Effects of Curing Conditions on the Self-Healing of Geopolymer Paste

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Abstract. Geopolymers are inorganic polymers produced by the reaction of aluminosilicates and alkaline solutions and show good mechanical and thermal features with a huge potential for use in the construction industry. Furthermore, geopolymers with self-healing properties can considerably decrease repair or maintenance costs and support economic and environmental sustainability. This study aimed to observe the self-healing capability of sodium silicate-containing agents in geopolymer pastes. Polyethylene glycol (PEG) and epoxy resin were used to encapsulate sodium silicate. The prepared healing agent was introduced into fly ash and metakaolin-based geopolymer samples. After curing for 28 days under room conditions, the samples were subjected to compressive loading to introduce cracks. The cracked samples were stored under three conditions: at 60°C under 100% relative humidity (RH), at room temperature under 100% RH, and at room temperature in water. After various durations, optical images were captured using a light microscope to determine the closure of the cracks. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) were used to identify healing products. Additionally, the change in compressive strength was used as an indicator of self-healing. The results showed that the sodium silicate agents could heal the cracks with narrow widths (<15µm) under all conditions and supported strength recovery. XRD and FT-IR results indicated that the main healing materials were aluminosilicate phases.

1 Introduction

Self-healing is the ability of materials to repair themselves and recover their properties after damage. Materials with self-healing features will have longer service lives and reduced maintenance costs [1]. The self-healing of cementitious materials is a promising phenomenon in terms of sustainability and durability, in addition to economic benefits. In the case of construction materials, the concern of using raw materials and energy sources with lower impacts on the world makes it necessary to find new strategies. In recent studies, researchers have focused on self-healing cementitious materials by repairing damage and recovering mechanical and durability-based properties [2, 3].

Several self-healing approaches have been applied, including bacterial self-healing and encapsulation technologies, such as mineral admixtures or crystalline admixtures [4]. Previous studies have demonstrated predominantly autogenous or autonomous healing of the cement mortar and concrete by evaluating crack sealing, permeability, or mechanical strength recovery [5-7]. However, few studies have been carried out about the self-healing of geopolymers which are eco-friendly alkali-activated aluminosilicate binders and have comparable features to cement-based materials. Kan et al. (2019) investigated the self-healing capability of fly ash and metakaolin-based geopolymers by exposure to air and wet-dry cycles and found that air exposure was more effective for self-healing [8]. In a study by Alshaer (2020), cracks were healed by non-soluble mineral phases due to the uptake of CO₂ from the air in vascular luffa fiber-reinforced geopolymer systems [9]. Doctolero et al. (2021) observed the self-healing of geopolymers through microbial-induced calcite precipitation by X-ray microtomography [10]. Kusbiantoro et al. (2016) used the self-healing agent of polyethylene vinyl acetate (PVA) to reduce the drying shrinkage of geopolymers at elevated temperatures. Their results showed that PVA has a promising potential for compressive strength development and crack-filling mechanisms [11].

In this study, fly ash and metakaolin-based geopolymers with sodium silicate-containing self-healing capsules were prepared. This study aimed to investigate the contribution of sodium silicate to the crack closure of geopolymer pastes under various healing conditions. The visual crack closure and water sorptivity properties of the geopolymer pastes were compared to determine the external and internal effects of the healing agents. The mechanical strength recovery was observed by comparing the compressive strength after different curing conditions. Moreover, the chemical identification of the crack fillers was performed by XRD and FT-IR techniques.
2 Experimental studies

2.1 Preparation of self-healing agent

The self-healing agents were produced by core-shell encapsulation. The procedure performed by Feng et al. [12] was modified for this study. The core consisted of a phase change material of polyethylene glycol (PEG) that was used as a carrier for the self-healing agent of sodium silicate. The core was covered with epoxy resin and a fly ash shell to avoid releasing the healing material before the desired time. Using fly ash aimed to increase the interaction between the interface of the healing capsules and geopolymer paste.

