Smart superplasticizers based on redox-responsive polymers for rheology control of cementitious materials

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Abstract

In this work, we introduce a new concept to control the rheology of cementitious materials using stimuli-responsive polymers. RAFT polymerization of methacrylic acid (MAA) and 2,2,6,6, tetramethyl-4-piperidyl methacrylate (TMPMA) was successfully employed to prepare poly(MAA-co-TMPMA) as a precursor for the preparation of poly(MAA-co-TEMPO), a redoxresponsive copolymer containing 2,2,6,6-tetramethylpiperidine-1-oxyl group. Poly(MAA-co-TEMPO) is soluble in alkaline water and undergoes a redox switch when triggered by an external voltage that oxidizes the TEMPO group to the oxoammonium cations (TEMPO⁺). This copolymer has been used as a smart superplasticizer that can induce rheology control to cement pastes in response to external electric fields, providing active stiffening control (ASC), which is hypothesized to result from adsorption of the negatively charged copolymer with the TEMPO side chains on cement particles and (partial) desorption of the zwitterionic copolymer with the TEMPO⁺ side chains. The results revealed that these new chemical admixtures could enhance the flowability of cement pastes at a low W/C ratio and sharply increase the storage modulus when applying an electric potential of 1 V. As such, the poly(MAA-co-TEMPO) acts as a smart superplasticizer that can efficiently enhance the workability of cement pastes and induce the stiffness upon applying an electric voltage. This feature could be of great interest in producing pre-cast concrete and 3D-printing technology.

Keywords: Superplasticizer, rheology, redox-responsive polymers, TEMPO, cement paste.

1. Introduction

Concrete is basically composed of three main constituents: cement, water, and aggregates [1]. However, concrete has become more complex in recent decades due to the advent of new ingredients such as filler materials and mineral and chemical admixtures to improve the quality of concrete without losing its properties [2]. The concrete casting process was improved using chemical admixtures that provided control over fresh concrete properties, such as workability and rheological properties [3]. The rheological properties of cementitious materials can be characterized by at least two parameters according to the Bingham model [4]:

$$\tau = \tau_o + \mu \dot{\gamma}$$

Where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μ is the plastic viscosity (Pa.s), and γ is the shear rate (s⁻¹). The rheological parameters that describe the flow behavior of cement

pastes according to the Bingham model are the plastic viscosity (μ) and the yield stress (τ_o). Other models, such as Modified Bingham and Casson models, have also been employed to study the flow characteristics of cement pastes in certain circumstances, where the Bingham equation cannot be obeyed [5-7]. Chemical additives could significantly influence the rheology of cementitious materials [8].

Oscillatory shear tests have been extensively used to study the viscoelastic properties of cement pastes [9]. This technique could be employed to study the structural build-up evolution during the cement hydration process [10, 11]. Monitoring the storage modulus (G'), the elastic component of the linear viscoelastic region (LVR), can shed light on the structural build-up and elasticity of cement pastes under the ongoing hydration process [10]. The linear increase in G' is related to colloidal interaction forces such as Van der Waals, electrostatic interactions, and steric effects in the early time after mixing (a few seconds) and to the C-S-H nucleation at later periods [12-14].

Concrete superplasticizers such as polycarboxylate ethers (PCEs) are usually added to the cement pastes or fresh concrete to enhance their workability and reduce the water uptake [15-18]. However, due to the retardation effect of superplasticizers, the setting time of cement pastes or concrete could be significantly affected. This behavior could exert more pressure on the formwork after casting. In modern concrete technology such as 3D-printing where the formwork is absent, it is desirable to have a pseudo-solid-like state directly after deposition so that a fast structural build-up could be achieved, which is essential in 3D-printing as many layers are required to be printed in a short time [19, 20]. In this perspective, It is essential to develop chemical admixtures that can enhance the workability during mixing and pumping processes and accelerate structuration after casting or deposition.

