

# Development and characterization of novel polymers for self-healing cementitious materials

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## ABSTRACT

In the present work, a polymer-based healing agent has been developed to be applied in self-healing of cementitious materials. Several key prerequisites of the healing agent such as viscosity, curing time, swelling capacity and elasticity were evaluated. The healing agent was manually injected into cracks of mortar samples to evaluate its potential to seal concrete cracks. After curing of the healing agent, the crack width was increased by 50, 100 and 150% in order to evaluate its elasticity and strain capacity. Interestingly, a strain of at least 150% could be achieved as no differences were observed in the microscopy images of the healed crack after each stepwise elongation. Therefore, the developed healing agent is a promising candidate to seal dynamic cracks in structures under cyclic load. Furthermore, the results indicate that the developed polymer has favorable self-healing properties including an adequate curing time, viscosity and mechanical properties.

## 1. INTRODUCTION

Due to its high compressive strength and relatively low cost, concrete is still one of the main materials used in the construction industry. However, cracking tends to occur in concrete as a consequence of its relatively low tensile strength. Since these cracks can provide entry channels for potentially aggressive liquids and gasses which can result in concrete deterioration, a mechanism for self-healing would be very beneficial to improve the durability of concrete. Several types of healing agents have already been used in research on self-healing of concrete. One-component and two-component healing agents, such as cyanoacrylates, epoxy, silicones, alkali-silica solutions, PU or PMMA were screened by different research groups [1].

The present study reports on the characterization of novel crosslinked polymers. The rheological properties, the curing time and the swelling capacity of the crosslinked polymers were determined. Furthermore, its elasticity and strain capacity were evaluated after injection in cracked mortar samples.

## 2. MATERIALS AND METHODS

### 2.1. Polymer precursor synthesis and characterization

Two polymer precursors (P200 and P400) with crosslinkable end-groups were in-house synthesized and characterized by FT-IR, <sup>1</sup>H NMR spectroscopy and gel permeation chromatography.

P200 and P400 are differentiated by the molecular weight of the spacer between the precursor backbone and the crosslinkable end-groups. The synthesis conditions as well as the chemical structure of the polymer precursors cannot be disclosed due to IP issues.

## 2.2. Healing agent characterization

Several healing agent compositions were prepared by combining the synthesized precursors (dissolved in a predetermined amount of solvent) with a crosslinker possessing complementary functionalities at different concentrations. The ratio of precursor/solvent used was 1g/0.5ml. For each polymer precursor, two molar ratios with respect to the crosslinker were evaluated (as indicated in the table 1).

Table 1: Molar ratio of precursor/crosslinker used.

|                   | Precursor /crosslinker ratio (mol) |
|-------------------|------------------------------------|
| P200_1 and P400_1 | 1:0.5                              |
| P200_2 and P400_2 | 1:0.25                             |

### 2.2.1. Rheological Properties and curing time

The viscosity of the mixtures was determined by means of rheology. The shear rate of the spindle was increased from 1 to 3000 s<sup>-1</sup>. The temperature during the measurements was 20 °C and for each mixture three repeated measurements were performed.

The same rheometer was used to determine the curing time. However, instead of rotating, the spindle was now oscillating.

### 2.2.2. Swelling capacity and crosslinking efficiency

Crosslinked polymers were, after weighing, incubated in water. After 24h, the swollen polymers were removed, gently surface dried with paper and weighed. The polymer swelling capacity (%) was calculated based on the following formula:

$$\text{Swelling capacity(\%)} = \frac{W_0 - W_{\text{swollen}}}{W_0} \times 100$$

in which  $W_0$  is the weight of dry polymer and  $W_{\text{swollen}}$  is the weight of the hydrated crosslinked polymer. For each sample, three repeated measurements were performed.

The efficiency of the crosslinking reaction was determined using HR-MAS <sup>1</sup>H NMR spectroscopy. The crosslinking efficiency can be calculated by comparing the intensity of the signals characterizing the protons of the crosslinkable end-groups with the integration of a signal that remains chemically inert during crosslinking.

### 2.2.4. Manual crack repair

Mortar specimens (40x40x160 mm<sup>3</sup>) with a water to cement ratio of 0.45 and a sand to cement ratio of 3 were made. In order to create controlled cracks, each specimen contained two steel reinforcement bars with a diameter of approximately 3 mm. At the age of 7 days, the mortar prisms were cracked by means of a crack width controlled 3-point-bending test. Cracks were injected with the healing agent immediately after crack formation. After 3 days, the healed cracks were widened in a stepwise fashion.

### 3. RESULTS

#### 3.1. Viscosity and curing time

The measured viscosity for each healing agent mixture is shown in Figure 1A. It can be noticed that upon increasing the molecular weight of the polymer precursor, the viscosity also increased, as anticipated. The viscosity measured for a shear rate of  $3000\text{ s}^{-1}$  was chosen for comparison of the different mixtures (Figure 1B). Dry [2] found that the viscosity of the healing agent should be between 0.1 and 0.5 Pa.s. It was noticed that the obtained viscosity values for P400 were double the values suggested by Dry. However, the viscosity can be adjusted by increasing the amount of solvent added.

