

Analysis of Bending Strength of Resin Mortars That Are at Risk of Long-Term Exposure to Environmental Corrosives

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Abstract. The results of the article are part of an extensive research on new building materials including cement-free polymer composites where the binder is epoxy resin modified with glycolyzates obtained from poly (ethylene terephthalate) waste (PET). The investigation conducted confirmed that there is a possibility of using waste materials in the production of mortar. Since they have always been an environmental problem, their utilization will help to apply the principles of sustainable development in the processes of obtaining new materials. The article discusses the results of a study of flexural strength of polymer mortars. Mortar specimens modified with propylene glycol and PET waste based glycolyzate were exposed to a 10% NaCl solution and their strength parameters were then examined after one month, six months and twelve months of immersion in this aggressive medium. The same characteristics were also determined for specimens that were not exposed to the NaCl solution. The results were presented as the trend function. The sections of the curve corresponding to the particular periods of exposure in aggressive medium vary in shape. Due to this, an attempt was made to adjust the spline function to the experimental data. The composites obtained show a deterioration in their strength properties which grows with the extension of their exposure to a corrosive medium. However, the chemical corrosion resistance of the mortars under investigation can be considered very good as it is still much higher than that of conventional cement mortars. Even after a year exposure to a corrosive substance, the mortars obtained still show high mean flexural strength values which equal about 30 MPa.

1. Introduction

Numerous research centres [1-20] try to make new polymer concretes which can successfully protect buildings against the adverse effect of aggressive media. Especially the study of the effect of different corrosive solutions on the strength characteristics of polymer composites has been carried out by many researchers all over the world [1, 3, 4, 7, 16, 21-27]. The most important selection criterion for the chemically aggressive solutions to be used in the experiments is a possibility of simulating the corrosive environments with which resin composites might potentially come into contact.

The article discusses the research on the effect of a 10% sodium chloride (NaCl) solution on the strength properties of mortar specimens modified with propylene glycol and PET waste based glycolyzate. The choice of this corrosive agent was due to the fact that it is one of the key components of de-icing salts that are usually used in some countries to remove ice from the surfaces of roads, bridges and concrete pavement slabs. Moreover, one of the possible applications of resin concretes is in the manufacture of bridge drainage elements and in the production of prefabricates for linear



drainage systems. Consequently, this type of resin prefabricates may be exposed to the harmful effect of de-icing salts.

As it was suggested by Lichołai and Dębska [28], there is a need for reliable and durable materials which can be used in conditions of a particularly high chemical aggression hazard. This requirement is met by polymer concretes, whose further advantages are short use readiness time, impermeability, resistance to frost and nice appearance. Their very high mechanical strength and good chemical corrosion resistance are due to replacing mineral binder by resin binder in their composition [1]. What is more, high cost of resins encourages research into a possibility of applying plastic waste for polymer concrete modification. Lichołai and Dębska [28] describe epoxy mortars modified by PET waste based glycolyzates. The mortars show relatively small mass changes after being exposed to chemically aggressive media as well as low water permeability. Due to the fact that the exposure of resin compounds to chemically aggressive solutions affects not only their mass and outward appearance but also impairs their mechanical strength. Therefore it was decided to examine a modified epoxy mortar also in this latter respect. The theory of experiment planning was used again as a part of the research plan. Like in the experiments described by Lichołai and Dębska [20], a composition central plan with a repetition of the experiment at the central point was chosen. In the case of the chemical resistance study the plan of the experiment took the form of a table (Table 1). Each of the ten columns of the table stands for one point of the plan and describes the content of the mortars under research.

Table 1. List of parameters describing mortar composition for particular points of experiment plan.

No of experiment plan point	1	2	3	4	5	6	7	8	9	10
Content of PET glycolyzate, % by weight	7.03	2.06	0.00	7.03	7.03	7.03	12.00	12.00	14.06	2.06
Resin-aggregate mass ratio	0.36	0.33	0.25	0.14	0.25	0.25	0.18	0.33	0.25	0.18

The flexural strength of the modified epoxy mortars was determined after being immersed for one, six and twelve months in this aggressive medium. The same characteristic was also determined for specimens that were not exposed to the NaCl solution. The results obtained were presented as the trend function.

