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Using Waste Limestone Powder as Filler in a Toxic Epoxy Resin Coating and Its Influence on Adhesive Properties

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Epoxy resin is very harmful to the environment, e.g. it affects aquatic organisms, irritates the skin and eyes and causes allergic reactions. Because, the epoxy resin is an expensive building material, this study presents research on reducing its mass needed to make a floor coating, through the use of waste limestone powder as a filler. This additionally supports the recycling of the mineral waste. The main aim of the research was to find the amount of waste limestone powder that would not adversely affect the adhesive properties of the epoxy resin coating. The tests were carried out on a concrete element, with two differently prepared substrate surfaces using grinding and left raw after concreting. The epoxy resin coating contained waste limestone powder in an amount of 0 to 29% was examined. The pull-off strength of the coating was examined at three points for each coating composition on both types of the surfaces. The aim of the research was achieved by obtaining the satisfactory results of the pull-off strength for epoxy resin filled with the waste limestone powder.

1. Introduction

In civil engineering, epoxy resin is commonly used as a floor coating, because it has excellent chemical resistance, i.e. it is resistant to, among others, mineral oils, fuels and dilute acids. That is mainly the reason why it is used as a floor coating, e.g. in large-scale production halls. However, epoxy resin ingredients are very harmful to the environment, they affect aquatic organisms, are toxic to reproduction in humans and animals, and cause skin and eye irritation. Epoxy resin is a bisphenol A (BPA) based material that is particularly hazardous. Xiao et al. (2020) presented a review of studies showing that BPA elicit toxicity to plants. Rahman et al. (2021) proved that gestational exposure to BPA has a multigenerational impact on the fertility of mice. Therefore, it is very important to reduce the production of epoxy resin and look for its substitutes. There are not any good alternatives to date for civil engineering epoxy resin coating. Therefore, it is a good idea to reduce the total mass of epoxy resin needed to make the coating by using fillers. An ideal solution would be to use a waste material as a filler. This would support the idea of the sustainable development, help to utilize the waste material and reduce the cost of the coating. Epoxy resin coating is a costly building material - it costs about 700 Euro / 100 kg, and for example cement (type CEM I) costs 6.7 Euro / 100 kg. According to the statistics published by Eurostat (2021), in 2018, 26.6% of all waste in the European Union was produced from mining and quarrying. 74% of the total waste generated was major mineral waste. Attempts have been made to utilize waste mineral powders as a substitute for cement in concrete (Galińska and Czarnecki, 2017). Studies of epoxy resin with mineral additives can also be found in the literature. Subhash et al. (2018) investigated the effect of waste granite powder on the properties of epoxy resin and obtained an improvement in hardness and a slight increase in impact strength. Ojha and Biswal (2019) also investigated epoxy resin with the addition of granite powder and obtained improvements in impact energy, Young's modulus and hardness, but decreased the tensile and flexural strength. Chowaniec et al. (2020) showed that the addition of waste glass powder has a positive effect on the pull-off strength of the epoxy resin coating. De Oliveira et al. (2009) showed that the addition of quartz sand to epoxy resin improves its abrasion resistance and compressive strength. Krzwiński et al. (2021) proved that recycled fine aggregate can be used as extender in the epoxy resin coating without affecting the compressive and flexural tensile strength of polymer-cementitious composite. Zhu et al. (2020) concluded that the addition of mesoporous silica to epoxy resin improves its tensile strength, impact strength and storage modulus. Yeasmin et al. (2021) proved that the addition of mesoporous silica increases the glass transition temperature of epoxy

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resin. Summarizing the aforementioned studies, mineral powders have positive effects on some of the properties of epoxy resin. However, these studies mainly focused on powders which were not wastes and subjected epoxy resins were not used as floor coatings. There are also insufficient tests for the pull-off strength of the epoxy resin coating with various waste mineral powders. The pull-off strength is of particular importance for the durability of the epoxy resin coating (Sadowski, 2019). Single pull-off strength results are required to be greater than 1.0 MPa and the average value of the minimum of three results should be a min. of 1.5 MPa (PN-EN 1504-2:2006) and it is required that one control measurement of the pull-off adhesion is carried out on a surface of no more than 3 m^2 (Czarnecki et al.). Therefore, it is crucial to examine whether the epoxy resin coating with waste mineral powders still meets these conditions. Potentially, waste limestone powder could be used as a filler for epoxy resin coating. Seghir et al. (2020) found waste limestone powder a good alternative to cement with an adequate amount up to 10%. This powder consists mainly of calcium carbonate, which, unlike the epoxy resin, is not harmful to the environment. The tests should also consider the effect of the type of surface treatment on the pull-off strength of the coating. Sadowski et al. (2016) showed that the roughness parameters of concrete substrate affect the adhesion to epoxy resin. Krzwiński and Sadowski (2019) investigated the effect of texturing the surface of a concrete substrate on the pull-off strength of epoxy resin coating. Summarizing, the main goal of the research is to find the amount of waste limestone powder that will not deteriorate the adhesive properties, in terms of the pull-off strength value, of the epoxy resin coating. The use of waste limestone powder, that is not harmful to the environment, as a filler will substitute toxic epoxy resin. These studies will help to fill the gap on the influence of waste limestone powders on the adhesive properties of epoxy resin used as floor coating.

