Materials and Design 98 (2016) 215–222

Contents lists available at ScienceDirect

Materials and Design

journal homepage: www.elsevier.com/locate/matdes

Cross-linkable polyethers as healing/sealing agents for self-healing of cementitious materials

Maria Araújo [a,b,c], Sandra Van Vlierberghe [b], João Feiteira [a], Geert-Jan Graulus [b], Kim Van Tittelboom [a], José C. Martins [d], Peter Dubruel [b], Nele De Belie [a,*]

[a] Magnel Laboratory for Concrete Research, Department of Structural Engineering, Faculty of Engineering and Architecture, Ghent University, Technologiepark Zwijnaarde 904, 9052 Ghent, Belgium
[b] Polymer Chemistry and Biomaterials Group, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Campus De Sterre, Building S4, Krijgslaan 281, 9000 Ghent, Belgium
[c] SIM vzw, Technologiepark Zwijnaarde 935, 9052 Ghent, Belgium
[d] NMR and Structural Analysis Unit, Department of Organic and Macromolecular Chemistry, Faculty of Sciences, Ghent University, Campus De Sterre, Building S4, Krijgslaan 281, 9000 Ghent, Belgium

ARTICLE INFO

Article history:
Received 12 November 2015
Received in revised form 19 February 2016
Accepted 2 March 2016
Available online 4 March 2016

Keywords:
Self-healing
Concrete
Hydrogel precursor
Michael-type addition reaction
In-situ curable hydrogels

ABSTRACT

To date, the potential of several types of polymeric materials as healing agents for self-healing of concrete has already been investigated. Generally, for self-healing concrete with encapsulated polymeric healing agents, the curing mechanism is triggered upon contact with moisture/air or upon reaction with a second component provided by additional capsules. The present work explores the use of *in-situ* curable hydrogels formed as a result of the elevated pH of the cementitious matrix, via a Michael-type addition reaction, as potential healing/sealing materials for concrete applications. For this purpose, a variety of acrylate-endcapped urethane-based precursors were synthesized and combined with a thiol-based cross-linker. Various properties including the viscosity, the curing time, the swelling capacity and the cross-linking efficiency have been evaluated. The potential of the developed materials to seal concrete cracks was assessed through manual injection. The results indicate that the cross-linking reaction can readily occur *in-situ* due to the alkaline environment of the cementitious matrix and that the hydrogels exhibit favorable sealing properties.

1. Introduction

Concrete is the most widely used construction material because of its high compressive strength, relatively low cost and broad availability. However, cracking tends to occur in concrete as a consequence of its limited tensile strength. For that reason, concrete is often combined with steel reinforcement to carry the tensile loads. These steel rebars can limit the crack width but do not completely prevent crack formation. The repair of these cracks is indispensable as they can provide easy entry channels for the penetration of water or other harmful substances into the concrete, which can lead to deterioration and to corrosion of the reinforcement [1]. Usually, cracks are repaired manually, which is very expensive and difficult when cracks are not visible or accessible. A smart cementitious material, which has the ability of repairing damage by itself, would be thus highly advantageous. Self-healing properties in concrete may be obtained by the addition of healing agents such as superabsorbent polymers (SAPs) [2], bacteria [3], fibers to limit the crack width [4] or encapsulated polymers [5]. Among the various healing agent types, encapsulated polymer-based systems have gained increasing attention. In the capsule-based approach, the self-healing mechanism is triggered upon crack formation, leading to capsule breakage followed by release and reaction of the healing agent in the zone of damage. Several commercial polymers such as cyanoacrylates [6–8], epoxy [9–11], silicones [7], polyurethanes [5,12–14] and poly(methyl methacrylate) [15–17] have already been tested in research on self-healing of concrete. Generally, these are one-component healing agents which react upon contact with moisture or air or due to heating or multi-component systems which react upon making contact with a second component that is present in the matrix or provided by additional capsules [18]. Although different polymeric healing agents have been explored for self-healing of concrete, the reported healing agents have some limitations. For one-component healing agents premature hardening of the healing agent inside the capsules may occur [6,19,20]. In the multi-component system proper mixing of the components is often required to obtain the prescribed properties of the hardened agent [20,21].

