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Synthesis and Performance of Polycarboxylate Superplasticizer Based on a Novel Redox System of Manganese Dioxide/Acid

Siyong CHENG [1], Xintang WANG [2], Si WU [3], Luyan WANG [4] *

[1] *Zibo Transportation Construction Development Center, Zibo 255020, China*
[2] *Shandong Hi-Speed Infrastructure Construction Co., Ltd., Jinan 250014, China*
[3] *Shandong Hi-Speed Engineering Test Co., Ltd., Jinan 250003, China*
[4] *School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China*

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This study aims to develop a novel redox system based on manganese dioxide (MnO_2)/acid for synthesizing polycarboxylate superplasticizers (MPCE) via solution copolymerization of acrylic acid (AA) and methallyl polyoxyethylene ethers (TPEG). The performance of MPCE synthesized using MnO_2 combined with different acids (citric acid, tartaric acid, oxalic acid) was compared with two conventional redox systems: ascorbic acid (VC)/H_2O_2 and ammonium persulfate. The MnO_2/citric acid system proved most effective, attributed to its one-step reaction to generate primary free radicals. Optimal reaction conditions were determined as a molar ratio of AA to TPEG (Mn=2400) of 3.5:1.0 and [MnO_2]:[citric acid] of 1:1. The longer side chains of MPCE enhanced adsorption on cement particles and dispersing performance via steric hindrance. Cement paste containing MPCE-2400 showed superior dispersing ability, retention capacity, clay resistance, and hardened mechanical properties. The findings highlight the critical role of the MnO_2/acid redox system in optimizing MPCE synthesis.

Keywords: manganese dioxide, acid, cement, dispersion, superplasticizer.

1. INTRODUCTION

Polycarboxylate superplasticizer (PCE) is an essential chemical admixture extensively employed in a wide range of cement and concrete applications, such as high-rise buildings and bridges [1]. It significantly improves the workability of cement at a constant water-to-cement (W/C) ratio or reduces the required water content and W/C ratio, thereby enhancing the strength and durability of cement while maintaining optimal workability [2 – 4]. Superplasticizers enhance workability by adsorbing onto cement particles and improving their dispersion, thereby reducing particle aggregation and promoting a more homogeneous mixture [5, 6]. PCE is a comb-type polymer synthesized from monomers containing carboxyl groups and other functional groups [7]. This polymer structure includes one or two anionic anchor groups and non-anionic, non-adsorbing side chains, typically composed of polyethylene oxide units [8]. The anionic groups facilitate the adsorption of PCE molecules onto the surface of cement hydrates [9, 10], while the side chains extend into the liquid phase, creating significant steric hindrance on the surface of cement particles [11 – 13]. Consequently, PCE enhances the dispersion of cement paste by interacting with cement particles, preventing the formation of flocculating structures, releasing entrapped water, and promoting uniform particle distribution [14 – 17].

Currently, PCE is predominantly synthesized through initiator-mediated polymerization of active monomers. This method leverages initiator-driven radical reactions to facilitate monomer crosslinking, thereby enabling the formation of PCE with precisely tailored carboxylic ether structures. The choice of initiator critically governs the polymerization kinetics, which in turn affects the molecular weight distribution and functional group density of the final product. Commonly used initiators include peroxides such as ammonium persulfate [18, 19], which facilitate the synthesis of PCE under heated conditions. Lin et al. [20] synthesized polycarboxylate superplasticizers using ammonium persulfate as the initiator at 50 °C. In contrast, Guan et al. [21] prepared ISC-PCE by dropwise addition of an aqueous solution containing acrylic acid, ammonium persulfate, and thioglycolic acid into an ISC aqueous solution over 5 hours at 70 °C, indicating that ammonium persulfate can successfully synthesize PCE under heating conditions. Besides, Star-like polycarboxylate superplasticizer (SPCE) was synthesized by Lai et al. [22] using a triethylamine-based initiator under 65°C and demonstrated superior dispersibility and enhanced colloidal interaction with cement particles. 2,2 '-Azoisobutyronitrile (AIBN) was also used as an initiator by Yu et al. [23] to synthesize a kind of block type PCE under 70 °C.

However, the high reaction temperature not only increases energy consumption but also leads to the easy volatilization of small monomers, such as acrylic acid, at elevated temperatures. This results in a strong odor and potential environmental pollution. To meet sustainable development goals, low-temperature synthesis of PCEs has become an industry focus due to its energy efficiency and operational simplicity. The H_2O_2-based redox systems have been identified as efficient initiators for triggering polymerization under low-temperature conditions [24 – 26].