2. Materials

The tests were carried out on a substrate made of concrete class C30/37, dimensions 2.5 m x 2.5 m, thickness 0.15 m and compressive strength 37.36 MPa. The surface of the substrate was divided into two areas with different treatment methods - the raw surface and the ground surface. Loose concrete fragments were removed from the raw surface only with a brush, and then this part of the sample was vacuumed. The second part of the surface was mechanically ground and vacuumed. As shown in Figure 1, the substrate was divided into measurement squares.

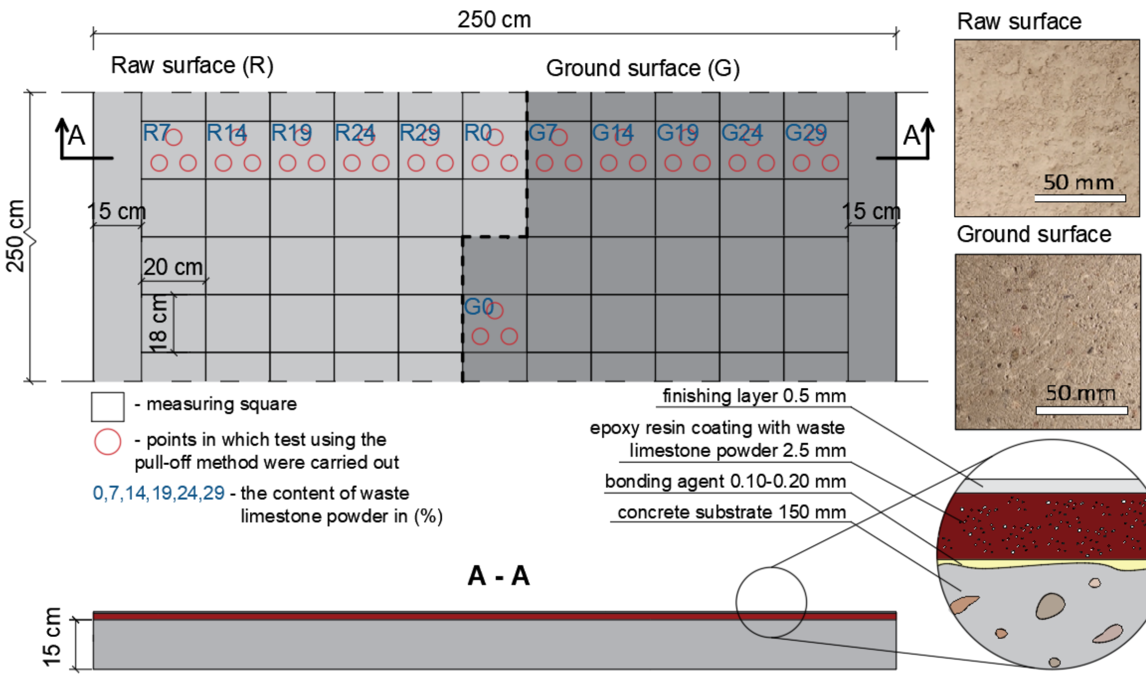

Figure 1: View of the concrete substrate with the division into surface treatment methods, measurement squares and coating layers