PEG 1000 was obtained from Carl Roth GmbH (Karlsruhe, Germany). Sodium silicate (SS) powder was provided by Wöllner GmbH (Ludwigshafen, Germany) under the brand name Sikalon A, with a SiO₂:Na₂O molar ratio of 2.1. The EpoFix resin and hardener were obtained from Struers (Cleveland, USA). To prepare the PEG 1000 and sodium silicate mixture, PEG was first heated to its melting point, and SS was added to the melted PEG at a ratio of 1:1 by mass. The core material was then solidified under room conditions and crushed to form granules. The prepared core granules were covered with epoxy resin and allowed to rest for 30 min to improve the waterproofing features of the shell. Subsequently, the surfaces of the epoxy-coated granules were completely covered with fly ash. To finalize the production of self-healing agents (SS@PEG capsules), the granules were kept at room temperature overnight and sieved. Granulates with the size of 2–4 mm were used in the geopolymer paste.

2.2 Characterization of self-healing agent

To investigate the survivability of the self-healing agent in water and alkaline solution SS@PEG capsules were immersed in water and Geosil (pH=13.5) for 7 days. The weight change in the capsules before and after immersion was measured. Three measurements were performed. Also, the surface deformation was detected via light microscope examination.

2.3 Preparation of geopolymer specimen

Fly ash (FA) and metakaolin (MK) were used as aluminosilicate sources in this study. Fly ash was obtained from Baumineral GmbH (Herten, Germany) and was F-type with a low CaO content. Metakaolin was supplied by Temcon Solutions GmbH (Winnweiler, Germany). The chemical components of the FA and MK are listed in Table 1.

First, FA and MK were dry mixed to homogenate and added into the Geosil. The materials were mixed in the following steps: low-speed mixing for 90 s, break for 30 s, and high-speed mixing for 90 s. After mixing the geopolymer paste, the pre-determined amounts of self-healing agents were added and the paste was mixed for an additional 30 s to ensure uniform dispersion of agents. Afterward, the pastes were poured into 2 cm cubic moulds and compacted in a compacting table for 1 min. The surface of the specimens was covered by stretch film to avoid evaporation of the alkaline solution. The specimens were cured at 22℃ for 28 d. The control samples were prepared without SS@PEG capsules and undergo the same procedure with capsule containing pastes.

2.4 Experimental method

To observe the self-healing effects of SS@PEG capsules, artificial cracks were introduced by applying compressive strength to the 28-d cured specimens. Firstly, samples were subjected to the compressive strength test to obtain the maximum load capacity. Then 80% of the max load was applied to the specimens to introduce cracks with various widths. After having cracks, the crack width was measured under an optical microscope (Zeiss Stemi SV 11). To understand the effects of different healing conditions, the healing

<table>
<thead>
<tr>
<th>Component</th>
<th>FA (wt.-%)</th>
<th>MK (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>6.19</td>
<td>10.18</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>26.56</td>
<td>38.55</td>
</tr>
<tr>
<td>CaO</td>
<td>3.83</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5.61</td>
<td>1.28</td>
</tr>
<tr>
<td>K₂O</td>
<td>3.37</td>
<td>0.19</td>
</tr>
<tr>
<td>MgO</td>
<td>2.86</td>
<td>0.08</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.91</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.84</td>
<td>0.14</td>
</tr>
<tr>
<td>SiO₂</td>
<td>48.68</td>
<td>47.51</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.05</td>
<td>1.41</td>
</tr>
</tbody>
</table>

Table 1. Chemical components of FA and MK

Table 2. Mix proportion of geopolymer pastes

<table>
<thead>
<tr>
<th>Sample</th>
<th>FA (g)</th>
<th>MK (g)</th>
<th>Geosil (g)</th>
<th>Healing agent/binder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>400</td>
<td>100</td>
<td>200</td>
<td>0</td>
</tr>
<tr>
<td>GP-SS@PEG</td>
<td>400</td>
<td>100</td>
<td>200</td>
<td>0.18</td>
</tr>
</tbody>
</table>

First, FA and MK were dry mixed to homogenate and added into the Geosil. The materials were mixed in the following steps: low-speed mixing for 90 s, break for 30 s, and high-speed mixing for 90 s. After mixing the geopolymer paste, the pre-determined amounts of self-healing agents were added and the paste was mixed for an additional 30 s to ensure uniform dispersion of agents. Afterward, the pastes were poured into 2 cm cubic moulds and compacted in a compacting table for 1 min. The surface of the specimens was covered by stretch film to avoid evaporation of the alkaline solution. The specimens were cured at 22℃ for 28 d. The control samples were prepared without SS@PEG capsules and undergo the same procedure with capsule containing pastes.
progress of the specimens was observed for water immersion, 100% relative humidity (RH)-room temperature (RT), and 100% relative humidity (RH)-60°C.

