the available literature data and the results of the author’s preliminary experiments it was decided that the range of the resin-aggregate ratio would be from 0.14 to 0.36, according to the adopted plan of the experiment. In the mortars obtained, the epoxy resin was partially replaced (0-14% by weight) by poly(ethylene terephthalate) glycolyzate. The glycolyzate used for the experiments was provided by the Organika-Sarzyna SA Chemical Plant. It was produced from PET waste and propylene glycol (propano-1,2-diol) in the ratio of 1/1.7(PET/glycol). The formula of the glycol applied is presented in Figure 1. The process of glycolysis was conducted at 210°C, with zinc acetate as a catalyst.

![Figure 1. Formula of propylene glycol (propane 1,2-diol)](image)

Appropriate amounts of epoxy resin and modifier were weighed and mixed for uniformity. After that, the ingredients were heated at 85°C for 60 minutes in order to enable the functional groups of the two ingredients to react. When the PET glycolyzate modified epoxy mixture reached the room temperature, an appropriate amount of Z-1 hardener (10 weight parts/100g of resin) was carefully mixed in until the mixture was uniform. Previously prepared resin mixtures were put into the bowl of the laboratory mixer and stirred with standardized sand, keeping up the same mixing time and rotational speed of the mixer. The mortar that was obtained was then put into 40x40x160 steel moulds. The specimens were left for curing for seven days under laboratory conditions.

2.2. Methods

Tests for flexural and compressive strengths were conducted in strength testing machines with appropriate inserts, on 40x40x160 specimens for flexural strength and on halves of those specimens for compressive strength, according to the PN-EN 196-1:2006 specification. Figure 2a presents a machine for compressive strength tests and an insert with a specimen prepared for the test (Figure 2b).
Table 1. Some chosen parameters characterizing Epidian 5 epoxy resin

| Parameters of hardened resin | Determination method | Epoxy resin Epidian 5 |
|-----------------------------|----------------------|-----------------------|
| Flexural strength, MPa      | PN-EN ISO 178: 2006  | 133                   |
| Modulus of elasticity at bending, MPa | PN-EN ISO 178: 2006  | 3230                  |
| Deflection, mm              | PN-EN ISO 178: 2006  | 8.1                   |
| Rupture stress, MPa         | PN-EN ISO 527-1: 1998 PN-EN ISO 527-2: 1998 | 86.3 |
| Modulus of elasticity at tension, MPa | PN-EN ISO 527-1: 1998 PN-EN ISO 527-2: 1998 | 3430 |
| Unit elongation at rupture,% | PN-EN ISO 527-1: 1998 PN-EN ISO 527-2: 1998 | 5.6 |
| Compressive strength, MPa   | PN-EN ISO 604: 2006  | 121                   |
| Unnotched impact strength, kJ/m² | PN-EN ISO 179-1: 2004 | 30 |
| Ball pressure checked hardness, MPa | PN-EN ISO 2039-1:2002 | 124 |
| Deflection temperature under load HDT, °C | PN-EN ISO 75-1: 2006 PN-EN ISO 75-2: 2006 | 107.8 |
| Barcol hardness, °B         | ASTM-D 2583-95: 2007 | 45                    |

Figure 2. View of strength testing machine during compressive strength test (a), on the right is a close-up on insert with specimen for the test (b)

3. Experimental results
3.1. Determination of mean flexural and compressive strengths values and standard deviation
The computations concerning the general characteristic of the mortar specimens submitted to strength tests were conducted based on the basic Statistics module and tables of the STATISTICA programme. Mean strength and the standard deviation values calculated for each time of exposure to NaCl solution were determined. The results of the investigation are shown in Table 2.
Table 2. List of mean values and standard deviation of compressive strength for modified epoxy mortar calculated before and after immersing specimens for 1, 6 and 12 months in a 10% Na Cl solution