In this work, we have developed a smart superplasticizer that could enhance the workability of cement paste before placement and increase the structuration after casting in response to an external electric field. As redox-responsive unit we have selected the 2,2,6,6tetramethylpiperidine-1-oxyl nitroxide radical group (further referred to as TEMPO). The TEMPO radicals are known to possess high stability and fast electron transfer kinetics, enabling a fast response triggering effect [21]. Thus, a novel concrete superplasticizer consisting of the redox-responsive nitroxide radical, TEMPO, and methacrylic acid (MAA) has been prepared using the RAFT polymerization technique. It is hypothesized that the bulky TEMPO radical acts as a steric stabilizing pendant groups, inspired by our earlier discovery that 2,2,6,6tetramethyl-4-piperidyl groups are efficient steric stabilizing groups [22], allowing synergistic effects between the steric stabilization induced by the TEMPO pendant groups and electrostatic forces induced by the COO⁻ groups and thus the desired features for a typical superplasticizer are obtained. While enhancing the cement fluidity before placement, the cement structural evolution after casting is hypothesized to occur upon applying an external electric potential that induces the oxidation of the TEMPO radical to the corresponding oxoammonium cation, TEMPO⁺, altering the physical properties of cement pastes by inducing soluble-insoluble and adsorbed-desorbed polymer transitions. In this way, it is hypothesized that we can induce active stiffening control (ASC) for the cement paste or concrete after the casting process using external stimuli [23].

2. Results and discussion

2.1. Polymer synthesis

The direct radical polymerization of TEMPO-based monomers could not be achieved as it acts

as a radical trap and inhibits the polymerization [24, 25]. For this reason, a random copolymer having MAA and 2,2,6,6-tetramethyl-4-piperidyl methacrylate (TMPMA) comonomers in a 1:1 ratio was first prepared as polymer precursor, using RAFT polymerization (Fig. 1). ¹H-NMR spectroscopy analysis showed the successful copolymerization process and the formation of near-ideal random copolymers as observed from the kinetics plots of both MAA and TMPMA during the copolymerization process (Fig. 2). The actual chemical composition was further evaluated by acid-base titration of pTMPMA and was found to be in good agreement with the theoretical composition (Table 1). The number average molar mass (M_n) determined by size exclusion chromatography (SEC) is significantly higher than the theoretical M_n of around 15 kg/mol, which can be ascribed to the use of a poly(methyl methacrylate) (PMAA) as calibration as the charged copolymer will have a significantly larger hydrodynamic size.

Table 1.

Conditions for pTMPMA synthesis and main structural details of the obtained polymers.

Entry	MAA	TMPMA	MAA	TMPMA	Conv.ª (%)	Composition (wt.%) ^b		$M_{n (SEC)}{}^{c}$	Ðď	Size ^e
	(mol.%)	(mol.%)	(wt.%)	(wt.%)		MAA	TMPMA	(kg/mol)		(nm)
1	50	50	27.6	72.4	86.5	27.9	72.1	33.4	1.17	5.73
^a Calculated based on ¹ H-NMR spectroscopy, and the average conversion of both monomers is used. ^b Determined by acid- base titration. ^c Obtained by SEC analysis using PMMA standards. ^d Measured by SEC (M _w /M _n). ^e Measured by DLS.										

The oxidation of the resulting poly(MAA-*co*-TMPMA) with H_2O_2 in the presence of Na₂WO₄.2H₂O/EDTA in methanol yielded the corresponding nitroxide polyradical, poly(MAA-*co*-TEMPO) (Fig. 1). This oxidation method is more economical and environmentally friendly than the commonly used *m*-chloroperoxybenzoic acid in an inert solvent such as CH₂Cl₂ or CHCl₃ [26]. In this work, poly(MAA₅₀-*co*-TMPMA₅₀) has been employed in which the subscripts refer to the number of repeating units of MAA and TMPMA units. The further oxidation of poly(MAA-*co*-TEMPO) to the oxoammonium cation analog, poly(MAA-*co*-TEMPO⁺), could be achieved by either chemical oxidation or electrochemical oxidation. The chemical oxidation of poly(MAA-*co*-TEMPO) was performed using NaOCl as an oxidant in water.



Fig. 1 Schematic representation for the synthesis of redox-responsive poly(MAA-co-TEMPO).



Fig. 2 ¹H-NMR spectra of purified poly(MAA-*co*-TMPMA) in D_2O (a) and first order kinetic plot for the synthesis of PCA by copolymerization of MAA and TMPMA; [MAA]:[TMPMA]:[CTA]: [AIBN] = 50:50:1:0.2, [M]= 1 M in EtOH/H₂O (80/20) at 70 °C (b).

