Study of polymer-based adhesive mortar with higher durability

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Abstract. This paper deals with the study and development of polymer-based adhesive with high filling ratio of secondary raw materials and waste materials. The goal of this paper is to develop adhesive mortar with the highest filling rate of secondary raw materials and waste materials as possible while preserving very high physical-mechanical properties, including flexural and compressive strength, pull-off bond strength and abrasion resistance. High-temperature fly ash, waste slag and waste packaging glass are used in this paper as fillers. The resulting mortar shows high physical-mechanical properties, including high abrasive resistance and very high bonding strength to a large variety of building materials including concrete, steel, glass, and tiles.

1. Introduction

Today, the construction industry is increasingly facing problems related to the ecological and economic demands of the production of building materials, which is also reflected in the demands on the construction of new structures. The materials used in the implementation of new buildings, but also in the implementation of remediation works are increasingly demanding in terms of strength characteristics, but also the consumption of material. Today, buildings are no longer built according to historical principles. Careful calculation is performed for each construction to ensure optimal usability of the structure while ensuring minimum material requirements. There are also economic demands attached to this. Thus, the construction industry is facing an increasing demand for high-quality materials, which, however, would be economically available and have a low environmental impact. One way to achieve this is to use secondary and waste raw materials as an available and inexpensive filler in polymeric materials, which are otherwise very economically and environmentally demanding. During 2021, the price of polymer binders rose by up to 100% in some parts of the world. For this reason, this issue is becoming increasingly relevant. Secondary and waste raw materials that can be used for this purpose include, for example, high-temperature fly ash, waste glass, or waste slag from a thermal power plant which are used in this paper. The chemical composition of used materials is shown in Table 2 and sieve analysis is shown in figure 2.

2. Materials

2.1. Epoxy resin

For the purposes of this work, an epoxy resin based on a combination of bisphenol A and F was used. Amine-based hardeners were used for curing. The mixing ratios of the resin and the hardener are as
follows: 62 parts of resin and 40 parts of hardener (by weight). The binder was then mixed with a filler component consisting of high temperature fly ash, waste glass and waste slag from a thermal power plant. The grain size of the fillers was adjusted by crushing and grinding to the required grain size of 0 - 500 µm. The epoxy resin used had the following properties:

Table 1. Epoxy resin properties.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity at 25°C [mPas]</td>
<td>1000-1400</td>
</tr>
<tr>
<td>Density at 20°C [g·cm⁻³]</td>
<td>1.07</td>
</tr>
<tr>
<td>Pot life (40°C after) [min]</td>
<td>20</td>
</tr>
<tr>
<td>Exothermic temperature [°C]</td>
<td>170</td>
</tr>
</tbody>
</table>

2.2. High-temperature fly ash (HFA)

High-temperature fly ash is formed during the burning of pulverized coal in thermal power plants. Combustion takes place at temperatures of 1200–1700°C. The fly ash used for this work comes from electrostatic precipitators, which capture the fly ash from the combustion flue gas. The fly ash meets the properties of the ČSN EN 450 standard, which prescribes the suitability of fly ash for use in concrete and mortar. This means that the fly ash contains at least 45% amorphous SiO₂ and at the same time the maximum amount of free CaO, MgO and alkalis is monitored. In addition to concrete and mortar, fly ash from high-temperature combustion can also be used as a microfiller in the production of polymer composites. The specific weight of the used fly ash reaches the range 2400-2500 kg·m⁻³. Due to the high content of SiO₂ and relative inertness to a number of chemical compounds, it is a suitable filler for the developed material [1].

2.3. Waste glass (WG)

Waste packaging glass is a type of glass that is created during the sorting of glass packaging and can no longer be recycled. This is due, for example, to its color inhomogeneity or the impossibility of perfect sorting on automatic lines, which prevents its further use to produce glass containers. However, it is still a glass phase, which is produced by a glass stem containing approximately 50% silica sand, 10% Na₂CO₃ (soda), 12% CaCO₃ (limestone), 18% crushed shards and about 4% other, additional components. Glass, which can no longer be used, is a significant environmental problem. Glass generally has a very high hardness, according to the Mohs scale about grade 6. At the same time, glass is very resistant to most chemical compounds, except hydrofluoric acid [2].

2.4. Waste slag from thermal power plant (WS)

When burning coal, flammable shale, or other solid fuels in thermal power plants on grids and in furnaces, solid fuel residues are formed, which are partially melted. The resulting material is contaminated with organic residues of the original fuels. Its further use can therefore cause certain problems in building materials. Waste slag from a thermal power plant contains, for example, residues of unburned coal, free CaO and MgO, or several soluble salts. Slag is landfilled in warehouses near thermal power plants. The quality of the slag increases in proportion to the landfill time. The longer the time, the higher the quality of the slag, as the residual soluble salts are washed away by the rain. However, if the repository is not maintained, grass and trees grow in the repository, which introduces other organic residues into the slag, which are not suitable for use in building materials [2].
Figure 1. Sieve analysis of used waste and secondary raw materials.