An epoxy-based bonding agent was applied to all measurement squares (on both types of surfaces) with a roller. The bonding agent improves the adhesion of subsequent coating layers to the substrate. After 24 hours, an epoxy resin coating with a gradually increasing filler content was applied to the measurement squares. The epoxy resin coating consisted of two components: epoxy resin based on bisphenol A (component A) and phenalkamine hardener (component B). The mixing ratio of the components was A: B = 100: 50. Waste limestone powder from the extraction and processing of mineral resources was used as a filler. The powder used consisted of 97.12 % $CaCO_3$, 1.00 % MgO, 1.50 % SiO_2, 0.08 % Fe_2O_3 and 0.30 % Al_2O_3. The powder size distribution was: 14.5% of the grains have diameter smaller than 0.1mm, 85% of the grains have diameter between 0.1 mm and 1.2mm and 0.50% of the grains have diameter between 1.2 mm and 2.0 mm. The waste limestone powder was first added to component A and thoroughly mixed. Then component B (hardener) was added to the mixture and the both components were mixed until a uniform consistency was obtained. The epoxy resin coating was stripped off with a serrated trowel. The thickness of the epoxy resin coating was 2.5 mm. The limestone powder filler content was from 7% to 29% of the mass of the epoxy resin coating. In addition, two reference squares with an unfilled epoxy resin coating were made. The symbol R0 denotes the reference sample on the raw surface, and the symbol G0 denotes the reference specimen on the ground surface. The mixing ratio and the corresponding marking of the measurement squares are shown in Figure 1 and Table 1.

Table 1: Mixing proportions of epoxy resin coating with waste limestone powder

Measuring square according to Figure 1	A weight ratio of A: B: waste limestone powder	Components calculated per 100g of the mixture		
		A (g)	B (g)	waste limestone powder (g)
R0 and G0	100 : 50 : 0	67	33	0
R7 and G7	100 : 50 : 12	62	31	7
R14 and G14	100 : 50 : 24	57	29	14
R19 and G19	100 : 50 : 36	54	27	19
R24 and G24	100 : 50 : 48	51	25	24
R29 and G29	100 : 50 : 60	48	24	29

R and G means the type of concrete substrate surface treatment (R- raw surface, G- ground surface)

The finishing layer of 0.5 mm thickness was applied using a roller 24 hours after the epoxy resin coating was made. It is also a two-component material based on the epoxy resin with a mixing ratio of 100: 15. Thanks to this layer, the selected color of the coating and gloss are obtained. The entire procedure of applying all aforementioned layers was performed under controlled laboratory conditions: at an ambient temperature of 20 °C ± 2 °C and a relative air humidity of < 65 %.

3. Methods

The epoxy resin coating needs a minimum of 7 days at 20 ºC to achieve full mechanical and chemical resistance. The pull-off strength tests were carried out 3 weeks after the last layer of the coating was applied. The tests were performed in accordance with the ASTM D4541 standard. According to this standard, measurements should be carried out in min. 3 points to obtain the average pull-off strength of the coating. Figure 2a shows a view of the test stand.

In the first stage, around each measuring point, the coating was cut to a depth of about 2-3 mm in the concrete substrate. The underside of the steel disc and the surface of the coating were first cleaned and degreased with acetone and then covered with epoxy glue. After two days, the epoxy glue was completely hardened. Pull-off strength measurements were made using an automatic device DY-216 (Proceq, Switzerland). The steel discs were firstly placed in the holder and then the device was leveled and the pull-off process was started. In the tests, steel discs with a diameter of 50 mm were used, and the speed of increasing the force was 0.050 MPa/s. The pull-off strength of coating was automatically calculated from formula (1) and presented as a *X* value in MPa.

$$X=4F/(\pi d^2) \tag{1}$$

where:
X = pull-off adhesion strength achieved at failure (MPa),
F = maximum force applied to the test surface at failure (N),
d = steel disk diameter (mm).