EPR spectra were employed to calculate the radical content in poly(MAA-*co*-TEMPO) copolymer and to monitor further oxidation to poly(MAA-*co*-TEMPO⁺). Fig. 3 shows the EPR spectra of poly(MAA-*co*-TMPMA), poly(MAA-*co*-TEMPO), and poly(MAA-*co*-TEMPO⁺). As can be observed, the signal intensity for poly(MAA-*co*-TMPMA) is absent due to the absence of radical species. On the other hand, poly(MAA-*co*-TEMPO) exhibited a hyperfine split spectrum at g = 2.005, which correlates with the oxygen-centered unpaired electron of the TEMPO nitroxide radical [27]. A sharp intense signal with mass normalized EPR intensity of 14.24 was obtained, which correlates with the high radical content of poly(MAA-*co*-TEMPO). Moreover, the mass normalized EPR intensity reduced to 0.26 after the chemical oxidation of poly(MAA-

co-TEMPO) to poly(MAA-*co*-TEMPO⁺), suggesting that around 98% of the nitroxide radicals were oxidized to the corresponding oxoammonium cations.



Fig. 3 EPR spectra of poly(MAA-*co*-TMPMA), poly(MAA-*co*-TEMPO), and poly(MAA-*co*-TEMPO⁺). (X-Band) with g=2.005.

The redox behavior of poly(MAA-*co*-TEMPO) was also assessed by cyclic voltammetry (CV) in 0.1 M NaOH solution. As displayed in Fig. 4, both anodic and cathodic peaks were observed at about 0.6V and 0.39V, respectively, versus Ag/AgCl screen-printed electrode. The CV results confirm the reversible redox-switching of poly(MAA-*co*-TEMPO) to poly(MAA-*co*-TEMPO⁺).



Fig. 4 Cyclic voltammetry (CV) data of poly(MAA-*co*-TEMPO) in 0.1 M NaOH solution (10 mg/ml) at a scan rate of 50 mV/s.

2.2. Flow curves

The flow curves of cement paste in presence of the copolymers before and after oxidation were investigated to assess the suitability of these redox copolymers as smart superplasticizers for active concrete rheology control. The Bingham model was used to determine the yield stress and plastic viscosity (Fig. 5). Reference cement paste, without added polymer, showed a yield stress and plastic viscosity of about 35 Pa and 1.25 Pa.s, respectively. The addition of 0.1% and 0.3% of the negatively charged poly(MAA-co-TEMPO) by weight of cement led to a lower yield stress and plastic viscosity that depended on the polymer concentration. The cement pastes with 0.1% poly(MAA-co-TEMPO) showed yield stress of 20 Pa and plastic viscosity of 0.87 Pa.s, indicating better fluidity of the cement paste. Increasing the poly(MAAco-TEMPO) content in the cement pastes to 0.3% bwoc sharply decreased both yield stress and plastic viscosity to 6.57 Pa and 0.37 Pa.s, respectively. In contrast, the addition of the zwitterionic poly(MAA-co-TEMPO⁺) resulted in higher yield stress and plastic viscosity than poly(MAA-co-TEMPO) at a low dosage. However, when the poly(MAA-co-TEMPO⁺) dosage was 0.3% bwoc, a similar yield stress value as observed for poly(MAA-co-TEMPO) was obtained, but the plastic viscosity of poly(MAA-co-TEMPO⁺) containing pastes was almost twice as those for poly(MAA-co-TEMPO). The flow curves suggest that poly(MAA-co-TEMPO) polymers could be used as potential superplasticizers, and their superplasticizing ability could be controlled by redox switching from poly(MAA-co-TEMPO) to poly(MAA-co-TEMPO⁺).



Fig. 5 Flow curves obtained by rheology of cement paste in presence of the copolymers before and after chemical oxidation (a) polymer conc.=0.1% (bwoc), and (b) polymer conc.=0.3% (bwoc) at W/C=0.35; pTEMPO = poly(MAA-*co*-TEMPO) and pTEMPO⁺=poly(MAA-*co*-TEMPO⁺).

