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Assessment of polyester concrete subjected to long-term exposure to an acidic environment

Ocena betonu poliestrowego poddanego wieloletniej ekspozycji na środowisko kwasowe

The article presents the results of the assessment of the durability of polyester concretes containing waste microfiller (obtained from the dedusting of road aggregate) made after many years of exposure of the elements to the sulfuric acid environment. Concretes with different quantitative compositions (waste dust partially or completely replaced the commercial quartz microfiller) were exposed to the H_2SO_4 environment with a concentration of 0.5 M for a period of 1 month and 8 years. The measure of concrete's acid resistance were changes in compressive strength compared to reference concretes tested immediately after obtaining technical efficiency. Additionally, 8-year-old concretes were subjected to NDT tests – the velocity of the ultrasonic wave passing through the composite was determined. It was experimentally confirmed that dust from road aggregate dedusting is a good partial substitute for commercial microfillers in polyester concretes in the context of their durability. After 8 years of exposure to H_2SO_4, the differences in the strength of concrete compared to analogous compositions exposed for 1 month amounted to an average of 4.9%, and compared to compositions not exposed to chemicals – an average of 9.5%. It was also shown that there is a clear relation between the ultrasonic wave velocity and the compressive strength of concrete, and any changes after exposure to acid (matrix discoloration and deposits) were only on the surface.

Keywords: concrete durability, chemical resistance, polyester concretes, polymer concretes, acidic environment, NDT

W artykule przedstawiono wyniki oceny trwałości betonów poliestrowych zawierających mikrowypełniacz odpadowy (pozyskany z odpylania kruszywa drogowego) dokonanej po wieloletniej ekspozycji elementów na działanie środowiska kwasu siarkowego(VI). Betony o różnych składach ilościowych (pył odpadowy częściowo lub całkowicie zastępował komercyjny mikrowypełniacz kwarcowy) zostały wyeksponowane na działanie środowiska H_2SO_4 o stężeniu 0,5 M przez okres 1 miesiąca oraz 8 lat. Miarą odporności betonu na działanie kwasu były zmiany w wytrzymałości na ściskanie w porównaniu z betonami referencyjnymi badanymi bezpośrednio po uzyskaniu sprawności technicznej. Dodatkowo 8-letnie betony poddano badaniom NDT – oznaczono prędkość fali ultradźwiękowej przechodzącej przez dany kompozyt. Potwierdzono eksperymentalnie, że w kontekście trwałości betonów poliestrowych pył z odpylania kruszywa drogowego to dobry częściowy substytut komercyjnego mikrowypełniacza. Po 8 latach ekspozycji na H_2SO_4 różnice w wytrzymałości betonów względem analogicznych składów poddanych ekspozycji przez 1 miesiąc wyniosły średnio 4,9%, a względem składów nieobciążonych chemicznie – średnio 9,5%. Wykazano też, że istnieje wyraźna zależność między prędkością fali a wytrzymałością betonu na ściskanie, a wszelkie zmiany po ekspozycji na kwas (przebarwienie matrycy i osady) były jedynie powierzchniowe.

Słowa kluczowe: trwałość betonu, chemoodporność, betony poliestrowe, betony polimerowe, środowisko kwasowe, NDT