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* Corresponding author: L. Wang
E-mail address: *chm_wangly@ujn.edu.cn*

Xiang et al. [24] reported the preparation of PCE at room temperature in the complex initiation system of H_2O_2, ascorbic acid (Vc) and ammonium persulfate. A series of PCEs were synthesized by Feng et al. [25] via copolymerization using a novel macromonomer, ethylene-glycol monovinyl pyolyethylene glycol (EPEG) through rapid reaction (20 – 30 min) at low temperature (5 – 20 ℃) with H_2O_2/2-mercaptoethanol initiator system. Dang et al. [26] synthesized a slow-release polycarboxylate superplasticizer using H_2O_2 as the initiator at room temperature.

Nevertheless, hydrogen peroxide, as a liquid oxidant, is difficult to transport and store in industry. Moreover, the elevated cost of ascorbic acid or 2-mercaptoethanol will lead to an increase in both the production expenses and practical application costs of PCE. Besides, cerium (Ce^{4+}) salts (mainly nitrate or sulfate) can also be combined with many organic compounds (such as alcohols, aldehydes, ketones, amines, or mercaptans, etc.) to form a redox system [27]. However, the high price of Ce^{4+} salt makes it difficult for this technology to be used in industrial production. Therefore, it is necessary to explore new initiator systems to meet the needs of energy saving, operation simplification, and product cost reduction.

In this work, manganese dioxide (MnO_2)/reductic acid were selected for the first time as the redox system to prepare polycarboxylate superplasticizers (MPCE). MnO_2/reductic acid systems (e.g., citric acid) offer low-cost, stable alternatives, with prior applications in graft polymerization [28, 29]. Methyl polyoxyethylene ethers (TPEG) and acrylic acid (AA) were chosen as monomers. The condition on preparation of MPCE was discussed and the performances of fresh and hardened cement doped with MPCE were proved to be better than the commercial product PCE1.The objective of this study is to employ an easy-to-operate redox system as an initiator, thereby providing a novel low-temperature synthetic pathway for PCE. In comparison with conventional methods, this approach not only reduces energy consumption and production costs but also holds promise for advancing the development of green and efficient water reducers.

2. EXPERIMENTAL

2.1. Material

2.1.1. Chemicals

Methyl polyoxyethylene ethers (TPEG) (Mw = 800, 1200, 2400) was obtained from Oxiranchem Inc (Liaoning, China). Acrylic acid (AA) was supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), and used without further purification. The polymer chain transfer agent mercaptoacetic acid (MPA) was obtained from Aladdin Reagent (Shanghai, China). The Na-bentonite was purchased from Fenghong Colloidal Co. Ltd. (Zhejiang Province, China). It contained 95 % montmorillonite and the major chemical components contained SiO_2, Al_2O_3, CaO, etc. Manganese dioxide (MnO_2), citric, tartaric, and oxalic acids were of reagent grade. A commercial product PCE1 (Methylallyl polyoxyethylene ether-based commercial polycarboxylate superplasticizer, dosage of 0.12 %) was from Shandong Zhuoxing Chemical Co., Ltd.

2.1.2. Cement

The cement used in the experiment was Portland cement (P.O 42.5) produced by Shandong Shanshui Cement Group Ltd. (Shandong, China). Its composition is shown in Table 1.

Table 1. Cement composition

Cement composition	Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
P.O 42.5	5.61	22.75	8.66	2.77	51.54	4.91	1.87

2.2. Preparation of MPCE

TPEG (28 g, 12 mmol) dissolved in 150 mL of deionized water and MnO_2 (0.13 g, 1.48 mmol) were placed in a reaction vessel and then stirred. Subsequently, reductic acid and AA (3 g, 0.042 mmol), along with a chain transfer agent (0.14 g, 1.52 mmol), were mixed with 25 mL of water. The resulting solution was then added simultaneously to initiate the polymerization reaction, which proceeded at 35 °C for 4 hours. After the reaction, the mixture was cooled to room temperature. The as-prepared MPCE solution was directly employed in subsequent tests without undergoing further purification.