2.5 Monitoring the self-healing efficiency

The optical microscopy analyses were carried out just before (1 d) and 28 d of exposure in each healing medium to observe the closure of the cracks. Various points on the cracks were marked and images in the same region were captured for a proper comparison. An image analysis software of Fiji (Image J) was used to calculate the crack closure efficiency (R) of each sample

\[ R = \frac{(W_0 - W_1)}{W_0} \times 100 \]  

where, \( W_0 \) and \( W_1 \) denote the width of cracks before and after healing for 1 d and 28 d, respectively [12].

The capability of strength recovery of damaged geopolymer specimens was investigated by comparing the compressive strength values before and after the healing process. The tests were carried out with the Toni Technik model 2060 from Zwick Roell. The capillary water absorption test was performed to analyze the performance of the self-healing agents under various healing environments [13]. Due to having small (2 x 2 x 2 cm) cubes, tests were carried out with some modifications in EN ISO 15148.

At the end of the specified healing period, X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FT-IR) techniques were used to identify healing products. The healing materials from the surface and internal region of the cracks were scratched under a microscope and ground for XRD and FT-IR analysis. XRD analysis was carried out by Empyrean XRD device from PANalytical with CuKα (\( \lambda = 1.54 \) Å) radiation at 40kV and 40 mA in the range of 5°-65°. Due to the small quantity of the samples, a specific sample holder made of Si single crystal for small quantities (approx. 20 mg) was used. The crystalline phases were determined with ICDD and ICSD databases. Structural analysis was done using FT-IR (Spectrum Two, PerkinElmer) using the attenuated total reflection (ATR) method in the range of 4000 and 400 cm\(^{-1}\).

3 Results and discussions

3.1 Characterization results of healing agent

The immersion of the healing agents into the water and alkaline solution caused no change in the weight of the samples, which can be proof of leak tightness. Also, as seen in Fig.1, the healing agents protected their shape in water and alkaline solution.

Fig. 1. Microscopy images of healing agents immersed in water (a) and alkaline solution (b).

The stability in weight and surface showed that there was no transition of components through the shell walls of the agent.

3.2 Microscope images

The crack sealing development for each curing condition is illustrated in Fig. 2.

Fig. 2. Crack closure of progress for different curing mediums
The microscope images showed that depending on the width of the cracks, partial or complete closure was achieved for all curing conditions. It is expected that when geopolymer samples were preloaded, the load caused cracks and ruptured the capsules. The released healing agent reacted with unreacted materials in the geopolymer matrix and sealed the cracks with these secondary geopolymerization products.

Microscopy investigation revealed about 10-100% crack sealing within 28 d. The healing agent might have reacted with unreacted aluminosilicate compounds in the geopolymer matrix and filled the crack faces with geopolymerization products.

However, as shown in Table 3, crack closing was not accomplished completely when the crack widths were > 20µm. That could be explained by the lack of enough leakage of the sodium silicate from the healing agent to the crack mouths. At this point, it is important to investigate the healing of the internal cracks in terms of the penetration of water.

### Table 3. Changes in the crack width before and after healing

<table>
<thead>
<tr>
<th>Healing conditions</th>
<th>Crack width (µm)</th>
<th>Crack closure efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%RH-60°C</td>
<td>4.8</td>
<td>14.32</td>
</tr>
<tr>
<td>100%RH-RT</td>
<td>1.8</td>
<td>44.0</td>
</tr>
<tr>
<td>WH</td>
<td>2.9</td>
<td>20.2</td>
</tr>
</tbody>
</table>

### 3.3 Compressive strength recovery

The compressive strength values before and after the healing process are given in Fig. 3. When the compressive strength values were compared, it was seen that using capsules caused decrease in the mechanical endurance. For control sample, the further curing supported the compressive strength. On the other hand, before introducing cracks, the mean compressive strength value of the GP-SS@PEG samples was 26 MPa. As shown in Fig. 3, after healing in the water for 28 d, the average value of the compressive strength showed a decrease. Healing under 100% relative humidity at 60°C caused an increase in compressive strength by 26%. This could be because of the accelerated reaction between the healing agent and the unreacted aluminosilicates.