As an alternative to the use of the aforementioned healing agents, we explore the use of a novel, *in-situ* curable hydrogel formed by the reaction of an acrylate-endcapped hydrogel precursor with a multifunctional thiol as potential material for self-healing of concrete. The curing of these prepolymers occurs via a Michael-type addition reaction in slightly basic conditions resulting in chemically cross-linked hydrogels [22–24]. *In-situ* formation of the network can thus readily

* Corresponding author.
E-mail address: nele.debelie@ugent.be (N. De Belie).

http://dx.doi.org/10.1016/j.matdes.2016.03.005
0264-1275/

occur due to the alkaline environment of the cementitious matrix. This is a unique advantage compared to other encapsulated polymers already investigated, as no premature hardening of the healing agent will occur (curing triggered by the high pH of the cementitious matrix) and no external stimuli (air, moisture, temperature, etc.) are required to activate the curing of the healing agent as the increase of pH upon exposure to the concrete is sufficient to trigger the cross-linking. Another advantage of this system is that proper mixing of the components can also be guaranteed, as encapsulation of both components of the healing agent into single capsules is possible if a latent cross-linker is applied [25]. Moreover, the reactivity of proposed healing agents is not affected in the presence of moisture/water, which may facilitate the encapsulation of these agents in comparison to moisture or air-curing healing agents since use of impermeable capsules is not absolutely necessary.

In order to develop the *in-situ* curable hydrogels, a variety of acrylate-endcapped urethane precursors have been first synthesized and characterized. Urethane-based acrylate oligomers are often used in UV-curable formulations [26–28] and have the potential to combine a wide range of properties exhibited by polyurethanes including excellent adhesion to most substrates, abrasion resistance and high impact and tensile strength together with the high reactivity of acrylates [26, 29]. Subsequently, the acrylate-functionalized precursors have been combined with a thiol-based compound to prepare cross-linked hydrogels. In addition, several key characteristics of the healing agents, such as their viscosity, the curing time required and their swelling capacity have been evaluated. In a final part, the various healing agent formulations have been injected into cracks of mortar samples and cured in the high pH environment. The healing/sealing efficiency was evaluated by determining the regain in water tightness of the healed cracks.

2. Materials and methods

2.1. Materials

All chemicals were used as received unless otherwise specified. Poly(ethylene glycol) (200 g/mol) (PEG200), hexamethylene diisocyanate (HDI, ≥98%), dibutyltin dilaurate (DBTDL), phenothiazine (≥98%) and pentaerythritol tetrakis (3-mercaptopropionate) (>95%) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Poly(ethylene glycol) (400 g/mol) (PEG400) and poly(propylene glycol) (425 g/mol) (PPG425) were obtained from Acros Organics (Geel, Belgium). PEG monoacrylate and PPG monoacrylate were kindly provided by Geo Specialty Chemicals (Hythe, UK). Chloroform (>99%) was obtained from Chem-Lab (Zedelgem, Belgium). Deuterated chloroform ($CDCl_3$) was purchased from Euriso-top (Saint-Aubin, France). PEG200, PEG400 and PPG425 were dried and degassed at 80 °C under reduced pressure for 2 h prior to use.