2.3. Characterization of MPCE

2.3.1. FTIR spectra

Fourier transform infrared (FTIR) spectra were obtained using a Bruker Vertex 70 spectrometer. Potassium bromide pellets containing MPCE were prepared as samples, and the spectra were recorded at a resolution of 4 cm^{-1} in the wavenumber range of 400 – 4000 cm^{-1}.

2.3.2. Fluidity of cement paste

The fluidity of cement pastes containing MPCE samples was evaluated in accordance with the Chinese standard GB/T 8077-2000: Methods for Testing Uniformity of Concrete Admixtures. Fresh cement pastes were prepared at a water-to-cement (W/C) ratio of 0.29 and a temperature of 25 °C, incorporating MPCE at a dosage of 0.12 % (P/C) by mass relative to the cement. Fluidity was assessed using a mini slump cone with dimensions of 60 mm in height, 36 mm in top diameter, and 60 mm in bottom diameter. The average spread diameter of the pastes was measured immediately after mixing.

2.3.3. Fluidity of cement paste with clay

87 g of water, a specified amount of MPCE, 297 g of ordinary Portland cement, and 3 g of Na-bentonite were added to the container. After mixing, the fluidity was measured. By adjusting the dosage of MPCE, the initial fluidity of the cement paste can reach 260 ± 5 mm.

2.3.4. Adsorption behaviors of PCE

The adsorption of MPCE samples onto cement was quantified using the depletion method [30]. Different concentrations of MPCE samples were introduced into cement suspensions (W/C = 0.35). The liquid phase was separated by agitating the suspensions in a wobbler (VWR International) at 2400 rpm for 4 minutes, followed by centrifugation at 8500 rpm for 15 minutes. The total organic carbon content was analyzed using a Shimadzu TOC-5000A total organic carbon analyzer (Japan). By comparing the PCE concentration in the aqueous phase before and after mixing with cement, the extent of MPCE adsorption onto the cement surface was determined.

2.3.5. Zeta potential test

Zeta potential measurement of cement paste is an effective approach to investigate the dispersion mechanism [31]. An Electroacoustic Spectrometer was utilized to measure the Zeta potential of cement paste incorporating varying dosages of MPCE. Herein, the samples were prepared by mixing cement and MPCE solution for 5 minutes (W/C = 50/1; P/C = 0.35).

2.3.6. Compressive strength

The compressive strength of cement specimens cured for 3, 7, and 28 days was evaluated using a YAW-300C testing machine. Specimens were fabricated with a W/C of 0.35 and an MPCE dosage of 0.3 %.

2.3.7. Morphology of hydrated products

The morphology of hydrated cement products was examined using a scanning electron microscope (SEM, model QUANTA PEG 250, FEI Co., Ltd.), with an accelerating voltage of 10.00 kV during this measurement.

3. RESULTS AND DISCUSSION

3.1. FTIR characterization

FTIR spectra of MPCEs derived from various MnO_2/reductant acid redox systems are presented in Fig. 1. As can be observed, these infrared spectra of MPCE exhibit remarkable similarity. Specifically, the peak near 1100 cm^{-1} is attributed to the C-O-C stretching vibration of the TPEG side chain in MPCE. The symmetric stretching vibration peak of the -COO- group appears at 1440 cm^{-1}, while the C=O stretching vibration peak is observed at 1732 cm^{-1}. The characteristic diffraction peak of the -COO- group from the AA side chain in MPCE corresponds to the expected position. Additionally, the peak at 1637 cm^{-1} is assigned to the C=C stretching vibration in AA; however, no such peak is present in MPCE, indicating the absence of the C=C double bond. These findings confirm the successful synthesis of MPCE.

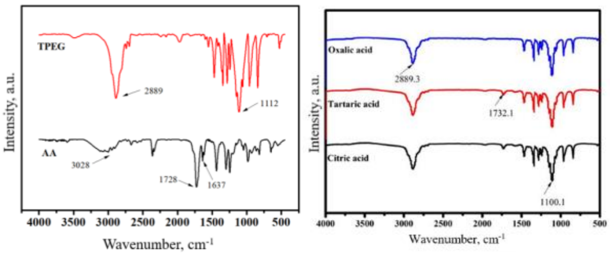

Fig. 1. FTIR spectra of monomers and MPCEs synthesized from different MnO_2/reductic acids redox systems.