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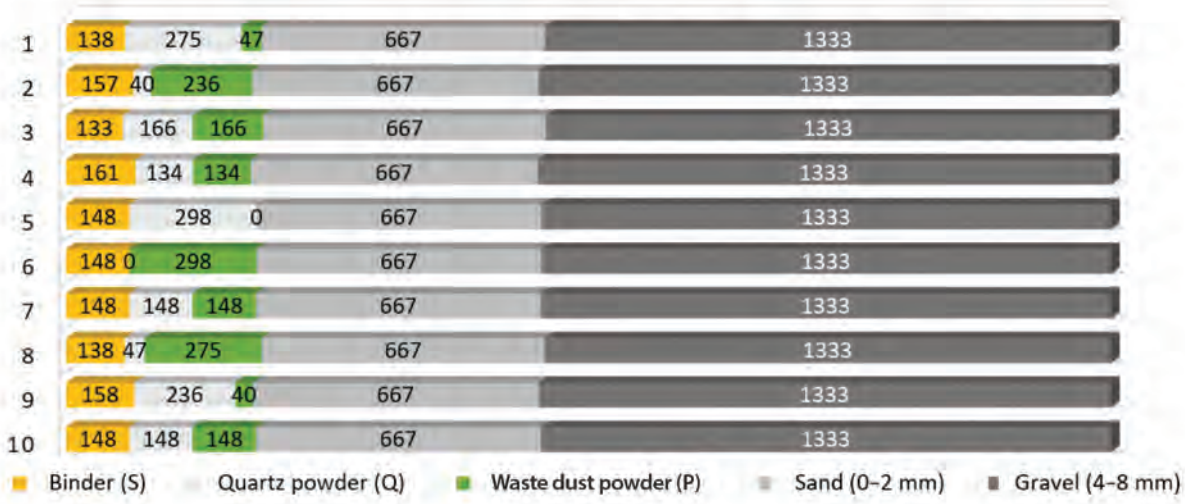

Fig. 1. Compositions of tested polymer concretes in kg per 1 m^3 of mix (calculated acc. to the statistical design, compositions 7 and 10 are the duplicated central point of the design)

Rys. 1. Składy badanych betonów polimerowych w kg na 1 m^3 mieszanki (obliczone wg DOE, kompozycje 7. i 10. to zduplikowany punkt centralny planu eksperymentu)

1. Introduction

Polymer concretes are characterized by high chemical resistance, which is mainly due to the polymer matrix and high-quality aggregate [1]. The important role plays finest fraction of aggregate, i.e. the so-called a microfiller that fills the synthetic binder and prevents its shrinkage. With appropriate material values of A/B and B/M coefficients (i.e. mass proportions of aggregate to binder and binder to microfiller), the hardened polymer properly coats the grains of mineral fillers, providing them with a tight, chemically resistant cover. This theoretically makes it possible to use a wide range of materials as fillers. In practice, however, it is assumed that materials analogous to those used in ordinary concrete technology are used as raw materials for the production of polymer concrete fillers, including crushed aggregates from rocks rich in silica (e.g. granite), fractionated, washed and dried natural aggregates – quartz gravels and sands and quartz powders (e.g. from crushed sand), which generally do not react with acidic environments. This is a safe approach, although unjustified from the economic and ecological point of view, but also from the point of view of the durability of composites with pure polymer matrices. Therefore, in recent years, attempts have been made to replace fillers made of natural rocks with powdered mineral industrial waste.

This article presents the results of assessing the durability of polyester (vinyl ester) concretes after long-term exposure to sulfuric acid. The concretes contained waste microfiller – mineral dust obtained from the dedusting of road aggregate, which partially or completely replaced the commercial microfiller (quartz powder). While the possibility of using this waste in polyester concrete had previously been confirmed in the context of short-term tests, it was not certain whether the dust rich in calcium compounds would cause degradation of the synthetic matrix after a long period of operation of the composite in a chemically aggressive environment (polymer concrete elements are used where chemical resistance is necessary, e.g. in tank structures, sewage treatment plants). The experiment discussed below was intended to simulate the long-term operation of a composite used as a lining of a tank for storing sulfuric acid with a concentration of 0.5 M.

