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Repairing composite using hazardous waste containing heavy metals

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Abstract. This research deals with the possibility of using hazardous waste in epoxy resin-based polymeric substances. More specifically, it is the use of neutralising galvanic sludge (NGS), which produces as a by-product in the surface treatment of metallic elements. The objective of the research was to incorporate as much as possible of this hazardous waste into a suitable polymeric substance because the further use of this waste is very problematic and is costly to treat and dump. Experiments carried out have shown that homogenisation of this hazardous waste with a suitable epoxy resin results in the coating of all filler particles in the form of waste by the binder and there is no release of heavy metals and other undesirable contaminants. From an ecological point of view, it is, therefore, possible to use the pre-treated neutralising sludge as suitable filler in the polymer-based repairing composite. On the basis of the assessment of the mechanical properties test evaluation, it can be stated that the most suitable seems the application of 40% quantity by weight of this hazardous waste type to be used in the repairing mortar. The perfect distribution of hazardous waste particles in the epoxy matrix was confirmed by the evaluation of scanning electron microscope (SEM) images. The distribution of the individual elements found in the filler was monitored by energy dispersive X-ray analysis (EDX).

1. Introduction

Repairing composite materials are materials used to repair various elements and structures from various materials (e.g. concrete, polymer, stone, etc.). Repairing materials may be silicate or polymer-based.

For the production of the highest quality composite materials, polymer-based binders are most commonly used and are characterised by very good adhesion to most materials [1]. For repairing composite materials, polymeric binders based on epoxy resins seem to be the most appropriate, as they exhibit excellent adhesion to most materials as well as excellent physical and mechanical properties, minimum shrinkage and good chemical resistance after curing [2]. For this reason, a polymeric substance based on epoxy resin was selected for this research. Hodul et al. [3] dealt with using epoxy resin as a binder for repairing material, where they watched the possibilities of using denitrified filter fly ash in the repairing materials.

In connection with the continuous production of hazardous wastes in the industry and the effort to avoid landfilling of these materials as much as possible, it is necessary to find appropriate use of such hazardous waste. Within this research, the use of hazardous waste as a filler in the polymeric repairing composite was experimentally checked. For this research, a neutralising galvanic sludge (NGS) was chosen as a by-product in the surface treatment of metallic elements. The purpose of the surface treatment of metals is to make metal coatings on mostly metallic-based materials, thereby creating a



protective anticorrosive layer which protects metallic products from environmental influences during their use and thus prolongs their service life. Galvanic plating produces a variety of waste products, which can be sludges or filter cakes, from a neutralising station containing dangerous substances. In order to use the neutralising sludge as a filler in polymeric substances, it is necessary to adjust it accordingly. The most common type of hazardous waste treatment is solidification (stabilisation) [4]. It involves the mixing of hazardous waste with reagents that bind dangerous substances to a solid matrix to avoid the release of contaminated components into the environment. The most commonly used reagents are lime, cement or power fly ash. This type of adaptation was dealt with by Hodul et al. [5] in their experiment, which involved the solidification of neutralising sludges. The solidification of other hazardous wastes was investigated by Lopéz et al. [6] who tried to stabilise hazardous waste containing large amounts of mercury. The effort is to maximise the use of all waste in order to limit their very costly treatment and landfill, which contributes to the protection of the environment.

2. Identification of the materials

2.1. Neutralising galvanic sludge (NGS)

A neutralizing galvanic sludge (NGS) is produced as a by-product in the surface treatment of metallic elements, namely galvanic plating. For this reason, it contains a considerable amount of pollutants, predominantly heavy metals, which need to be successfully incorporated into a suitable matrix to avoid leaching them. According to the waste catalogue, this hazardous waste can be classified in group 19 02 05 Sludges from physical and chemical treatment containing dangerous substances. This neutralisation sludge exhibits several hazardous properties such as H5 (Harmfulness to health), H14 (Ecotoxicity), H15 (Ability to release dangerous substances to the environment during or after removal).

