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Interaction of Polycarboxylate-Based Water-Reducing Admixture Molecular Structure with Fly Ash Substituted Cementitious Systems: Marsh-Funnel and Mini-Slump Performance

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Abstract: Polycarboxylate ether-based high-range water-reducing admixtures (PCE) play a crucial role in enhancing the workability of fly ash-substituted cementitious systems. Alterations to the chemical structures of both the main and side chains can particularly enhance the electrostatic repulsion and steric hindrance effects of PCEs. As a consequence, this results in improved performance within cementitious systems containing fly ash substitutions. This study investigated the compatibility of the altered molecular structure of polycarboxylate ether (PCE) with cementitious systems containing fly ash substitutions. To achieve this, five polymers were synthesized, varying the side chain length, molecular weight, main chain length, and main chain lengths of PCEs while maintaining other properties constant. Cement pastes were then prepared using the synthesized PCEs with fly ash replacements at three different rates. Marsh-funnel flow time and mini-slump values were measured in the prepared mixtures. The study revealed that in mixtures without fly ash, PCEs with a long main chain (40k) and short side chain length (1000 g/mole) exhibited the lowest Marsh-funnel flow and mini-slump performance among PCEs with diverse molecular structures. For the other PCEs in these mixtures, the change in molecular structure did not significantly affect their performance. However, as the fly ash replacement rate increased, PCE having a medium main chain (21k) and side chain (2400 g/mole) length outperformed other PCEs in terms of Marsh-funnel flow and mini-slump performance.

Keywords: Fly ash replacement rate, Polycarboxylate-based water-reducing admixture (PCE), change in PCE side chain length, change in PCE main and side chain length.

Introduction

Fly ash, a waste material released in production industries that use coal as fuel, is substituted in certain proportions instead of cement to enhance the long-term strength and durability of concrete mixtures (Yao et al., 2015). The spherical shape and smooth surface of fly ash generally enhance fluidity, reducing the demand for water-reducing admixtures in mixes. However, it has been emphasized that the water need of mixes increases with the use of some fly ash types in certain proportions (Toledano-Prodos et al., 2013; Mardani-Aghabaglou et al., 2014; Karakuzu et al., 2021). Additionally, substitution of fly ashes with different particle size distributions (PSD) instead of cement causes the PSD of the fly ash-cement mixture to change. This affects the need for water / water-reducing additives, causing the fluidity properties of the mixtures to change (Karakuzu et al., 2021). Since fly ash particles are negatively charged, the adsorption amount of polycarboxylate-based water reducing additive (PCE) on the fly ash surface is lower compared to cement. According to Ng and Justnes (2016), at lower substitution rates, fly ash acted as a filler and did not exert a substantial impact on the efficiency of PCE. However, it was stated that PCEs showed poor performance with replacement of fly ash above 40%. It has been reported that increasing the fly ash replacement rate in mortar mixtures up to a certain point (30% by cement weight) reduces the need for additives for target spreading (Toledano-Prodos et al., 2013; Altun et al. 2021). In fly ash substituted systems, it has been observed that the molecular structure of PCE also affects workability (Ozen et al., 2022; Altun et al., 2023). Özen et al. (2022), in their study where they investigated the impact of PCEs with varying chain lengths on the properties of fly ash substituted systems, reported that among the synthesized PCEs, the one with medium main and side chain length exhibited the best flow performance. As a result, it has been observed that the impact of fly ash on the fluidity properties of cementitious systems may vary depending on the substitution rate, fineness and morphological properties of fly ash, as well as the structural characteristics of PCEs used in fly ash substituted mixtures.

In this study, the effect of PCE chain lengths on Marsh-funnel flow time and mini-spread performance in paste mixtures with different fly ash replacement ratios was examined. In this context, five different PCEs were synthesized by changing their chain lengths. A grand total of 20 paste mixtures were meticulously concocted with synthesized PCEs and fly ash substituted cements at three different rates (15, 30 and 45%).

Material and Methods

Materials

In this study, CEMI 42.5R Portland cement, which complies with the EN 197-1 Standard, and class F fly ash, meeting the EN 450-2 Standard, were employed. Detailed information about the properties of these binders is provided in Table 1.