The chemical composition of the secondary and waste raw materials used is shown in the following table 2.

<table>
<thead>
<tr>
<th></th>
<th>Cl</th>
<th>P</th>
<th>SiO₂</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>MnO</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFA</td>
<td>&lt;0.40</td>
<td>&lt;0.05</td>
<td>55.6</td>
<td>0.4</td>
<td>&lt;0.1</td>
<td>26.4</td>
<td>1.5</td>
<td>5.9</td>
<td>1.9</td>
<td>1.05</td>
<td>0.06</td>
<td>0.29</td>
</tr>
<tr>
<td>WG</td>
<td>-</td>
<td>-</td>
<td>71.0</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
<td>10.4</td>
<td>0.7</td>
<td>0.3</td>
<td>2.3</td>
<td>-</td>
<td>13.0</td>
</tr>
<tr>
<td>WS</td>
<td>-</td>
<td>-</td>
<td>51.0</td>
<td>1.1</td>
<td>0.34</td>
<td>22.4</td>
<td>4.3</td>
<td>0.9</td>
<td>3.3</td>
<td>1.7</td>
<td>-</td>
<td>1.77</td>
</tr>
</tbody>
</table>

For the purposes of this work, pre-treatment of secondary and waste raw materials was performed using a jaw crusher and a laboratory ball mill. The grain size of the filler was adjusted to a fraction of 0–500 µm and the grain size was decomposed according to the following sieve analysis curve (figure 2).

Figure 2. Sieve analysis of used waste and secondary raw materials.

The above sieve analysis curves have been adjusted to approximate ideal granularity curves. Only the filler consisting of high-temperature fly ash achieves a finer curve, as this raw material achieves a very high fineness without pre-treatment. For the purposes of this research, the highest possible level of filling with individual types of fillers was carried out, while maintaining the workability in the masonry way, with a spatula. In general, fillers whose specific surface area is higher, or whose absorbency is higher, can be dosed in a significantly smaller dose than in the case of non-absorbent fillers. The following recipes describe the recipes used.
Table 3. Composite formulations.

<table>
<thead>
<tr>
<th>Filling rate</th>
<th>WS</th>
<th>WS, HFA</th>
<th>HFA</th>
<th>HFA, WG</th>
<th>WG</th>
<th>WG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin [wt%]</td>
<td>30.4</td>
<td>28.0</td>
<td>25.5</td>
<td>23.1</td>
<td>18.2</td>
<td>18.2</td>
</tr>
<tr>
<td>Hardener [wt%]</td>
<td>19.6</td>
<td>18.0</td>
<td>16.5</td>
<td>14.9</td>
<td>11.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Filler [wt%]</td>
<td>50.0</td>
<td>54.0</td>
<td>58.0</td>
<td>62.0</td>
<td>66.0</td>
<td>70.0</td>
</tr>
</tbody>
</table>

3. Methods

Epoxy resin and hardener were mixed to prepare the samples. The ingredients were mixed thoroughly with a low-speed stirrer (300-400 rpm) for 2 minutes. A slow-running stirrer was used to prevent bubbles from entering the mass. The entire contents of the filler were slowly mixed into the liquid component and mixed for the necessary time to ensure perfect homogeneity. This time was longer than two minutes. After mixing, the mixtures were placed by masonry or casting in test moulds measuring 20x20x100 mm to determine flexural tensile strength and compressive strength, then into test moulds measuring 70x70x50 mm to determine wear resistance and the materials were applied to concrete and steel base for determining pull-off bond strength.

3.1. Apparent density
After curing of the 20x20x100 mm samples, the apparent density was determined according to ČSN EN ISO 845 standard by weighing the test samples and measuring its dimensions [3].

3.2. Compressive and flexural strength
Polymer composite was applied and compacted into silicon moulds of dimensions 20x20x100 mm. The samples were used for the determination of compressive strength and three-point flexural strength. Support distance for three-point flexural strength was 80 mm. For the determination of compressive strength, the 20x20 mm loading plates were used to distribute force evenly on the test sample sides. Three test samples of each filling rate and each filler were prepared. All test samples were cured in a laboratory environment (21°C and 55% relative humidity) for 7 days. Samples are shown in figure 3.

3.3. Pull-off bond strength
The pull-off bond strength was determined on test samples applied to concrete tiles and steel sheets. The strength was determined according to the ČSN EN 1542:1999 standard by using the Dyna pull-off tester with hand crank. All materials were applied to dry and clean surfaces. Materials were applied in thickness of approximately 3mm. The pull-off bond strength was tested after 7 days of curing [4].

3.4. Wear resistance
The wear resistance was determined on samples of dimensions 70x70x50 mm according to the ČSN EN 13892-3:2015. The wear resistance was tested on Böhm disk. Three test samples of each filling rate and type of filler were used. The wear resistance was tested after 7 days of curing [5].
4. Results
For each filler, the maximum filling rate was verified while maintaining workability in a masonry manner. This led to a different maximum filling for different types of fillers. Compressive and flexural strength was determined by a modified method according to ČSN EN 13892-2 used by Hermann et al. [6, 7].