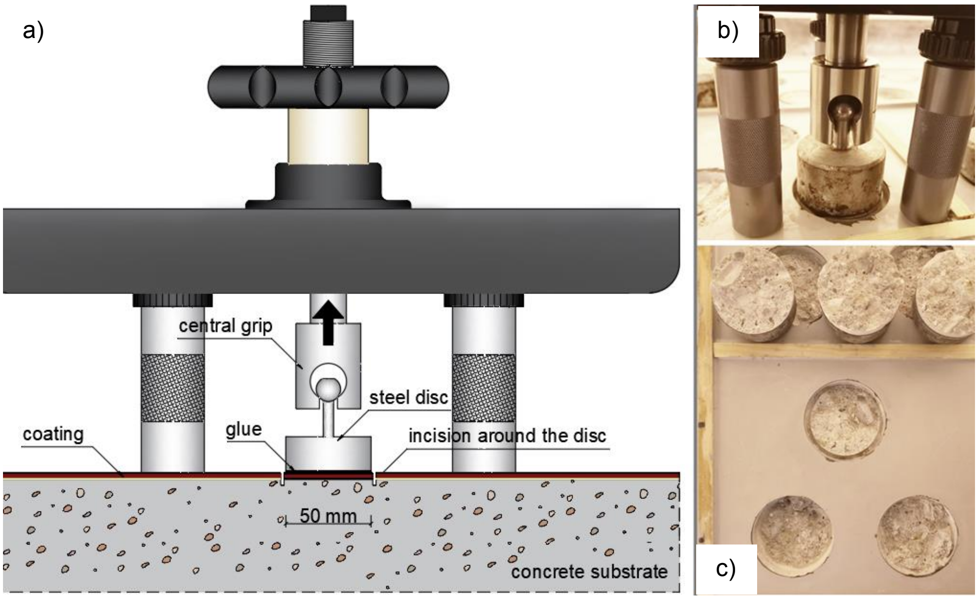

Figure 2: a) View of the pull-off test stand, b) the process of pulling off the steel discs, c) steel discs after pull-off test

4. Results

Three pull-off tests were performed in each measuring square. These results are summarized in Table 2. The failure mode was determined for each measuring point in accordance with the ASTM D4541. This standard distinguishes 3 modes of cohesive failure in the substrate, which are shown in Figure 3a, and adhesive failure, as shown in Figure 3b. Cohesive failure substrate A was obtained at almost all measuring points, which means that the destruction occurred at a certain depth in the concrete substrate, and the steel disc was pulled-off with a bulk cement paste and aggregate (Figure 3c). At three measuring points on the raw surface, the adhesive failure was obtained, which means that the failure occurred at the coating/substrate interface (Figure 3d). This failure mode was most likely due to the lack of mechanical treatment of the substrate and thus less local pull-off strength.

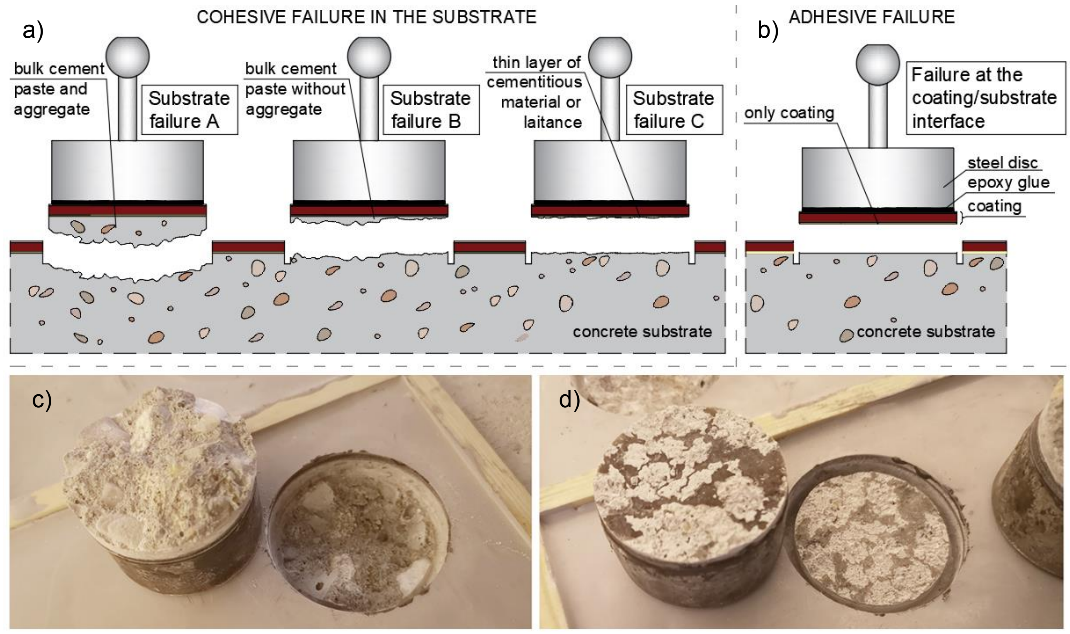

Figure 3: a) Three cohesive failure modes, b) adhesive failure mode, c) substrate failure A obtained during pull-off tests, d) adhesive failure obtained during pull-off tests