3.2. Effect of reaction conditions on MPCE

In MnO_2/acid system, MnO_2 reacts with the acid to generate primary free radicals. The specific types and properties of the acid determine the formation and diversity of various free radicals [28, 29]. Based on the reaction mechanism of the initiation system composed of MnO_2 and citric acid (Eqs. 1 and 2), the interaction between MnO_2 and citric acid initially produces primary free radicals, which subsequently react with TPEG macromonomers and AA monomers, ultimately leading to the formation of PCE. In the initiation systems involving oxalic acid and tartaric acid with MnO_2, there is an additional step that consumes primary free radicals: the initially formed radicals can either initiate polymerization by reacting with monomers to produce PCE or further react with MnO_2. This consumption of radicals slows down the polymerization process, affects the generation of PCE, and reduces the chain growth rate of PCE molecules. Consequently, the theoretical yield of primary free radicals in the entire reaction system follows the order: citric acid > tartaric acid > oxalic acid. The molecular weight of MPCE produced through reactions initiated by varying numbers of primary free radicals (as shown in Eq. 1 and Eq. 2 differs, thereby influencing its dispersion performance in cement, as illustrated in Fig. 2.

$$MnO_2 + C_6H_8O_7 \xrightarrow{redox} Mn^{2+} CO_2 + R; \qquad (1)$$

$$TPEG + AA \xrightarrow{polymerization} MPCE. \qquad (2)$$

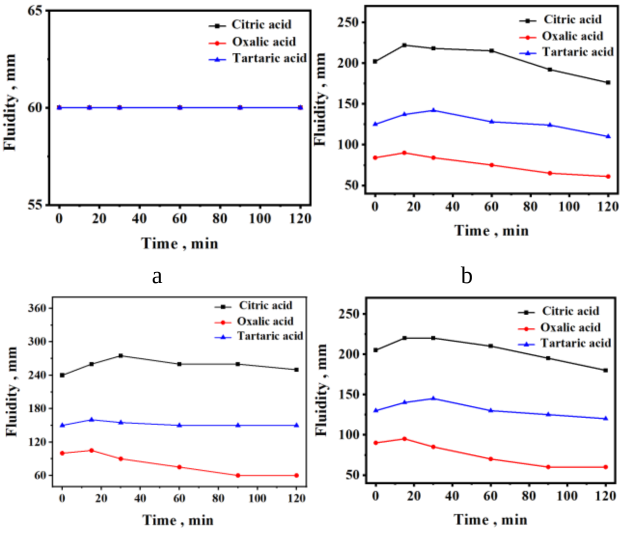
a
b
c
d

Fig. 2. Effect of MPCE from different redox systems on the fluidity of cement paste. Reaction conditions: a – $[MnO_2]$:[Acid]=1:0; b – $[MnO_2]$:[Acid]=1:0.5; c – $[MnO_2]$: [Acid]=1:1; d – $[MnO_2]$:[Acid]=1:1.5; polymerization time: 4 h; reaction temperature: 35 °C; MPCE dosage: 0.12 % by weight of cement (bwoc)

Fig. 2 illustrates the influence of acid type and dosage on the fluidity of cement paste doped with MPCEs synthesized via different redox systems. Alone, MnO_2 shows no significant effect without acid. When acid is added to form an initiation system with MnO_2 for PCE synthesis, the fluidity of cement slurry containing these PCEs improves markedly. Among tested acids, citric acid has the most pronounced effect: as its dosage increases and the $[MnO_2]$:[acid] ratio rises from 1:0.5 to 1:1, the initial fluidity of MPCE-doped cement paste increases from 200 to 240 mm. However, fluidity declines when the ratio exceeds 1:1. Similarly, increasing the dosage of tartaric acid and oxalic acid in the other two reaction systems up to a [MnO_2]:[Acid] ratio of 1:1 significantly improves the fluidity of the cement paste, while further increases in acid dosage lead to a reduction in fluidity. The fluidity of cement pastes containing MPCEs synthesized by these three MnO_2/acid redox systems follows the order: citric > tartaric > oxalic. This trend can be attributed to three primary factors: (1) the inherent properties and reactivity of the primary free radicals generated from the acids, (2) the interactions between these radicals and other components in the system, and (3) the half-life characteristics of these primary free radicals [29]. Future research should focus on a more comprehensive investigation of the reaction process to further elucidate these structure-performance relationships.