<mark>2.3. Mini-slump tests</mark>

The fluidity of cement pastes containing pTEMPO copolymer in terms of spread diameter as a function of time is represented in Fig. S1 and Fig. 6 and compared to Glenium 27, as commercial PCE-type superplasticizer, at the same dosages. It can be seen from Fig. S1 and Fig. 6 that pTEMPO has high dispersion and workability retention with performance comparable to the Glenium 27, indicating its potential performance as concrete superplasticizer. The adsorption measurements of pTEMPO on cement particles confirmed its high adsorption capacity that could reflect the high initial dispersion behavior (Fig. S3). Moreover, the performance was compared to pMAA homopolymer at a dosage of 0.5% bwoc to assess the steric stabilization effects induced by the TEMPO pendant groups. Initial spread diameter for

pMMA homopolymer showed a spread diameter of 74 mm, compared to 103 mm for pTEMPO, which indicates that pMMA can enhance the initial dispersion to a certain extent. However, cement pastes that contain pMMA suffer a rapid loss in fluidity and the pastes become not workable after a short time. These results agree with previously reported research [28]. On the contrary, cement pastes that contain pTEMPO has a good workability retention that could be attributed to the steric stabilization effects of the TEMPO pendant groups. On the other hand, cement pastes that contain pTEMPO⁺ are not workable due to their low adsorption capacity and limited solubility (Fig. S2).



Fig. 6 Spread diameter of cement pastes containing pTEMPO or Glenium 27 over time at W/C=0.35 and a polymer concentration of 0.5% bwoc.

2.4. Dynamic light scattering (DLS) study

Next, dynamic light scattering (DLS) was used to assess the solubility of both poly(MAA-co-TEMPO) and poly(MAA-co-TEMPO⁺) in cement pore solution (Fig. 7). poly(MAA-co-TEMPO) showed a polymer size of 5 nm while poly(MAA-co-TEMPO⁺) had a size of 55 nm, indicating that poly(MAA-co-TEMPO⁺) tends to aggregate in cement pore solution, most likely due to electrostatic aggregation of the zwitterionic copolymer, confirming that the oxidation of poly(MAA-co-TEMPO) could result in different physical properties of the copolymers. This finding agrees with the results of the flow curves and mini-slump tests where cement with poly(MAA-co-TEMPO) showed a higher fluidity than cement with the less soluble poly(MAAco-TEMPO⁺).



Fig. 7 Dynamic light scattering measurements of pTEMPO; poly(MAA-co-TEMPO) and pTEMPO⁺; poly(MAA-co-TEMPO⁺) at a polymer concentration of 5 mg/ml in cement pore solution.

2.5. Zeta potential studies

Zeta potential measurements were also performed for cement suspensions with different concentrations of poly(MAA-*co*-TEMPO) and poly(MAA-*co*-TEMPO⁺) to assess the stability of the cement suspensions containing these polymers and the effect of TEMPO oxidation on the charge characteristics. Cement particles usually show a very low zeta potential (i.e., close to zero mV) as they tend to instantly agglomerate due to their electrostatic potentials [29]. Fig. 8 shows that the addition of poly(MAA-*co*-TEMPO) increases the absolute zeta potential value of cement suspensions between -18 mV and -23 mV depending on the concentration of poly(MAA-*co*-TEMPO). On the other hand, the addition of poly(MAA-*co*-TEMPO⁺) also increases the negative zeta potential in the range of -10 mV to -22 mV. As the zeta potential is a measure of the overall charge distribution in the system and does not necessarily indicate the extent of adsorption or desorption of a particular component, cement suspensions containing pTEMPO⁺ may be forming aggregates or complexes with other negatively charged components in the system, such as ions or cement particles. Thus, resulting in high zeta potential values.



Fig. 8 Zeta potential measurements of cement particles in the presence of poly(MAA-*co*-TEMPO) copolymers at different polymer concentrations (% bwoc) at W/C=50; the average of five measurements was represented; pTEMPO = poly(MAA-*co*-TEMPO) and pTEMPO⁺=poly(MAA-*co*-TEMPO⁺).

2.6. Effect on cement hydration

The addition of poly(MAA-*co*-TEMPO) to cement paste induced a slight retardation effect on the cement hydration (Fig. 9), while poly(MAA-*co*-TEMPO⁺) showed a slightly lower retardation effect than poly(MAA-*co*-TEMPO) on the cement hydration process. Nonetheless, these retardation effects are both minor and are not expected to strongly influence the cement hydration process.



Fig. 9 Time-dependent heat flow (a) and total heat (b) liberated by cement pastes (W/C = 0.4) at a temperature of 20 °C in the presence of 0.1% bwoc of pTEMPO; poly(MAA-*co*-TEMPO) and pTEMPO⁺; poly(MAA-*co*-TEMPO⁺) copolymers and compared to reference cement paste, as

determined by isothermal calorimetry.