The experiment consisted in assessing the durability of polyester concretes with different quantitative compositions (including different contents of waste material – the dust partially or completely replaced the quartz microfiller), which were exposed to the environment of sulfuric acid at a molar concentration of 0.5 M for a period of 1 month and 8 years. The acid resistance of concrete was measured by changes in the compressive strength of chemically loaded composites compared to unloaded composites prepared from the same mixtures and tested immediately after obtaining technical efficiency (after 2 weeks of curing in a dry conditions). The results obtained in the first stage of the experiment, i.e. after 1 month of exposure of the specimens to sulfuric acid, were presented in 2018 [2]. The results obtained in the second stage (after 8 years) presented below were also analyzed in the context of previous observations. Additionally, the external surface was inspected before and after cleaning from chemical deposits accumulated during the test period and after destructive testing. The cleaned specimens were also subjected to ultrasonic tests. The values of the speed of ultrasonic waves passing through the composites were determined using a direct method, and the relation between the ultrasonic pulse velocity and compressive strength was developed.

2. Materials and subject of the study

The subject of the study was 9 polyester concretes, the quantitative compositions of which were designed according to the statistical experimental design. The plan assumed 2 material variables and 9 experimental points (two-factor rotational design with the central point repeated twice for greater accuracy). The material variables were the previously mentioned ratio B/M = B/(Q + P) (relative ratio of the mass of the polymer binder and the total mass of the microfiller consisting of commercial quartz filler, Q, and/or waste dust powder, P) and P/M = P/(Q + P) (relative mass ratio of waste dust powder and total microfiller fraction). The first variable was in the range of 0.40–0.60 (i.e. recommended by Czarnecki for concretes with synthetic resin matrices [1]); the second in the range of 0.0–1.0, i.e. substitution of a commercial quartz microfiller,

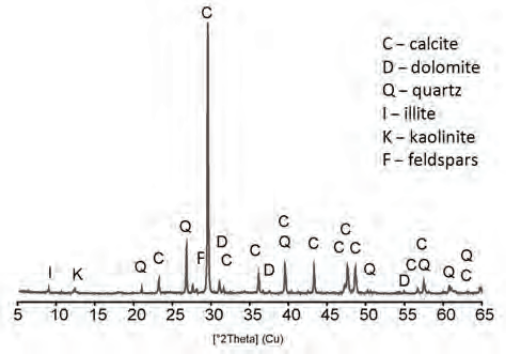

Fig. 2. XRD pattern of waste mineral dust from limestone aggregate for MMA used in the tested polyester concretes

Source: based on [2, p. 493].

Rys. 2. Dyfraktogram XRD odpadowego pyłu mineralnego z kruszywa wapiennego do MMA zastosowanego w badanych betonach poliestrowych

Źródło: opracowanie własne na podstawie [2, s. 493].

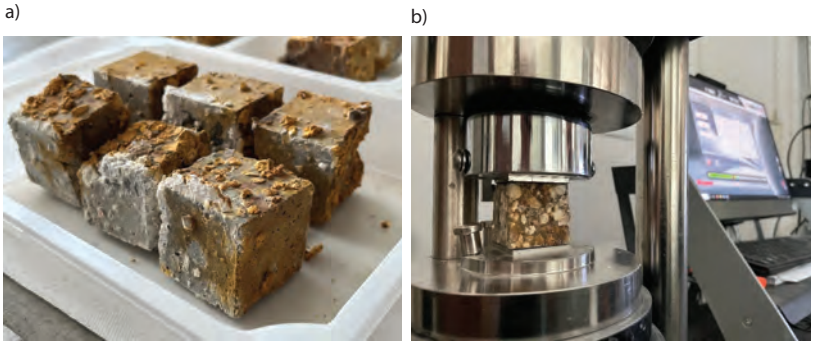

Fig. 3. Polymer concrete specimens (halves of beams with dim. of 40 × 40 × 160 mm remaining after the bending test): a) after 8 years of contact with the H_2SO_4 environment – after removal from the acid, b) after cleaning from sediments during the compression test

Rys. 3. Próbki betonów polimerowych (połówki belek o wymiarach 40 × 40 × 160 mm pozostałe po próbie zginania): a) po 8-letnim kontakcie ze środowiskiem kwasu siarkowego – po wyjęciu z kwasu, b) po oczyszczeniu z osadów podczas próby ściskania