Since this sludge is produced with a high content of physically bound water (pasty consistency), it had to be dried (105 °C) before using as a filler into the polymer mass. Subsequently, the dried sludge (figure 2), milled to a desired fraction (figure 3). Figure 1 shows the distribution curve of the particle size distribution of the dried and grounded sludge. The density of this sludge is 2960 kg/m³ and the specific surface is 880 m²/kg. The loss of drying at 105 °C was 34.7% and the pH of the sludge was 11.6. The high pH of the sludge is due to the neutralisation of the acid solutions used in the galvanic plating process when calcium hydroxide (Ca(OH)₂) is added to the solution. Table 1 presents the concentration of pollutants in the dry matter and table 2 presents the results of the leachability test carried out according to EN 12457-4 (Characterisation of waste. Leaching. Compliance test for the leaching of granular waste materials and sludges. One stage batch test at a liquid to solid ratio of 10 l/kg for materials with particle size below 10 mm (without or with size reduction). Determination of the pollutants concentration in dry matter and the leachability of waste results from Decree No. 294/2005 Coll. on the landfilling conditions of waste and its use on the terrain surface, and amending Decree No. 383/2001 Coll. on waste management details, which also includes limits for individual leachate classes. Based on the results of the leachability test, this waste can be classified in leachate class III because the limit for leachate class IIb for chlorides (2500 mg/l) and dissolved substances (6000 mg/l) has been exceeded.

Table 1. The concentration of specific heavy metals in the NGS sludge [mg/kg dry matter].

As	Cd	Cr	Ni	Pb	V
1.51	0.37	171	112	2110	8.36

Table 2. Results of the leaching test of the NGS sludge [mg/l].

DOC ¹	Chlorides	Fluorides	DS _{dried} ²	SO ₄	Ba	Cr	Cu	As	Mo	Pb
19.7	2950	0.2	6340	5.82	0.027	0.009	0.071	0.0014	0.019	< 0.001

Explanations: ¹Dissolved Organic Carbon, ²Dissolved Substances.

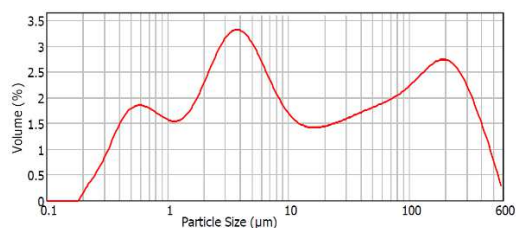


Figure 1. Particle size distribution of the pre-treated filler NGS.



Figure 2. Dried hazardous waste NGS (dryer: 105 °C).



Figure 3. Prepared filler (milled NGS).

2.2. Reference filler – silica sand

It is perfectly pure silica sand with the ideal grain shape that makes it possible to create a perfectly dense structure in the polymer substance. It is commonly used as filler in various polymer composites, mortars, fillers, polymeric substances and polymer concrete. This sand contains 99.6% of SiO_2 and has a density of 2660 kg/m^3 . As part of the research, this sand was used in reference samples to compare the parameters with the values of the developed repairing materials containing pre-treated hazardous waste.

2.3. Binder component – epoxy resin

As a binder the low viscosity solvent-free epoxy-based material with the polyamine (2,4,6-tris-(dimethylaminomethyl) phenol, and 4,4-methylenebis (cyclohexylamine)) based hardener was used. Epoxy resin is a very good binder to achieve high strength and minimal shrinkage [7]. A large amount of filler can be incorporated into this substance due to its very low viscosity.

3. Examinations carried out

3.1. Determination of compressive strength and three-point bending strength

These tests were carried out according to standard EN 13892-2 Methods of test for screed materials - Part 2: Determination of flexural and compressive strength. A filling of 40% and 45% of repairing substance by hazardous waste NGS was selected. Silica sand reference samples were created to compare the properties. The tests were carried out on $20 \times 20 \times 100 \text{ mm}$ test joists (figure 4) made of epoxy-based polymeric substance and neutralisation sludge or reference sand with different percentages of filling [8].

3.2. Determination of hardness

The hardness of the repairing composite was measured using a Shore method, which is based on inserting the spike of a type A (use for softer materials) or type D (harder materials) durometer. In our case, a type D durometer was used (figure 5). The test was performed according to standard EN ISO 868 Plastics and ebonite - Determination of indentation hardness by means of a durometer (Shore hardness). For the test, a TQC durometer, model LD0551, was used.

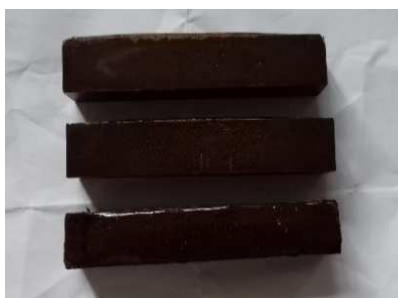


Figure 4. Samples for determination of bending and compressive strength.