Geopolymerization reactions are accelerated at elevated temperatures, supporting mechanical endurance recovery. However, if it was not cured under high relative humidity, the increase in the temperature could cause drying shrinkage [11].

### 3.4 Water sorptivity

The mean capillary water absorption coefficients of the specimens healed in various conditions are shown in Fig. 4. The self-healing of the internal cracks plays a significant role in water migration [7]. Thus, the closing of the internal cracks was monitored by the water uptake. The presence of SS@PEG capsules improved the water tightness of geopolymer samples when it compared with control samples. The capillary sorption coefficient of the samples was reduced as 56.9%, 40%, and 42.1% of control samples for the healing conditions of 100%RH-60°C, 100%RH-RT, and WH, respectively. These results showed us that initial cracks were healed by the SS@PEG capsules. As presented in Fig. 4, the specimens healed under 100%RH-60°C had the best water tightness with a water sorption coefficient of 0.249 kg/m²h⁰.⁵, proving a high degree of crack sealing. In conformity with the compressive strength results, when geopolymer samples were cured in water, the presence of the water inhibited the crack closure, which has a reverse situation in cement-based materials. Similar to this study, Kan et al. (2019) found that subjecting geopolymer samples to water showed lower healing efficiency since the presence of the water could hinder geopolymerization due to the chemical equilibrium. Water could be a medium for ion exchange instead of being the main reactant for different healing mediums [8]. Moreover, carrying out the healing process in water might cause the dissolution of the crack fillings.
3.5 XRD analysis

For chemical analysis of the healing compounds, the fillings along the crack areas were collected and analysed by XRD. The XRD patterns of the healing are given in Fig. 5. The patterns for healing products show that the main crystalline phases were mullite and quartz for all samples. These results show that no significant amount of a new different crystalline phase was formed during the healing process and the crack filler compounds have an amorphous structure which can be explained by the amorphous nature of the geopolymers.

3.6 FT-IR analysis

Fig. 6 presents the FT-IR spectra of healing compounds in the cracks and aluminosilicate sources of fly ash and metakaolin. All spectra for crack fillers showed similar bands because of similar geopolymerization products in the crack sealing.

In FT-IR spectra, the bands between 2360 and 2160 cm⁻¹ are due to hydrogen bridge bonds between Si(OH)₄ tetrahedra and a silicate network [14]. As seen in Fig. 6, the peaks in that region decreased for the geopolymer samples due to the polymerization of the silicates.

The bands around 1640 cm⁻¹ indicate the presence of the stretching (–OH) and bending (H–O–H) of the amorphous gel products containing (H)–OH groups. The peaks related to the asymmetric stretching and vibrations of Si–O–Si, and Si–O–Al of metakaolin and fly ash are observed around 1077 cm⁻¹ and 1020 cm⁻¹, respectively. For healing products, these peaks shift to a lower frequency. That is a verification of the leakage of the healing agent through the crack and its contribution to polymerization. The band corresponds to the split-in-plane bending vibration of CO₃²⁻ is observed at 872 cm⁻¹ and the region of 667–424 cm⁻¹ indicates the symmetric stretching of Si–O and bending modes of Si–O–Si and O–Si–O [14, 15].

4 Conclusion

The self-healing functionality of the geopolymer pastes under various healing conditions was investigated in this study. SS@PEG capsules were incorporated into the mixes as healing agents. Based on obtained results, the following conclusions may be drawn:

1. The healing agents could seal the surface cracks if the crack width is <15 µm independent of the curing condition.
2. Healing SS@PEG containing geopolymer samples under 100%RH-60°C significantly ensured compressive strength recovery compared to other curing conditions. Furthermore, the water sorptivity test showed that 100%RH-60°C condition supported having a denser microstructure. When all the geopolymer samples had the same formulation, the change in the water sorptivity coefficient could prove that healing samples under 100%RH-60°C promoted the closing of internal cracks more efficiently.
3. The structural and chemical analysis of XRD and FT-IR showed that the crystalline fillings in the cracks were mainly mullite and quartz. Also, FT-IR spectra proved the formation of aluminosilicate materials.
4. In further studies, the distribution of the self-healing agents in the geopolymer matrix should be improved to achieve higher self-healing capability. Also, to compare mechanical strength recovery results uncracked references with self-healing agents can be prepared.

References

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