Q, with waste was carried out in the entire range. Mass substitution was possible because the densities of the quartz filler and waste dust powder did not differ significantly – they were 2650 kg/m^3 and 2621 kg/m^3, respectively. Modified polyester (vinyl ester with a viscosity of 300–400 Pa · s and a flexural strength of 130 MPa – according to the manufacturer's specifications [3]) used as a binder and CEN standard sand and river gravel of 4–8 mm fraction (washed and dried) used as the basic aggregate The compositions of the tested composites are presented in Fig. 1.

As mentioned above, waste dust powder is the residue left after crushing and fractionating limestone aggregate into mineral-asphalt mixtures (MMA). XRD (Fig. 2) and EDS analyzes of the dust carried out in the first stage of the experiment [2] confirmed that the main mineral component of the dust (approx. 85%) was calcite supplemented with noticeable amounts of dolomite and quartz and trace amounts of clay minerals (illite and kaolinite).

However, the PSD analysis [2] of both microfillers showed that the mean and maximum (60 µm and 394 µm) grain size of waste dust were twice as large as in the case of quartz powder (28 µm and 152 µm, respectively), but at the same time the waste material contained particles smaller than 0.5 µm, which made the specific dust surface more than twice as large. Therefore, mass substitution of commercial filler with waste 1 : 1 in extreme cases could imply the need to use larger amounts of polymer to ensure proper coverage of dust grains and good workability of the mix, and consequently high mechanical strength of the composite. This was reflected in the results of testing the compressive strength of ready-made concrete.

3. Compressive strength as a measure of durability after chemical attack

Already in the first stage of the research, it was shown that concretes containing small amounts of polymer binder (composition No. 3) and/or a lot of waste material (compositions No. 6 and 8; Fig. 1, Table 1) were characterized by significantly lower compressive strength than the other ones. None of the abovementioned concretes did reach 70 MPa before the chemical resistance test, while the remaining concretes were characterized by strengths in the range of 74–97 MPa.

After exposure to 0.5 M H_2SO_4 acid concretes No. 3 and 8 additionally suffered the greatest damage: after 1 month of exposure to acid, their strength decreased by 15–31% and after 8 years by 18–34% (Table 1). These are very high values, but it should be emphasized that halves of beams with dimensions of 40 × 40 × 160 mm remaining after the 3-point bending test were introduced into the aggressive environment (Fig. 3). Therefore, each specimen characterized by one (fracture) surface with an open structure and an exposed phase of limestone microfiller. The acid therefore had open access to the reactive grains, which in an undamaged element are tightly closed in the polymer matrix. The approach used was to simulate the situation of a damaged element and demonstrate its ability to maintain strength during contact with acid, i.e. during the reaction between $CaCO_3$ and H_2SO_4 taking place on the fracture surface, producing hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$) visible on the uncleaned specimens (Fig. 3).

The analysis of the compressive strength of the remaining concretes showed that in the case of composites containing larger amounts of polyester binder, there was no such significant reduction in strength even after 8 years of contact with H_2SO_4. In the case of concretes with B/M ≥ 0.50, even with a very high share of waste in the microfiller (85–100%), the decrease in strength ultimately amounted to 13.6–16.1%, and with a lower share of waste there was even an increase in strength. The best effect – a change *in plus* 7.8% – occurred in the case of concrete with B/M = 0.60 and a microfiller consisting of half of commercial and waste materials (composition No. 4). The results therefore confirm that the use of fine-grained chemically active waste in polyester concrete requires an increase in the share of polymer that will tightly protect it in the event of a failure. This can be compared to the "encapsulation" process used in polymer processing [4]. However, the increase in strength indicates that the microstructure of selected composites has additionally strengthened, which could be the result of delayed and prolonged polymerization of the binder in a matrix highly saturated with a microfiller rich in calcium compounds – a phenomenon described in more detail by the authors in [5].