Figure 5. Determination of Shore D hardness.

3.3. Monitoring of microstructure using scanning electron microscope (SEM)

The distribution of the filler (neutralising sludge NGS) in the epoxy matrix was monitored using the Tescan Mira3 LM scanning electron microscope by supporting of energetic dispersion X-ray analysis (EDX), which is a function that allows the elemental composition of the material to be determined. This function has been used to determine the amount of representation of some elements (Fe, Ca) and their distribution in the substance. This microscope is equipped with a high brightness of Schottky emitter, which ensures high resolution and low noise imaging. The accelerating voltage of this SEM is from 200 V to 30 kV and provides a magnification from 3.5x to 1,000,000x.

4. Results and discussion

4.1. Compressive strength

Figure 6 below graphically illustrates the resulting compressive strength values of the verified repairing composite samples. As seen in figure 6, with the increasing percentage of the substance filling with the NGS neutralisation sludge, the compressive strength was reduced, unlike the reference substance where, with increasing percentage of filling, the tensile strengths increased slightly to over 120 MPa.

The developed repairing composite with hazardous waste exhibited the best compressive strength at 40% filling, evidenced by a compressive strength of almost 80 MPa, which is a relatively high strength. The reference substance has better properties mainly due to better physical-mechanical properties of the filler, namely silica sand, and also because of a substantially smaller specific surface of the sand, which results in a better coating of the sand grains of the binder component and thus the improvement of the resulting properties. Higher incorporation of the NGS filler into the epoxy matrix results in inhomogeneity of the cured repairing composite and in attenuation of the bonding of filler and binder. Above all, these facts result in a considerable deterioration of the physical-mechanical properties of the composite. However, 40% of filling by this hazardous waste is a significant ecological and economic benefit from the perspective of the repairing composite production.

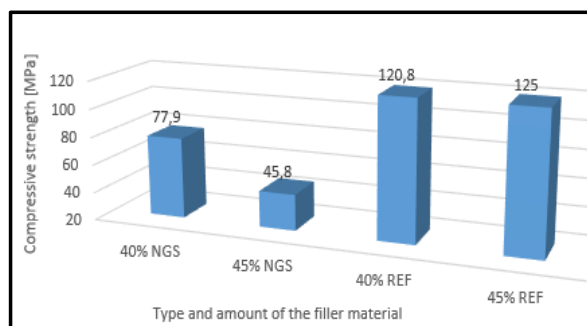


Figure 6. Compressive strength of the samples with NGS filler and reference sand.

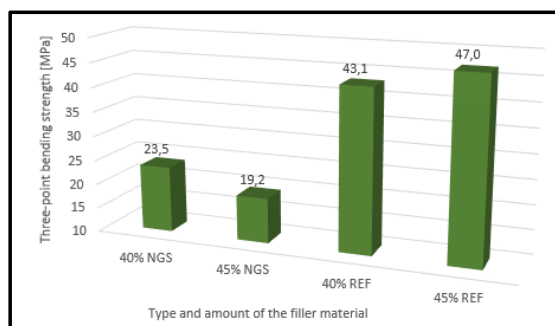


Figure 7. Three-point bending strength of the samples with NGS filler and reference sand.

4.2. Three-point bending strength

The resulting bending strength values of the test samples are graphically shown in figure 7. Here, it can be seen that the tendency of the resulting properties with the increasing percentage of filling is the same as that of the compressive strengths. Also, with the neutralising sludge NGS, the increasing filling percentage reduces workability and strength, with the reference substance increasing the three-point bending strength. The reference samples strengths ranged from 43 MPa to 48 MPa (figure 7). For the developed NGS repairing composite with hazardous waste, the flexural strength values ranged around 20 MPa. Better mechanical properties of the reference substance are also likely due to a more suitable particle size distribution and an optimal shape index of reference silica sand.

4.3. Shore hardness

The determination of the hardness of the developed composite with hazardous waste was done by measuring the shore-durometer at several locations on the test surface. It is generally known that the resulting hardness of epoxy resin-based materials depends largely on the curing time and the type of hardener. Composites with higher curing time in combination with polyamine-based hardeners typically have a high Shore D hardness. From the measured values, the average hardness of the repairing composite with 40% content of hazardous waste NGS was determined to be 90/100. It is, therefore, a material with a high surface hardness and is thus expected to be highly resistant to abrasion, impact and mechanical damage. For a reference sample containing 40% content of silica sand, a hardness value of 87/100 was recorded. Based on the evaluation of the hardness results, it can be said that the developed repairing composite will also be possible to use in places and operations where there is considerable mechanical stress in the form of inserting devices and sharp-edged objects.