3.3. Effect of MPCE on the fluidity of cement paste

To systematically evaluate the impact of different redox systems on the fluidity of cement paste, MPCE samples were synthesized using VC/H_2O_2 and ammonium persulfate redox systems, respectively, while maintaining all other reaction conditions constant. As illustrated in Fig. 3, the dispersion performance of the as-synthesized MPCE in cement was significantly superior to that of MPCEs derived from other redox systems at a dosage of 0.12 % by weight of cement (bwoc).

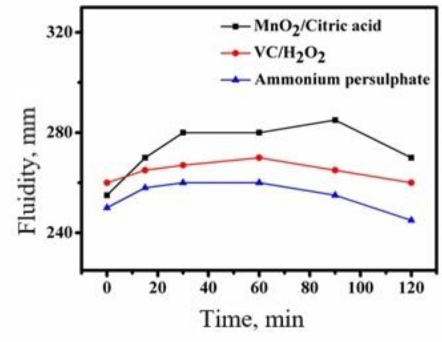

Fig. 3. Effect of MPCE prepared by different redox systems on the fluidity of cement paste

Among them, the 1 hour fluidity can reach 280 mm, while the 1 hour fluidity of the other two systems is 270 mm and 260 mm, respectively. Therefore, in the next work, the condition on preparation of MPCE synthesized by MnO_2/citric acid redox system was discussed, and the performances of MPCE in cement were assessed.

Fig. 4 illustrates the impact of MPCE samples, synthesized from macromonomers with varying molecular weights, on the fluidity of cement paste at a dosage of 0.12 %. When the acid-ether ratio is maintained constant during synthesis, a higher molecular weight of monomer TPEG leads to a longer side chain in MPCE. Consequently, this results in increased steric hindrance between cement particles upon the incorporation of MPCE into cement. As shown in Fig. 4, the variation in side chain lengths of MPCEs significantly influenced their dispersing performance. The initial fluidity improves markedly with increasing side chain length. Specifically, among the tested samples, the cement slurry containing MPCE-2400 exhibits the highest fluidity. Specifically, its fluidity reaches 280 mm within one hour and further increases to 285 mm at 90 minutes.

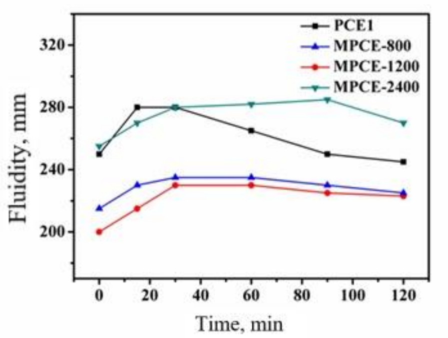

Fig. 4. Effect of different MPCEs and PCE1 on the fluidity of cement paste

In contrast, the fluidity of the slurries with MPCE-800 and MPCE-1200 are significantly lower than that of MPCE-2400. Their respective fluidities after one hour are 235 mm and 230 mm, and both begin to deteriorate slightly after 30 minutes. Additionally, comparative experiments with the commercial PCE1 reveal that the initial fluidity of the cement paste incorporating the synthesized MPCE-2400 is comparable to that of PCE1. However, MPCE-2400 demonstrates superior flow retention, maintaining a fluidity range of 280 – 285 mm between 30 and 90 minutes. In contrast, the fluidity of the cement paste mixed with PCE1 peaks at 280 mm within 15 minutes but subsequently decreases significantly. These results further highlight the outstanding performance of the synthesized MPCE-2400 in cement applications.

3.4. Fluidity of cement paste with clay

Herein, the dosages of different MPCE samples required to achieve a spread flow of 260 ± 5 mm for cement paste containing clay were compared. As shown in Fig. 5, the side chain lengths of MPCEs significantly influenced their dispersing performance in the presence of clay.

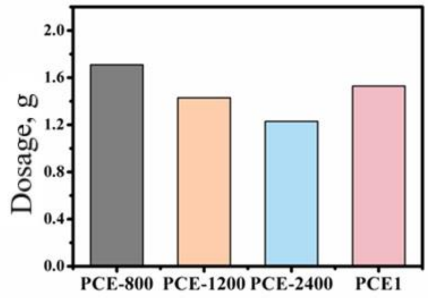

Fig. 5. Effect of different MPCEs and PCE1 on the dispersion of cement in the presence of clay

Specifically, the dosage of MPCE-2400 polymer was notably lower than that of MPCE-800 and MPCE-1200 in cement paste with clay. This indicates that the longer side chains of MPCE-2400, derived from the larger macromonomer TPEG, enhance the clay-resistance of PCE. This is because, in the presence of clay, PCE can be consumed through surface adsorption and intercalation adsorption. With longer side chains, PCE is less susceptible to intercalation adsorption on clay, thereby reducing its consumption. Compared with MPCE-800 and MPCE-1200, a smaller amount of MPCE-2400 is needed to acquire the same fluidity of cement. In addition, the data suggests that MPCE-2400 performs better in cement containing clay than the commercially available PCE1 superplasticizer.