2.2. Synthesis and characterization of acrylate-endcapped, urethane-based PEG/PPG precursors

Dry PEG (M_w 200 and 400 g/mol) or PPG (M_w 425 g/mol) and hexamethylene diisocyanate (HDI) were poured into a round-bottom flask equipped with a mechanical stirrer. The catalyst DBTDL (300 ppm) was diluted in dry toluene and added to the reaction vessel. The reaction proceeded for 3 h at room temperature under nitrogen atmosphere. The urethane-based prepolymer was subsequently endcapped by dropping PEG- or PPG-acrylate into the flask. Phenothiazine was used as an inhibitor for spontaneous polymerization at a 1000 ppm level based on the mass of the acrylate. The reaction end was determined by the disappearance of the peak correspondent to the isocyanate group (at 2240 cm^{-1}) in the Fourier Transform Infrared (FT-IR) spectrum. In Table 1, an overview of the chemical composition of the different polymer precursors developed is shown.

The chemical composition of the precursors was investigated using infrared (IR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. A Bio-Rad FT-IR spectrometer FTS 575C was used to perform attenuated total reflection infrared (ATR-IR) spectroscopy analysis. ^{1}H NMR spectra of the polymer precursors were recorded in $CDCl_3$ with a Bruker Avance 300 MHz instrument.

Table 1
Overview of chemical composition of the developed polymer precursors.

Sample name	Polyol (mol)			HDI (mol)	End-capping acrylate (mol)	
	PEG200	PEG400	PPG425		PEG-acrylate	PPG-acrylate
PE200	1	–	–	2	2	–
PE400	–	1	–	2	2	–
PP425	–	–	1	2	–	2

2.3. Healing agent formulations

Three healing agent formulations (HA_1, HA_2 and HA_3), each consisting of polymer precursor (PE200, PE400 or PP425), a solvent (chloroform) and a thiol-based cross-linker (pentaerythritol tetrakis(3-mercaptopropionate)) were prepared. A stoichiometric molar ratio of 1:1 of thiol to acrylate was used to prepare all formulations. The amount of solvent used was 0.5 ml per gram of polymer precursor.

2.3.1. Rheological properties

The viscosity of the formulations was determined using a rheometer type Physica MCR 310 (Anton Paar, Belgium). The gap width between the lower fixed plate and the rotating spindle was set to 0.4 mm. The shear rate of the spindle was increased from 1 to 3000 s^{-1}. The temperature during the measurements was 20 °C and for each mixture the measurements were performed in triplicate.

2.3.2. Hydrogel fabrication and characterization

Cross-linked hydrogels were obtained upon increasing the pH of the healing agent mixtures using a sodium hydroxide solution (NaOH, 0.5 M).

The straightforward tube inversion method was used to determine the gel transition time. Briefly, 20 μl of the NaOH solution was added to 500 μl of the healing agent mixture thereby creating a pH of approximately 9. The tube was then inverted at regular intervals and the gelation time was determined as the point at which no flow under the action of gravity could be observed.

2.3.2.1. Cross-linking efficiency. The efficiency of the cross-linking reaction was determined using high-resolution magic angle spinning (HR-MAS) ^{1}H NMR spectroscopy. HR-MAS analysis of the cross-linked hydrogels was performed on a Bruker Avance II 700 spectrometer (700.13 MHz) using a HR-MAS probe tunable to ^{1}H, ^{13}C, ^{119}Sn and equipped with a gradient coil. The spinning rate was adjusted to 6 kHz. Samples were prepared by placing a small amount of the cross-linked hydrogels inside a 4 mm zirconium oxide MAS rotor (50 μl). $CDCl_3$ was then added to the rotor, allowing the samples to swell. Homogenization of the samples was accomplished by manual stirring. A Teflon® coated cap was used to close the rotor.

2.3.2.2. Swelling capacity. Cross-linked polymers (0.5 g) were incubated in 100 ml of tap water. After 24 h, the swollen polymers were removed, gently surface dried with paper and weighed. The polymer swelling capacity (%) was calculated based on Eq. (1):

$$\text{Swelling capacity}(\%) = \frac{W_{\text{swollen}} - W_0}{W_0} \times 100, \quad (1)$$

W_0 is the weight of the dry polymer and W_{swollen} is the weight of the hydrated, cross-linked polymer. For each sample, three repeated measurements were performed.