2.7. Redox switchability behavior

The time-dependent rheological behavior was investigated to study the structural evolution of cement pastes containing poly(MAA-*co*-TEMPO) when triggered by an external electric field of 1V, using the setup that is schematically shown in Fig. 10.



Fig. 10 Experimental setup for the small-amplitude oscillatory shear (SAOS) test for cement pastes under the effect of an external electric field of 1 V.

Fig. 11 displays the storage modulus (G') curves related to the purely elastic response of the viscoelastic cement pastes. The G' value of reference cement paste, without added polymer, increased gradually over time and showed similar values and similar time evolution under 0 V and 1 V triggers. This indicates that a low potential value (1 V) does not significantly influence the cement paste structure evolution. The addition of poly(MAA-co-TEMPO) (1% bwoc), resulted in lower G' values in the first 150 s, indicating superplasticizing behavior, after which a pronounced increase in the G' was observed, leading to G' values that were higher than those for blank cement paste. On the other hand, cement pastes containing poly(MAA-co-TEMPO) in the presence of a 1V stimulus behaved similarly at the start of the test. However, after 50 seconds, a sharp increase in the G' was observed, which can be attributed to the cement paste rearrangements, i.e., desorption and/or aggregation of the formed poly(MAA-co-TEMPO⁺) in response to the applied electric potential. The G' sharply increased after about 6 min, and the G' reached about 50 MPa in 15 min compared to 20 MPa for cement pastes containing poly(MAA-co-TEMPO) without applied voltage and 10 MPa for blank cement pastes. This large observed effect of the application of the 1V electrical stimulus confirms that the redox responsive superplasticizers can be used to induce active stiffening control (ASC).



Fig. 11 Storage modulus of cement pastes containing 1% pTEMPO; poly(MAA-*co*-TEMPO) (bwoc) before and after applying an electric potential of 1 V as compared to blank cement paste at W/C = 0.35. percent standard deviation of three measurements lies between 10.5% and 16%.

Fig. 12 displays the proposed adsorption mechanism of poly(MAA-*co*-TEMPO) and poly(MAA*co*-TEMPO⁺) on cement surfaces. In **Fig. 12a**, the poly(MAA-*co*-TEMPO) polymer chains are extended and could be easily adsorbed to the cement particles via electrostatic attractions due to the presence of the COO⁻ groups. The steric hindrance effects of the bulky TEMPO pendant groups are hypothesized to stabilize and disperse the cement particles. On the other hand, the oxidation of the nitroxide containing polymer leads to the formation of poly(MAA*co*-TEMPO⁺) copolymers with both negative and positive charges on the polymer chain. These polymers have both anionic and cationic groups that could interact with each other through electrostatic attraction forces inducing polymer dehydration and aggregation [30] that lead to high structural buildup due to the fast dispersion loss of cement pastes (Fig. 12b).



Fig. 12 Schematic representation of the mode of action for (a) poly(MAA-*co*-TEMPO) shows an extended polymer chain adsorbed into cement particles, and (b) poly(MAA-*co*-TEMPO⁺) forms coils due to the intramolecular interactions between the positive and negative charges in the polymer chains causing dehydration and aggregation that may also result in the desorption of the copolymers and lead to fluidity loss. (For reasons of clarity, cement particles and polymers are not drawn at the same scale).

3. Conclusions

For the first time, the concept of smart superplasticizers that could be triggered by an external electrical stimulus has been demonstrated. A redox-responsive polymer, poly(MAA-*co*-TEMPO), has been prepared successfully by the RAFT polymerization process of MAA and TMPMA, followed by oxidation. Based on rheological measurements, the prepared copolymer showed high dispersion capacity for cement paste. In the presence of an external electric voltage of 1 V, poly(MAA-*co*-TEMPO) could be oxidized to poly(MAA-*co*-TEMPO⁺), enabling fast redox-response features that altered the physical and chemical properties of the polymer and the properties of the corresponding cement paste. The storage modulus revealed that a very high and fast structural build-up could be obtained in response to the applied electric field, allowing a swift transition from liquid-like behavior to solid-like behavior (stiffness). This confirms that the double stimuli-responsive effect of the prepared copolymer before and after applying an external electric field, providing the first example of a switchable superplasticizer for active rheology control. This redox copolymer could be of high potential for applications that require high fluidity (e.g., during mixing and pumping) and early stiffness (e.g., precast concrete and 3D printing).

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