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 2. 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 (Table1). 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 process of glycolysis was conducted at 210°C, with zinc acetate as a catalyst. 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

Test for flexural strength were conducted in strength testing machine with appropriate insert, on 40x40x160, according to the PN-EN 196-1:2006 specification.

3. Experimental results

3.1. Determination of mean flexural 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.

3.2. 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 (27- 30). The option selected was the one which used the method of characteristics weighing, observation numbers being the weights. The graph of the trend function for flexural strength is shown in Figure 1. The sections of the curve corresponding to the particular periods of exposure in aggressive medium vary in shape. Due to this, an attempt was made to adjust the spline function to the experimental data. The principles of approximating the data using the function are given by Jakubczyk [29].

Table 2. List of mean values and standard deviation of flexural strength for modified epoxy mortar calculated before and after immersing specimens for 1, 6 and 12 months in a 10% NaCl solution

No of experiment plan point	Content of PET glycolyzate, %	Resin/ aggregate ratio R/A	Flexural strength before immersion $\bar{f}_f \pm \sigma_{\bar{x}}$	Flexural strength after 1 month of exposure $\bar{f}_{f,1} \pm \sigma_{\bar{x}}$	Flexural strength after 6 month of exposure $\bar{f}_{f,6} \pm \sigma_{\bar{x}}$	Flexural strength after 12 months of exposure $\bar{f}_{f,12} \pm \sigma_{\bar{x}}$
–	%	–	MPa			
1	7.03	0.36	25.77 ± 1.15	28.70 ± 1.31	29.90 ± 1.74	28.10 ± 0.61
2	2.06	0.33	19.53 ± 0.49	27.47 ± 0.35	29.04 ± 1.34	28.70 ± 0.87
3	0.00	0.25	21.10 ± 0.26	29.21 ± 0.55	23.52 ± 0.68	35.80 ± 0.20
4	7.03	0.14	32.17 ± 0.32	31.50 ± 0.98	31.68 ± 0.03	27.23 ± 0.42
5	7.03	0.25	32.20 ± 1.06	33.60 ± 1.28	33.57 ± 0.64	33.43 ± 1.25
6	7.03	0.25	32.13 ± 0.99	34.17 ± 0.87	35.23 ± 0.11	34.70 ± 0.53
7	12.00	0.18	31.43 ± 1.07	32.53 ± 1.30	28.74 ± 1.37	25.55 ± 0.07
8	12.00	0.33	27.03 ± 2.33	29.47 ± 0.68	29.07 ± 0.64	25.97 ± 0.75
9	14.06	0.25	30.57 ± 0.29	31.07 ± 1.66	28.69 ± 1.85	28.43 ± 0.71
10	2.06	0.18	26.37 ± 1.11	34.13 ± 2.35	33.41 ± 0.01	31.20 ± 0.30
Total			27.83 ± 4.61	31.19 ± 2.55	30.37 ± 3.21	30.06 ± 3.54

The real function s is called spline function or spline of grade m with nodes:

$$a = x_0 < x_1 < \dots < x_n = b \quad (1)$$

if in each of the $[x_i, x_{i+1}]$ intervals the function is a nominal of a grade not higher than m .

In practice, the most often used spline functions $s(x)$ are third grade multinomials. They are first grade multinomials outside interval $[a, b]$. This approach was also applied in this paper. Attempts were made to find such a third grade spline function which in given x_i nodes takes fixed y_i values and which in each of the $[x_i, x_{i+1}]$ intervals is a nominal of a degree not higher than 3. In range $[x_i, x_{i+1}]$, function s can be written as:

$$s(x) = \frac{M_{i+1} - M_i}{6(x_{i+1} - x_i)}(x - x_i)^3 + \frac{M_i}{2}(x - x_i)^2 + \left[\frac{y_{i+1} - y_i}{x_{i+1} - x_i} - \frac{M_{i+1} + 2M_i}{6}(x_{i+1} - x_i) \right](x - x_i) + y_i \quad (2)$$