Table 1. The physical, chemical, and mechanical characteristics of the binders

Oxides (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Cl^-	*Free CaO*	*LOI*	Specific gravity	Specific surface (cm^2/g)
Cement	18.9	4,.3	5.5	61.7	1.6	2,8	0.04	0.75	3.33	3.21	3786
Fly Ash	59.2	22.9	6.3	3.1	1.3	0.2	0.001	-	3.2	2.31	4300

Throughout the synthesis process, a consistent free non-ionic content and an anionic/non-ionic group ratio of 2.78 moles and 3 moles per mole, respectively, were maintained for all PCEs. The primary chain lengths of the PCEs were determined based on the number of non-ionic groups they contained, while the anionic/non-ionic group ratio remained constant for each polymer. The nomenclature for each PCE was derived from their respective primary and side chain lengths. As an example, a PCE having 21 non-ionic groups, a main chain length of 21k, and a side chain length of 1000 g/mole would be denoted as MC21k-SC1000. Table 2 contains the characteristics of the synthesized PCEs.

Table 2. Some characteristics of PCEs

PCE	Density (g/cm^3)	Mw (g/mole)	PDI (Mw/Mn)	Main chain length	Side chain length (g/mole)
MC21k-SC1000	1.09	26,000	2.3	21k	1000
MC21k-SC2400	1.10	56,000	2.1	21k	2400
MC21k-SC3000	1.08	69,000	2.0	21k	3000
MC17k-SC3000	1.08	57,000	2.1	17k	3000
MC40k-SC1000	1.09	56,000	2.3	40k	1000

To assess Marsh-funnel flow times, paste mixes were formulated using a water-to-binder (W/B) ratio of 0.35. This methodology is in accordance with the protocols described in the following references: Mardani-Aghabaglou, 2016; Altun et al., 2021; Özen et al., 2022; Kobya et al., 2022; Kobya et al., 2023.a). The mixture formulated for the Marsh funnel test was also utilized for the mini-flow test, with procedures in line with the guidelines presented in references (Aïtcin, 2004; Kantro, 1980). The nomenclature for the paste mixtures was established based on both the fly ash replacement rate and the specific PCE utilized. For instance, a mixture created using the additive MC21k-SC1000 and having no fly ash replacement (0% fly ash) is designated as FA0-MC21k-SC1000.

Results and Discussion

Table 3 contains the Marsh-funnel flow times, while Table 4 displays the mini-slump values for all paste mixes. It is observed that the Marsh-funnel flow times of all mixtures increased as the fly ash replacement ratio increased. Within cementitious systems that incorporate fly ash as a substitute, various mechanisms influence workability, either positively or negatively, depending on the properties of the fly ash. Since fly ash particles are typically finer than the cement particles they replace, this results in increased surface area, potentially causing agglomeration and an elevated demand for PCE and/or water, as indicated by studies like Ozen et al. (2022), and Sha et al., (2018). These conditions tend to have an adverse impact on workability. Conversely, the spherical shape of fly ash particles can introduce a lubricating effect, leading to increased workability, as suggested by Tkaczewska et al. (2014) and Wang et al. (2021). However, this beneficial effect may be somewhat limited, possibly due to the prevailing presence of irregular fly ash particles in comparison to spherical ones. It is worth noting that the factors negatively influencing workability appeared to be predominant in all paste mixes used in the Marsh-funnel experiment. In mixtures without fly ash, the side chain length of the PCE molecule did not cause a notable change in the saturation point flow time. However, the saturation point flow time of mixtures containing MC21k-SC1000 with 15, 30, and 45% fly ash substitution was increased by 19%, 13%, and 28% in comparison to those that contain MC21k-SC2400. PCE might create a bridging effect by adsorbing to multiple fly ash particles simultaneously (Wang et al., 2021).