On the basis of the single results, the average pull-off strength and standard deviation were calculated for the epoxy resin coating with each content of waste limestone powder filler on the two types of surface (raw and ground). For the reference coatings (without filler), higher average pull-off strength was obtained for the raw surface (2.77 MPa) compared to the ground surface (2.43 MPa). The lowest pull-off strength value for the coating with waste limestone powder was obtained on the raw surface and with 14% filler content (2.19 MPa). In opposite, the highest pull-off strength for ground surface was obtained for the coating with 14% content of waste lime powder. The average value of the pull-off strength of the coating for the raw surface is 2.45 MPa with an average standard deviation of 0.38 MPa. The average value of the pull-off strength of the coating for the ground surface is almost the same (2.42 MPa), but with a smaller average standard deviation (0.27 MPa).

Table 2: Summary of the pull-off strength of the epoxy resin coating with waste limestone powder

Type of surface	Measuring square according to Figure 1	The content of powder (%)	Results (MPa)	The average pull-off strength (MPa)	Standard deviation (MPa)	Type of failure
Raw surface	R0	0 %	2.89; 2.70; 2.72	2.77	0.10	all failure A
	R7	7 %	2.27; 2.48; 2.50	2.42	0.13	2x adhesive failure, 1x fail. A
	R14	14 %	2.64; 1.50; 2.42	2.19	0.61	1x adhesive failure, 2x fail. A
	R19	19 %	2.31; 2.79; 2.69	2.60	0.25	all failure A
	R24	24 %	1.64; 2.68; 2.65	2.32	0.59	all failure A
	R29	29 %	2.06; 3.08; 2.00	2.38	0.61	all failure A
		Average for raw surface		2.45	0.38	
Ground surface	G0	0 %	2.95; 2.42; 1.92	2.43	0.52	all failure A
	G7	7 %	2.57; 2.32; 1.86	2.25	0.36	all failure A
	G14	14 %	2.74; 2.90; 2.55	2.73	0.18	all failure A
	G19	19 %	2.47; 2.38; 2.08	2.31	0.20	all failure A
	G24	24 %	2.44; 2.35; 2.42	2.40	0.05	all failure A
	G29	29 %	2.23; 2.74; 2.23	2.40	0.29	all failure A
		Average for ground surface		2.42	0.27	

All obtained values for both types of the surfaces are in the range of 2.19 MPa to 2.77 MPa. All results obtained during the tests are above the required minimum value of the pull-off strength of the coating, which is 1.5 MPa for epoxy resin coating. There was no negative influence observed of the waste limestone powder filler on the pull-off strength of the epoxy resin coating. There was not also any significant difference between the results obtained for both types of substrate surface. The lack of a significant difference in the results between the raw and ground surfaces may be caused by the use of a bonding agent, which improved the adhesion of the epoxy resin coating to the substrate.

5. Conclusions

Based on the tests performed the following conclusions can be stated:

- The epoxy resin coating with a waste limestone powder filler in the amount of up to 29% of the coating mass is characterized by a pull-off strength of coating above 2.19 MPa, i.e. above the required minimum value of 1.5 MPa.
- Waste limestone powder can be used as a filler for an epoxy resin coating in an amount of up to 29% by mass of the coating, without deteriorating its pull-off strength and thus without deterioration of its durability.
- Replacing epoxy resin (containing bisphenol A) in the coating with waste powder will reduce the amount of toxic ingredients. Especially since the waste limestone powder is not harmful.
- The use of a filler in an epoxy resin coating may reduce the costs of making this coating.
- The utilization of waste material (waste limestone powder) supports the sustainable development and recycling of mineral waste.
- The tests showed that the lack of mechanical treatment of the surface of the concrete substrate (raw surface) did not reduce the pull-off strength of the coating as compared to the ground surface. This is presumed to be due to the use of the bonding agent that improves the adhesion of the coating to the substrate.
- The newly designed epoxy resin coating containing waste limestone powder is fulfilling the requirements of the construction practice and fits in with the idea of sustainable construction. Thus it is a competitive alternative to the currently used solutions.

The research filled the research gap on the influence of waste limestone powders on the adhesive properties of the coating. However, it is not known what effect the smaller particle size waste limestone powders would have. It is also unknown what effect other waste mineral powders would have on the adhesion properties of the epoxy resin coating. The effect of these powders on other properties of the epoxy resin coating is also unknown. Therefore, it is worth considering a more extensive research on the influence of waste mineral powders on the properties of epoxy resin used as floor coatings.

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