| No of experiment plan point | Content of PET glycolyzate, % | Resin/aggregate ratio R/A | Compressive strength before immersion | Compressive strength after 1 month of exposure | Compressive strength after 6 month of exposure | Compressive strength after 12 months of exposure |
|-----------------------------|-------------------------------|---------------------------|----------------------------------------|---------------------------------------------|---------------------------------------------|-----------------------------------------------|
| 1                           | 7.03                          | 0.36                      | 100.73 ± 1.32                          | 90.62 ± 1.21                               | 95.07 ± 1.71                               | 69.30 ± 1.95                                 |
| 2                           | 2.06                          | 0.33                      | 84.67 ± 2.08                          | 93.92 ± 2.78                               | 96.12 ± 1.53                               | 75.57 ± 3.07                                 |
| 3                           | 0.00                          | 0.25                      | 96.95 ± 1.22                          | 96.08 ± 4.48                               | 102.22 ± 1.14                               | 109.88 ± 6.09                                |
| 4                           | 7.03                          | 0.14                      | 111.98 ± 3.86                          | 104.74 ± 1.31                               | 101.78 ± 5.34                               | 87.20 ± 3.15                                 |
| 5                           | 7.03                          | 0.25                      | 115.73 ± 1.49                          | 106.60 ± 2.75                               | 105.18 ± 1.83                               | 100.77 ± 2.45                                |
| 6                           | 7.03                          | 0.25                      | 114.52 ± 2.15                          | 109.35 ± 3.60                               | 104.35 ± 4.15                               | 107.62 ± 3.32                                |
| 7                           | 12.00                         | 0.18                      | 112.95 ± 1.86                          | 106.43 ± 7.99                               | 99.88 ± 5.41                                | 86.67 ± 4.44                                 |
| 8                           | 12.00                         | 0.33                      | 105.60 ± 2.33                          | 94.53 ± 1.70                               | 95.70 ± 2.96                                | 76.82 ± 1.79                                 |
| 9                           | 14.06                         | 0.25                      | 112.52 ± 2.20                          | 104.10 ± 2.21                               | 101.97 ± 3.89                               | 94.73 ± 4.39                                 |
| 10                          | 2.06                          | 0.18                      | 103.77 ± 3.73                          | 110.65 ± 5.39                               | 95.07 ± 1.71                               | 92.05 ± 5.38                                 |
| Total                       |                               |                           |                                        | 105.80 ± 9.64                               | 101.52 ± 7.81                               | 100.77 ± 5.09                                |

3.2. Difference significance assessment for parameters investigated depending on exposure period
The nonparametric Kruskal-Wallis test was applied to determine whether the compressive strength has changed significantly as a result of the exposure to a corrosive medium for fixed periods of time. Its results are given in Table 3.

Table 3. Kruskal-Wallis ANOVA rang test results for compressive strength

| Test duration, months | Number of valid observations | Sum of ranges | Mean range value |
|-----------------------|------------------------------|---------------|------------------|
| 0                     | 59                           | 9408.50       | 159.47           |
| 1                     | 58                           | 7319.00       | 126.19           |
| 6                     | 59                           | 7007.00       | 118.76           |
| 12                    | 60                           | 4231.50       | 70.53            |

The choice of the test was the consequence of normal distribution of the parameters investigated. The normality assessments for the distributions were carried out based on the Shapiro-Wilk test. Test statistics in the Kruskal-Wallis test for compressive strength are statistically very significant (p=0.000, test value H(3, N=236) = 51.61)). Thus, it can be concluded that for the particular exposure times in a 10% NaCl solution compressive strength achieved values that differed significantly between each other. The higher the range sum, the greater the strength values. The module Nonparametric statistics → Comparison of many independent tests also enables a display of a table with the significance level values p for repeated comparisons (bilateral). This allows assessing for which monitoring times the strengths values significantly differed (Table 4).