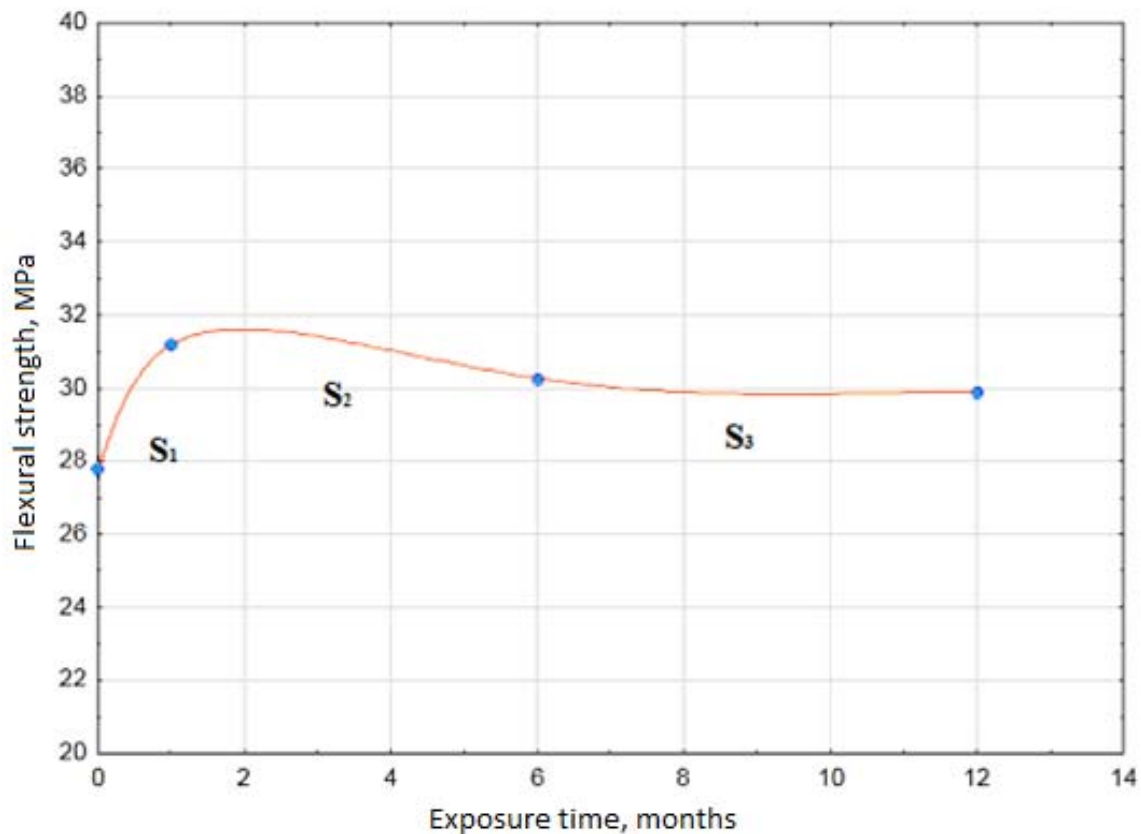


Figure 1. Trend function for flexural strength (spline method)

The coefficients appearing in the equation are calculated from:

$$M_i = q_i M_{i+1} + u_i \quad (i = n-1, n-2, \dots, 1, 0) \quad (3)$$

$$M_n = u_n \quad (4)$$

It is assumed that:

$$M_0 = M_n = 0 \quad (5)$$

$$\lambda_0 = 0 \quad (6)$$

$$d_0 = 0 \quad (7)$$

$$\mu_n = 0 \quad (8)$$

$$d_n = 0 \quad (9)$$

These are the conditions defining the natural spline function. However, the parameters:

$$q_0 = -\frac{\lambda_0}{2} \quad (10)$$

$$u_0 = \frac{d_0}{2} \quad (11)$$

$$q_i = -\frac{\lambda_i}{\mu_i q_{i-1} + 2} \quad (12)$$

$$u_i = \frac{d_i - \mu_i u_{i-1}}{\mu_i q_{i-1} + 2} \quad (i = n-1, n-2, \dots, 1, 0) \quad (13)$$

$$u_n = \frac{d_n - \mu_n u_{n-1}}{\mu_n q_{n-1} + 2} \quad (14)$$

$$\lambda_i = \frac{x_{i+1} - x_i}{x_{i+1} - x_{i-1}} \quad (15)$$

$$\mu_i = 1 - \lambda_i \quad (16)$$

$$d_i = \frac{6}{x_{i+1} - x_{i-1}} \left(\frac{y_{i+1} - y_i}{x_{i+1} - x_i} - \frac{y_i - y_{i-1}}{x_i - x_{i-1}} \right) \quad (17)$$

Like in the case of solving a system of equations by the Gauss elimination method, the values of M_i coefficients were determined in the sequence $M_{n-1}, M_{n-2}, \dots, M_0$, which was taken into account in the diagram of the algorithm in Figure 2. The results of the computation of the parameters determined in loops 1 and 2 of the spline function which approximates the results of the flexural strength tests of specimens exposed to an aggressive medium, according to the algorithm in Figure 2, were given in Table 3. The values of the coefficients of the approximation equations calculated in loop 3 are listed in Table 4.

Table 3. Parameter s necessary for determining spline function approximating the data with the third grade multinominal

i	0	1	2	n = 3
x_i	0	1	6	12
y_i	27.83	31.19	30.37	30.06
λ_i	0	0.833	0.545	—
μ_i	0	0.167	0.455	—
d_i	0	-3.524	0.061	0
q_i	0	-0.417	-0.301	—
u_i	0	-1.762	0.315	—
M_i	0	-1.893	0.315	0

Table 4. Multinomial coefficients for particular time intervals, for three approximating multinomials $s_1(x)$, $s_2(x)$ and $s_3(x)$

	a	b	c	d
$s_1(x)$	-0.3155	0	3.6755	27.8300
$s_2(x)$	0.0736	-1.1673	4.8423	27.4414
$s_3(x)$	-0.00875	0.3150	-3.5167	42.0202

The selection appropriateness of the parameters of the approximation equations was checked by putting x_i values equal 0, 1, 6, 12 in them. The calculations confirmed that at the splined points the values of z_i are exactly the same as those obtained from the measurements.