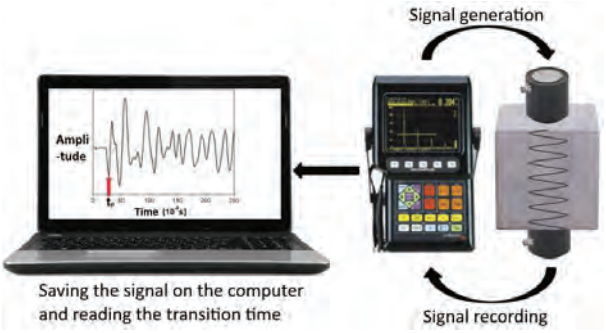

Fig. 4. Scheme of longitudinal wave velocity measurements using the direct method and the Panametrics EPOCH 4 flaw detector with a set of piezoelectric heads

Rys. 4. Schemat pomiarów prędkości fali podłużnej metodą bezpośrednią za pomocą defektoskopu EPOCH 4 firmy Panametrics i zestawu głowic piezoelektrycznych

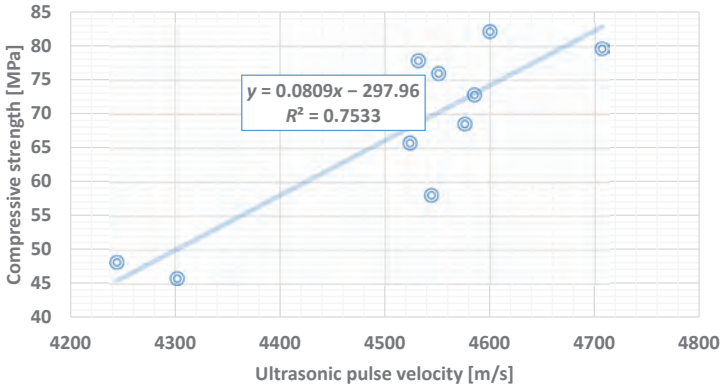

Fig. 5. The relation between the compressive strength of polymer concretes after 8 years of exposure to sulfuric acid and the ultrasonic pulse velocity (C_p [m/s])

Rys. 5. Zależność między wytrzymałością na ściskanie betonów polimerowych po 8-letniej ekspozycji na środowisko kwasu siarkowego i prędkością fali ultradźwiękowej (C_p [m/s])

Table 1. Compressive strength of polymer concretes (mean values from 4 or 2 results) determined after achieving technical efficiency (f_{c0}) and after exposure to the H_2SO_4 for 1 month (f_{c1}) and 8 years (f_{c8}) and changes compared to the initial strength values

Tabela 1. Wytrzymałość na ściskanie betonów polimerowych (wartości średnie z 4 lub 2 wyników) oznaczona po osiągnięciu sprawności technicznej (f_{c0}) i po ekspozycji na środowisko H_2SO_4 przez 1 miesiąc (f_{c1}) i 8 lat (f_{c8}) oraz zmiany względem wytrzymałości początkowej

No.	B/M [kg/kg]	P/M [kg/kg]	f_{c0} [MPa]		f_{c1} [MPa]	f_{c8} [MPa]	Δf_{c0-1} [%]	Δf_{c0-8} [%]
			mean	σ	mean	mean		
1	0.43	0.15	87.09	7.70	79.39	72.82	−8.8	−16.4
2	0.57	0.85	76.04	7.05	69.73	65.73	−8.3	−13.6
3	0.40	0.50	69.02	4.95	47.44	45.79	−31.3	−33.7
4	0.60	0.50	76.25	9.14	85.63	82.16	+12.3	+7.8
5	0.50	0.00	80.80	7.64	84.29	79.62	+4.3	−1.5
6	0.50	1.00	69.18	3.71	66.31	58.03	−4.1	−16.1
7	0.50	0.50	75.67	4.31	79.47	77.85	+5.0	+2.9
8	0.48	0.85	58.94	4.69	49.94	48.18	−15.3	−18.3
9	0.57	0.15	75.26	6.33	79.96	75.97	+6.2	+0.9
10	0.50	0.50	73.91	11.08	68.02	68.54	−8.0	−7.3