4.4. Monitoring of microstructure using scanning electron microscope (SEM)

The scanning electron microscope (SEM) was used to determine the distribution of filler particles, namely hazardous waste NGS in the polymer matrix. With a magnification of 500x, it can be seen in figure 8 that some particles are substantially larger than the others, but no clumps are formed, and the particles are distributed evenly throughout the polymer matrix volume. Additionally, energy dispersive X-ray analysis (EDX), which is a supplement to SEM, has monitored the presence and amount of some elements contained in the sample with 40% NGS content. Figure 9 shows the distribution of iron (Fe) in individual NGS particles and figure 10 shows the distribution of calcium (Ca) in the neutralising sludge particles. The high calcium (Ca) presence in the NGS sludge is caused by the neutralisation of waste galvanic solutions using $\text{Ca}(\text{OH})_2$. The presence of heavy metals could not be proven by EDX analysis because their amount was negligible compared to other elements, and a more sensitive EDX analysis would be needed to determine their distribution. However, it has been proved that the distribution of the individual elements in the epoxy matrix is uniform and the hazardous waste particles have been successfully incorporated into the closed solution structure while avoiding their leaching.

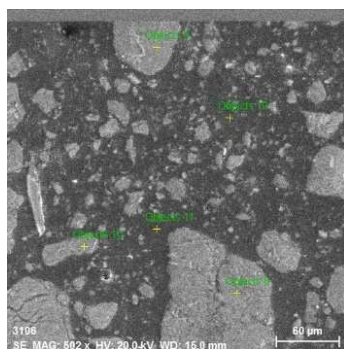


Figure 8. Distribution of the NGS particles in the epoxy matrix (40% NGS).

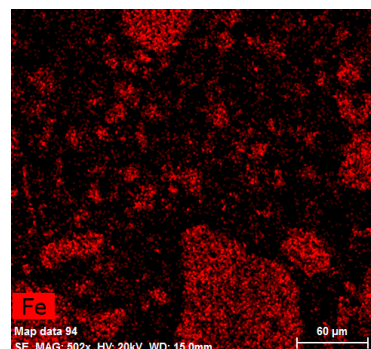


Figure 9. Distribution of iron (Fe) element in the composite with 40% NGS filler.

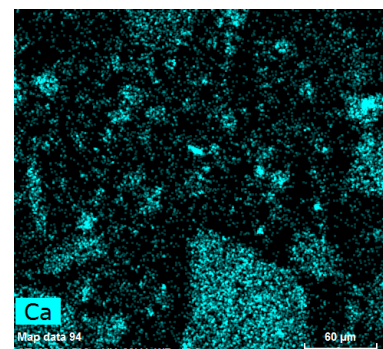


Figure 10. Distribution of calcium (Ca) element in the composite with 40% NGS filler.

5. Conclusion

Research on the possibilities and suitability of the use of hazardous waste, namely neutralisation galvanic sludge (NGS), has found that properly pre-treated hazardous waste can be used very

efficiently and advantageously as a filler in the polymer repairing composite. The repairing composite with a relatively high content of pre-treated hazardous waste NGS (40%) exhibited compressive strength of about 80 MPa and three-point bending strength of about 25 MPa. These values are high enough for the use of this composite as a repairing substance for the rehabilitation of concrete structures or for the manufacture of prefabricated fittings. The repairing composite material has also been subjected to a Shore D surface hardness test, which has been found to be a material of high surface hardness and can therefore also be used in operations where a high resistance to surface deformation is required. From an ecological point of view, this repairing composite has a very positive environmental benefit because it uses a significant amount of hazardous waste that is perfectly integrated into the substance and there is no longer any release of hazardous substances that could otherwise get into the surrounding environment in the event of imperfect landfilling. By using this waste, there is an increase in environmental protection by limiting the very expensive and problematic landfilling of these hazardous wastes. In addition, using hazardous waste reduces the producer costs associated with its landfill and all in all the production of this repairing composite eliminates the use of fillers based on primary raw materials, so even the producers will reduce direct costs.

Acknowledgements

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