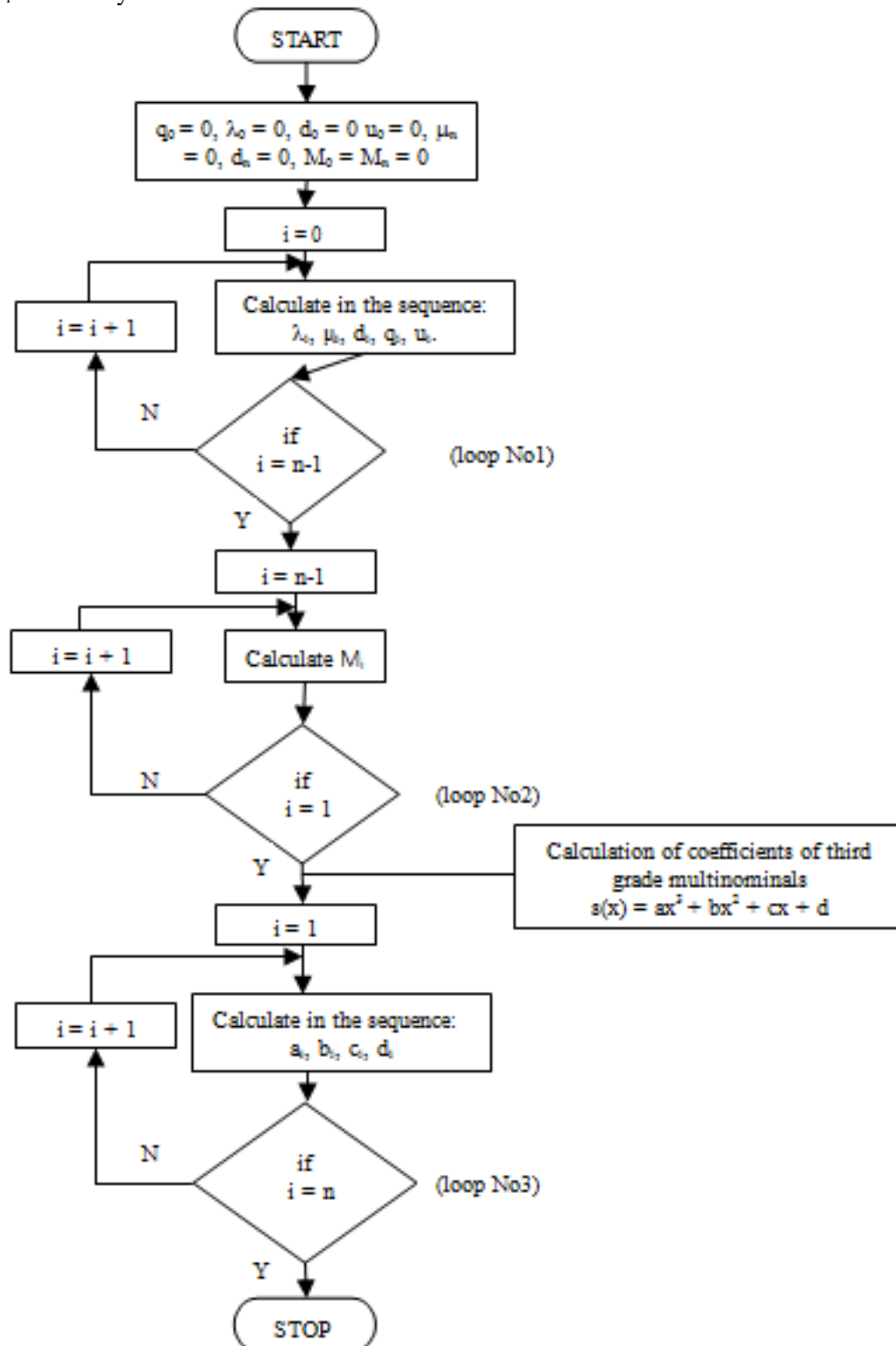


Figure 2. Calculation algorithm for spline function equation coefficients

4. Discussion

The trend function representing flexural strength changes depending on the duration of exposure to an aggressive medium (Figure 1), which makes it possible to notice an increase in the characteristics under investigation from 27,83 to 31,19 MPa. It means that in the initial phase of the exposure flexural strength was still growing slightly, whereas the effect of the modifier still could not be seen. Water particles of the NaCl solution may have got into the pores of the mortar and act as a “buffer”, which, at the beginning, made flexural strength higher than that of the mortars not submitted to the effect of a corrosive medium. However, further detailed determinations seem to be necessary in order to confirm the above conclusions. Tests carried within the time spans from 1 to 12 months show a slight decrease with time for the parameter determined. The medium flexural strength decreased by 2,6% within the time interval of 1-6 months, and by 1,03% within the 6-12 months, which proves the stability of the parameter in time.

The results obtained allow a conclusion that specimens containing more resin are less resistant to the 10% sodium chloride solution and the strength drop may be due to the reduction of the ordered binder phase. The tests carried out after a year of exposure showed that the minimum of the flexural strength value is characteristic of specimens containing as much as 12% of the modifier, whereas those without it show maximum of flexural strength value. This may suggest a negative effect of PET glycolyzate additive on the chemical resistance of mortars submitted to a longer exposure to the 10% NaCl solution. Additionally, in the case of mortars that were not modified, flexural strength grew with time despite the specimens being subjected to chemical aggression.

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 corrosion resistance of epoxy mortars.
- Even after a year exposure to a corrosive substance, the mortars obtained still show high mean flexural strength values which equal about 30 MPa.

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