3.5. Adsorption behavior

The adsorption behavior of PCEs on cement is one of the most effective methods to investigate the interaction between PCEs and cement particles. PCEs molecules can be adsorbed and fixed to the surface of the positively charged regions of cement particles through the electrostatic attraction of carboxyl groups, destroying the flocculation structure on the surface. Moreover, they extend from the main chain to the solution through the polyoxy side chains, forming a solvated water film with water molecules, which plays a steric hindrance role in the dispersion of particles, releasing more free water and promoting the dispersion of cement particles [18].As illustrated in Fig. 6, the PCE sample exhibited a clear Langmuir-type isothermal adsorption behavior on the cement surface, with the adsorption capacity decreasing as the side chain length increased.

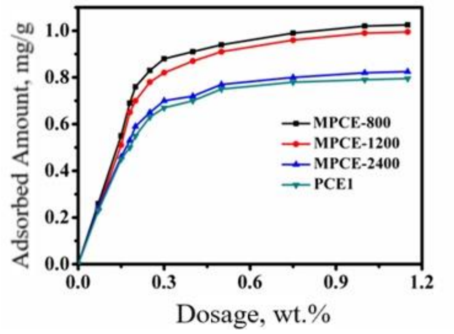

Fig. 6. Adsorption behavior of MPCEs and PCE1 on the cement surface

This trend can be attributed to the fact that longer side chains tend to extend more, thereby increasing spatial repulsion among polymer molecules and particles. Consequently, the adsorption of PCE molecules on cement particles decreases as the side chain length increases. Additionally, all three MPCEs demonstrated higher adsorption saturation and adsorption amounts compared to the commercial product PCE1.

3.6. Zeta potential

The zeta potential of cement pastes is influenced by the adsorption behavior of PCE on cement particles, and therefore, changes in zeta potential can serve as an indicator for investigating the interaction between PCE and cement. As illustrated in Fig. 7, the presence of aluminum-containing mineral phases causes the zeta potential of the blank cement slurry to be positive. This is attributed to the fact that, within the blank cement slurry system, positively charged regions dominate the surface of the cement particles, thereby leading to an overall positive zeta potential for the cement particles. The addition of MPCE-2400 resulted in a significant decrease in the zeta potential of the cement suspension, shifting from + 7.6 mV to –7.7 mV as the dosage of MPCE increased.

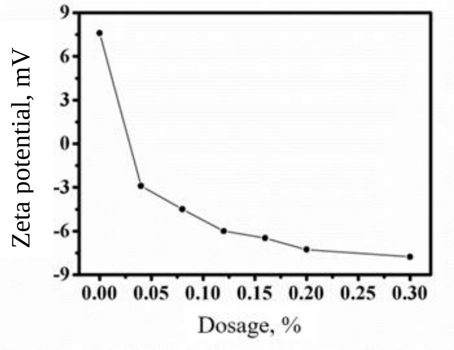

Fig. 7. Effect of MPCE-2400 dosage on the zeta potential of cement paste

This suggests that in the pore solution of cement slurry, MPCE molecules can be adsorbed onto the positively charged regions of cement particles via electrostatic attraction and onto the negatively charged regions through bridging with calcium ions. As a result, the Zeta potential of cement particles exhibits a significant downward trend, transitioning from a positive charge to a negative charge [18].

3.7. The action of MPCE in cement paste

MPCE, a type of polycarboxylate superplasticizer with a comb-like structure, exhibits unique adsorption behavior on cement particles. As illustrated in Fig. 8, the anionic groups on the main chain of MPCE can adsorb onto cement particles through electrostatic interactions, effectively anchoring the main chain to the particle surface.