In the absence of fly ash, the flow time at the saturation point of the mixture containing PCE with a moderate main and side chain length (MC21k-SC2400) was 12% and 8% shorter compared to PCEs with longer main chain and shorter side chain length (MC40k-SC1000) and PCEs with shorter main chain and longer side chain length (MC17k-SC3000), respectively. In fly ash substituted mixtures, the saturation point flow times of MC21k-SC2400 decreased by 28-37% and 3-9%, respectively, in comparison to MC40k-SC1000 and MC17k-SC3000. As the fly ash substitution ratio increased, the performance degradation of MC40k-SC1000 with long main and short side chains became more significant. The worst performance of the aforementioned PCE was associated with the inability of maintaining its stretched structure (Zhang et al., 2020), weak dispersion effect due to short side chains (Kobya et al., 2023.a- 2023.b). Regardless of the PCE variety, an increment in the saturation point flow times was observed with the increment in the substitution ratio. With 15%, 30% and 45% fly ash replacement, flow times increased by an average of 31%, 63%, and 89% compared to mixtures without fly ash prepared with the same PCEs.

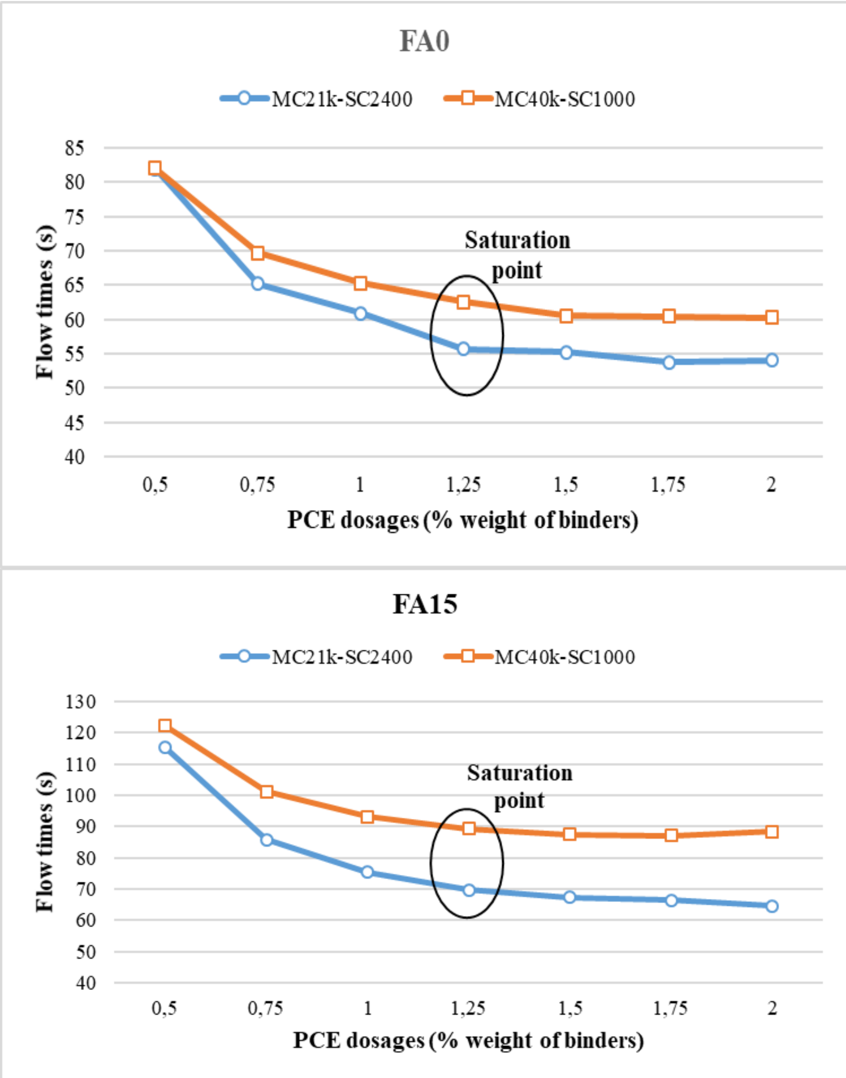
Table 3. Marsh-funnel flow times of mixes