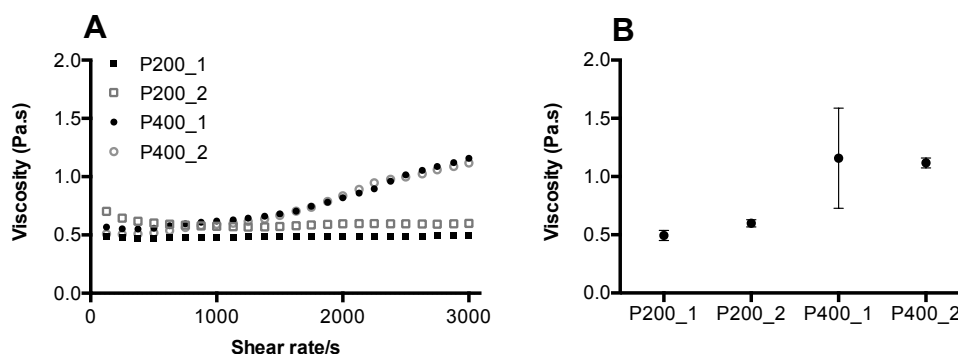


Figure 1: Measured viscosity for each healing agent mixture.

The gel point values obtained for the different mixtures are shown in Figure 2. It can be noticed that the curing time was shortened from 15 to 5 min by increasing the crosslinker concentration. For P400, the gel point could not be determined as the mixtures showed premature crosslinking.

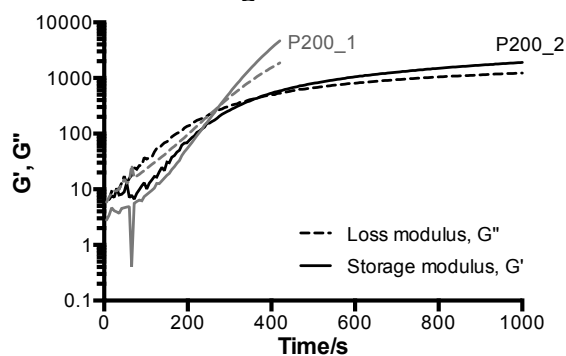


Figure 2: Gel point values for P200 mixture.

#### 3.2. Crosslinking efficiency and swelling capacity

A precursor/crosslinker molar ratio of 1:0.5 was selected to obtain a completely crosslinked polymer. HR-MAS  $^1\text{H}$  NMR spectroscopy was used to determine the efficiency of the crosslinking reaction. As expected, a crosslinking efficiency of approximately 100% was obtained for both P200\_1 and P400\_1. Upon decreasing the crosslinker concentration by half, a crosslinking efficiency of 53% and 49% was determined for P200\_2 and P400\_2, respectively.

In Figure 3 the swelling capacity of the crosslinked polymers is shown. It can be noticed that the swelling capacity increases when the degree of crosslinking decreases (P200\_2 and P400\_2). Furthermore, crosslinked polymers with higher molecular weight (P400) showed higher swelling capacity values.

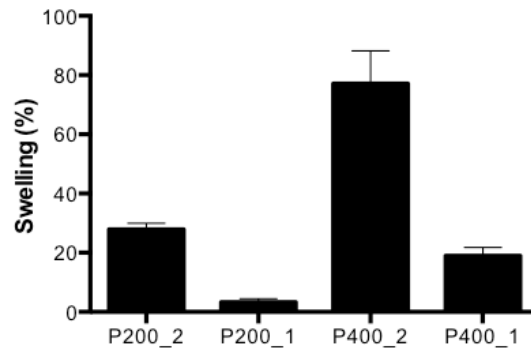


Figure 3: Mean swelling capacity measured for each healing agent mixture.

### 3.3. Manual crack repair

To evaluate the potential of the synthesized crosslinked polymers to seal concrete cracks, the mixtures were manually injected into cracks of mortar samples. After curing the healing agent, the crack width was increased up to 50, 100 and 150% in order to evaluate the polymer elasticity and its strain capacity. In Figure 4, images of the polymer in the healed crack recorded after each stepwise elongation are shown. A strain of at least 150% was achieved without observing any differences in the microscopy images of the healed cracks after each stepwise elongation.

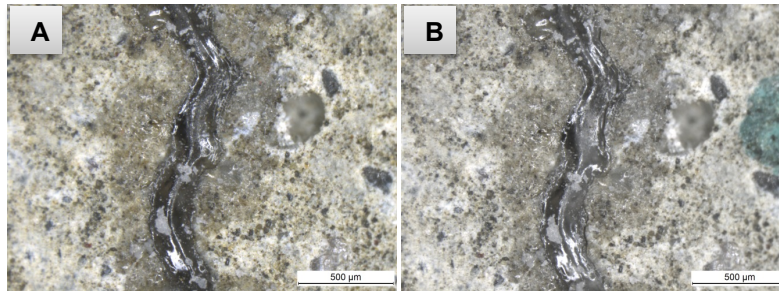


Figure 4: Images of the healed cracks: A – after healing; B – after crack widening by 150%.

## 4. CONCLUSIONS

In the present study, crosslinked polymers have been successfully developed and characterized. Interestingly, the polymers showed the ability to bridge cracks of increasing width, which is a key prerequisite in case of occurrence of dynamic cracks in structures under cyclic load. Moreover, the properties of the crosslinked polymers can be adjusted by varying the concentration of the crosslinker and the spacer length between the precursor backbone and the crosslinkable end-group.

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