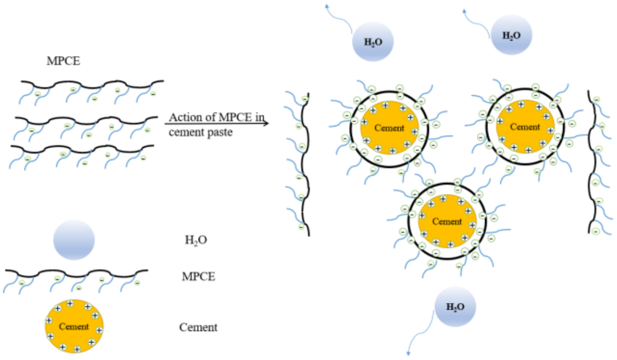

Fig. 8. Diagram for the action of MPCE in cement paste

Meanwhile, the side chains of MPCE extend into the interstitial spaces between cement particles, forming a molecular adsorption layer on their outer surfaces. Consequently, this configuration induces steric hindrance repulsion between cement particles, which serves as the primary mechanism by which MPCE achieves cement dispersion.

3.8. Compressive strength

Table 2 presents the compressive strength of hardened pastes both with and without PCE. The compressive strengths of samples containing MPCE-2400 at 3, 7, and 28 days were significantly higher than those of both the blank samples and samples containing PCE1. Therefore, this confirms that the incorporation of MPCE-2400 can effectively enhance the strength of cementitious materials.

Table 2. Compressive strengths of hardened cement with MPCE

Pastes	Compressive strength, MPa		
	3 days	7 days	28 days
Blank	40.4	51.2	67.7
MPCE-2400	47.3	76.5	83.0
PCE1	44.3	64.4	71.7

3.9. Morphology of hydrated products

Fig. 9 illustrates the morphological characteristics of cement hydration products in the absence and presence of MPCE-2400, respectively. In Fig. 9, the blank sample morphologies depicted in A-1 and A-2 feature a relatively loose structure with high porosity. In contrast, the morphologies of the sample containing MPCE-2400, as shown in B-1 and B-2, demonstrate a substantially denser microstructure with markedly reduced porosity, resulting in a more compact and cohesive hardened block. This microstructural evidence further corroborates that the incorporation of MPCE-2400 can effectively enhance the mechanical strength of cementitious materials.

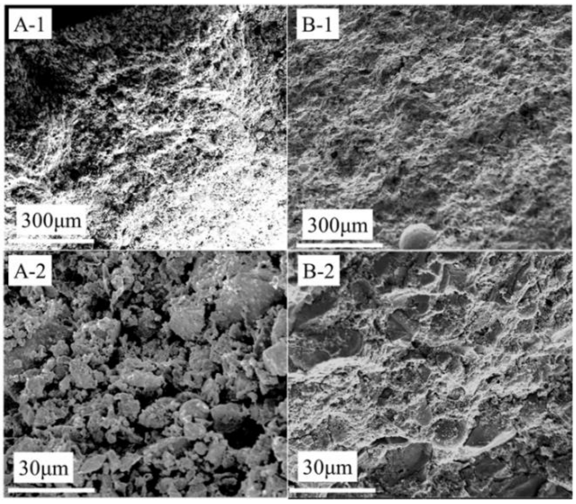

Fig. 9. SEM images of hydrated cement products for 24 h: A-1, A-2 – the blank sample; B-1, B-2 – the cement block with MPCE-2400

4. CONCLUSIONS

This study employed a novel MnO_2/acid redox system for the synthesis of polycarboxylate superplasticizers. The interactions between acid and MnO_2 significantly influence the generation of primary free radicals, which is crucial for MPCE synthesis. Among various combinations, the MnO_2/citric acid system was found to be optimal. The optimal reaction conditions were determined as follows: a molar ratio of acrylic acid/TPEG (Mn = 2400) of 3.5:1.0 and a $[MnO_2]$:[citric acid] ratio of 1:1. Increasing the molecular weight of TPEG leads to longer side chains in the synthesized MPCEs, thereby enhancing cement adsorption and dispersion performance through steric hindrance effects. MPCE-2400 exhibited superior dispersing ability, retention properties, and mechanical strength compared to other MPCEs and a commercial PCE1. Additionally, it demonstrated excellent resistance to clay contamination. This study underscores the significance of the redox system in the synthesis of high-performance PCEs and provides valuable insights into the preparation of advanced PCE materials. And future research should focus on scaling up this synthesis method for industrial applications, evaluating long-term durability in practical concrete systems, and exploring modifications with different functional monomers to further improve performance.

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