4. Ultrasonic pulse velocity vs. compressive strength of polyester concrete

This research used one of the simplest and most frequently used ultrasonic methods applied in concrete diagnostics, i.e. the transit time measurement method, which involves introducing a longitudinal ultrasonic wave into the tested medium and assessing its transit time along a known path between the transmitter and receiver located on opposite surfaces (the so-called direct measurement according to the European standard PN-EN 12504-4). This method enables obtaining very precise results because the maximum of the wave energy propagates perpendicularly to the surface of the transmitting head. The direct method is used primarily to assess the homogeneity of concrete (ordinary/heavy [6], PCC [7] and polymer [8]) in structures, estimate their compressive strength and monitor its changes over time. In the presented research ultrasonic measurements were carried out using a Panametrics EPOCH 4 flaw detector with a set of piezoelectric heads with a frequency of 100 kHz (Fig. 4). Acoustic coupling between the concrete surface and the heads was provided using a coupling gel. Measurements were made in the direction perpendicular to the smoothed surface of the above-mentioned specimens (halves of 40 × 40 × 160 mm beams) before their destruction in the compressive strength test.

During the measurement, signals were recorded in the form of a relation between wave amplitude and time, with each recorded signal being the result of the average of three readings. On that basis, from the position of the ultrasonic wave front, the transit time between the transmitting head and the receiving head was read and the velocity of the longitudinal ultrasonic wave C_p aka. UPV (ultrasonic pulse velocity) was calculated according to the formula:

$$C_p = s/t \text{ [m/s]},$$

where: s – distance between heads [mm], t – ultrasonic wave transit time [ms].

Taking into account all tested concretes, pulse velocities were determined in the range of 4200–4700 m/s. The lowest values were obtained in the case of concretes with a large or complete share of waste dust in the microfiller with a simultaneous small share of polyester binder (compositions No. 3, 6 and 8; Table 1), which generally confirms that these were composites with the least dense structure, and therefore the weakest mechanically. Generally, the analysis of the NDT test results showed that there is a clear relation between the pulse velocity and the compressive strength of chemically loaded polyester concrete. Fig. 5 presents this relation in the form of a linear function well suited to the empirical data (correlation coefficient $R = 0.87$ and determination coefficient $R^2 = 0.75$). The obtained results therefore confirm the possibility of using the ultrasonic method to predict the mechanical strength of polyester concretes in existing structures – including those exposed to aggressive environments.

5. Conclusions

The results of a multi-year experiment indicate that mineral dust from road aggregate dedusting is a good partial substitute

for commercial microfillers in polyester (vinyl ester) concretes in terms of their durability. After 8 years of continuous exposure to sulfuric acid, the differences in the strength of concretes compared to concretes with similar compositions subjected to chemical attack for 1 month amounted to an average of 4.9%, and compared to compositions not exposed to chemical attack at all – an average of 9.5%, while in the composits rich in polymer binder (binder/microfiller proportion ≥0.50), even an increase in strength was achieved (by a maximum of 7.8%). The analysis of the non-destructive testing results showed that there is a clear relation between the ultrasonic wave velocity and the compressive strength of tested concrete, which confirms that the ultrasonic method can be used to predict the mechanical strength of polyester concrete in existing structures – also those exposed to aggressive environments. Additionally, visual inspection of the specimens fractures showed that any changes (such as matrix discoloration and hydrated calcium sulfate deposit visible in Fig. 3) were only on the surface.

CRediT authorship contribution statement

Joanna Julia Sokołowska: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Kamil Załęgowski: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

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