4.1. Apparent and bulk density
The apparent density (D) of epoxy resin was 1.05 g cm$^{-3}$ in a laboratory environment (21°C). The bulk density of used fillers is shown in table 4.

<table>
<thead>
<tr>
<th>Table 4. Bulk density of used fillers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filler type</td>
</tr>
<tr>
<td>High-temperature fly ash (HFA)</td>
</tr>
<tr>
<td>Waste glass (WG)</td>
</tr>
<tr>
<td>Waste slag (WS)</td>
</tr>
</tbody>
</table>

The apparent density (D) of test samples is shown as blue line in figure 4.

4.2. Flexural and compressive strength
The results of flexural ($\sigma_t$) and compressive ($\sigma_c$) strength of test samples are shown in figure 4. The flexural and compressive strength was determined according to modified testing method stated in ČSN EN 13892-2. The flexural strength was tested, and the compressive strength was tested on the halves of samples, which resulted from the test of flexural strength.

![Figure 4. Flexural and compressive strengths and apparent density of test samples.](image)

From the above figure it can be determined that with the increase of filling ratio, the flexural strength tends to decrease, while the compressive strength increases. This is due to different behaviour of epoxy resin and fillers. The epoxy resin has very high flexural strength while relatively low compressive strength, which is increased by the filler. The apparent density increases with the increase of filling ratio. When the maximum filling ratio is achieved, there are several bubbles introduced into the mass of samples and the apparent density does not increase anymore.
4.3. Pull-off bond strength
The pull-off bond strength of all tested samples was greater than tensile strength of tested concrete tiles, which was between 3.3 N mm\(^{-2}\) and 3.6 N mm\(^{-2}\). The bond strength to steel sheets of all test samples was greater than the maximum tensile force of DYNA pull-off tester, which is 16 kN. The pull-off bond strength was tested on a circle area of 50mm diameter. Which, according to the 16 kN maximum cap of pull-off tester is approx. 8.1 N mm\(^{-2}\). The samples after testing are shown in figure 5.

![Figure 5. Samples after the pull-off bond strength test.](image)

4.4. Wear resistance
The wear resistance was tested on samples with dimensions 70x70x50 mm on laboratory Böhme disc according to the ČSN EN 13892-3:2015. The results are shown in following figure 6.

![Figure 6. Wear resistance of test samples.](image)

In the above figure, the wear resistance of samples is shown. The wear resistance decreases (the volume of abraded material is higher) with the increase of filling ratio. Which implies, that the bearer of the wear resistance is the epoxy resin itself and when the filling ratio is increased, the wear resistance decreases.

5. Summary
In this paper the possibility of using waste and secondary raw materials as filler in epoxy polymer composite was studied. Maximum filling ratio of each filler was determined by a workability test. The requirement was that the polymer composite would be still applicable in a masonry way by spatula. The A/F epoxy resin in combination with amine-based hardener was thoroughly mixed and then filled by waste and secondary raw fillers with a grain size of 0-500 μm (figure 2.). For purposes
of this paper, the waste slag from nearby power plant, high-temperature fly ash and waste packaging glass were used. It was found that all the selected materials can be used as fillers in epoxy-based mortar/adhesive up to a point. The lowest filling ratio was achieved with waste slag. That is probably due to a large number of impurities and organic residues which exhibit high absorption; therefore, the epoxy resin was absorbed into the material and could no longer function as a binder between grains of filler. The high-temperature fly ash has very low absorption and the filling ratio of this material was higher. The material also exhibits very high specific surface area; therefore, it needs a lot of binder to wet all of grains. The high-temperature fly ash had also the highest amount of very fine grains. The highest filling ratio was observed when waste packaging glass was used. The same behaviour can be observed in cementitious materials. This is probably due to shape of grains of this material and very low absorption. The flexural and compressive strengths were determined. With increase of amount of filler in the composite, the flexural strength tends to decrease, this is due to the fact, that the epoxy resin is the carrier of flexural properties. With the increase of filler in the material, the compressive strength increased, this is due to the fact, that the filler in combination with resin is the carrier of compressive strengths. It was determined that the maximum filling ratio, at which the physical-mechanical properties do not decrease too severely, was 54% for the waste slag, 66% for the high-temperature fly ash and 70% for the waste packaging glass. The pull-off bond strength was tested. The results show that all the test samples shown very good adhesive properties to both concrete and steel sheets. The pull-off bond strength to concrete was greater than the tensile strength of used concrete and was above 3.3 N·mm⁻² and the adhesion to steel sheets was greater than 8.1 N·mm⁻². The wear resistance was also tested, which confirms the results of flexural and compressive strengths. The lower values of physical-mechanical properties of the highest tested filling ratios are due to insufficient workability and inability to compact the samples, which resulted in porous samples with lower overall properties.

6. References

Acknowledgements
This paper was supported by the FAST-S-21-7228 project “Analysis of the influence of the size and morphology of microfiller particles from primary and secondary raw materials on the resulting properties of composite materials”.

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