Table 4. p values for repeated comparisons for compressive strength

| Test time, months | 0             | 1             | 6             | 12            |
|-------------------|---------------|---------------|---------------|---------------|
| 0                 | –             | 0.0500335     | 0.007217      | 0.000000      |
| 1                 | 0.0500335     | –             | 1.000000      | 0.0000057     |
| 6                 | 0.007217      | 1.000000      | –             | 0.000698      |
| 12                | 0.000000      | 0.000057      | 0.000698      | –             |
The compressive strength calculated after the 12 months’ exposure significantly differed from that obtained for the other immersion periods (before immersion, after 1 month and after 6 months of immersing the specimens in the NaCl solution). Significant differences occurred also between the compressive strength values calculated before the immersion and after 6 months of exposure to the aggressive medium.

3.3. Description of the parameters under research with the trend function
Changes in the strength values were described with the trend function. It was decided to analyse trend changes based on mean values. In fact, there were only four of them, but each was followed by a greater number of data (58-60 specimens). The option selected was the one which used the method of characteristics weighing, observation numbers being the weights.

In the case of compressive strength, the trend function for mean values, using the method of weighing characteristics, assumes the form of a straight line of the equation:

\[ z = 105.2111 - 1.1698 \cdot x \]  

so this parameter decreases by about 1.17 MPa in each month of the exposure. The curve of the trend function for the mean compressive strength values, using the method of weighing characteristics, is shown in Figure 3. The model is of high statistical significance. The determination coefficient is 0.9037.

![Figure 3. Trend function for mean compressive strength values considering weighing characteristics](image)

4. Discussion
Compressive strength of specimens in direct contact with a 10% NaCl solution changes with the time of the exposure. The dependence is linear and compressive strength decreases with an increase in the time of immersion by 1.17 MPa a month (Figure 3). Points of maximum and minimum compressive strength in the case of specimens that were not submitted to the corrosive effect of the substance are at the levels of 84.67 and 115.73 MPa. After 1 and 6 months of exposure, the minimum compressive stress values, 90.62 and 95.07 MPa, respectively, were observed at the experiment plan point characterized by the highest content of aggregate. However, the maximum compressive strength values, 110.65 MPa after 1 month and 105.50 MPa after 6 months can be observed at the point at which the PET glycolyzate content is 2% and the value of Z/K is one of the lowest, i.e. 0.18. Extending the duration of the experiment to one year confirmed the fact that a great amount of binder in the composite deteriorates its strength properties as the minimum strength, 69.30 MPa occurred at
the experiment plan point for which it was assumed that the resin-aggregate ratio will be at a level of 0.36. The maximum placed itself at the point that represents the unmodified mortar.

5. Conclusion
Based on the experiments carried out the following conclusions can be drawn about the composites analysed:

- Strength study conducted after 1, 6 and 12 months of exposing the mortar specimens to the 10% NaCl solution confirmed the general tendency of strength properties to deteriorate with the extension of immersion time.
- Modifier impairs the chemical Compressive strength of specimens in direct contact with a 10% NaCl solution changes with the time of the exposure. The dependence is linear and compressive strength de-creases with an increase in the time of immersion by 1.17 MPa a month.
- Even after a year exposure to a corrosive substance, the mortars obtained still show high mean compressive strength values which equal about 90 MPa.

Assuming limiting simulation on the basis of the linear trend function obtained for compressive strength under the 10% NaCl solution adverse effect conditions, it could be expected that this strength is likely to decrease in successive years. Were it so, it would mean significantly smaller application of modified epoxy mortars as layers in the contact with de-icing agents or as outer layers of wharfs. At the same time, it is difficult to state explicitly if, with the duration of exposure, compressive strength will really decrease in the way that is indicated by the extrapolation of the determined trend function as there may occur a hydrolysis process or other chemical reactions with the environment containing carbon dioxide. In fact, composites are only seasonally, mostly in winter, exposed to NaCl solutions of varied concentration. On the other hand, solutions of low concentration are sometimes more aggressive than those of high concentration due to diffusion or viscosity differences. Solutions of higher concentration have higher viscosity and due to this the determined trend functions show only the direction of the changes in strength properties of the composites under investigation.

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