	PCE dosage (%)						
Mixes	0.5	0.75	1	1.25	1.5	1.75	2
FA0-MC21k-SC1000	85.1	69.3	62.4	57.7[a]	55.6	54.8	55.2
FA0-MC21k-SC2400	81.9	65.2	60.9	55.7	55.2	53.7	54
FA0-MC21k-SC3000	98.4	70.4	61.2	56.7	53.5	50.8	51.1
FA0-MC17k-SC3000	102.1	74.4	64.1	59.9	57.9	57.6	57.2
FA0-MC40k-SC1000	82	69.7	65.3	62.5	60.5	60.4	60.2
FA15-MC21k-SC1000	136.5	98.4	88.1	82.9	80.3	76.7	76.6
FA15-MC21k-SC2400	115.3	85.8	75.3	69.7	67.3	66.3	64.6
FA15-MC21k-SC3000	121.9	90.1	75.3	70.9	68.6	68.5	68.1
FA15-MC17k-SC3000	148.1	100.9	83.8	74.1	73.2	72.4	72.1
FA15-MC40k-SC1000	122.3	101.2	93.2	89.3	87.4	87.1	88.3
FA30-MC21k-SC1000	171.1	120.4	105.3	98.4	95.4	93.6	92.1
FA30-MC21k-SC2400	147	105.5	92.7	87.3	84.8	82.2	81.8
FA30-MC21k-SC3000	162.8	111.7	93.7	91.9	91.6	91.8	92.4
FA30-MC17k-SC3000	172.5	119.8	103.1	90.1	88.3	85.6	84.7
FA30-MC40k-SC1000	157.2	128.8	118.1	114.3	112.7	112.1	113
FA45-MC21k-SC1000	214.8	147.6	130.8	124.1	121.9	121.3	123
FA45-MC21k-SC2400	193.8	151.2	104.7	97.2	94.3	92.8	93.1
FA45-MC21k-SC3000	188.9	124.5	107.7	99.3	93.8	91.3	91.1
FA45-MC17k-SC3000	194.7	130.4	114.7	105.5	104	104	107
FA45-MC40k-SC1000	187.6	151.2	138.9	133.2	132.9	132.1	135

a. The saturation point flow time is highlighted with the bolt.

Table 4. Mini- slump values of mixes

Mixes	0,5	0,75	1	1,25	1,5	1,75	2
FA0-MC21k-SC1000	17,3	19,3	19,2	**19,9**	20,5	21,0	20,3
FA0-MC21k-SC2400	17,6	18,9	20,2	**20,1**	20,3	20,3	19,1
FA0-MC21k-SC3000	17,1	18,5	18,6	**18,5**	18,8	19,2	18,2
FA0-MC17k-SC3000	19,0	20,0	21,5	**22,5**	22,6	22,4	22,2
FA0-MC40k-SC1000	18,0	18,8	19,0	**20,2**	20,6	19,8	19,9
FA15-MC21k-SC1000	16,1	18,0	18,7	**20,0**	20,5	21,5	21,8
FA15-MC21k-SC2400	17,8	18,2	18,5	**19,3**	19,4	19,6	19,2
FA15-MC21k-SC3000	18,8	19,5	19,6	**20,0**	21,4	21,6	21,5
FA15-MC17k-SC3000	19,2	20,8	21,0	**21,1**	21,5	21,5	22,0
FA15-MC40k-SC1000	19,9	21,9	21,0	**21,2**	21,0	21,3	21,6
FA30-MC21k-SC1000	17,3	18,0	19,1	**19,6**	20,2	21,7	21,8
FA30-MC21k-SC2400	17,6	18,0	18,2	**18,1**	18,5	18,7	18,2
FA30-MC21k-SC3000	18,4	19,0	19,2	**19,4**	20,1	20,8	21,4
FA30-MC17k-SC3000	18,5	20,9	21,5	**21,0**	21,2	21,4	21,8
FA30-MC40k-SC1000	18,8	19,7	19,2	**19,7**	20,0	20,1	19,3
FA45-MC21k-SC1000	16,3	18,1	19,0	**19,4**	19,7	19,8	20,4
FA45-MC21k-SC2400	16,9	17,6	18,2	**19,0**	18,8	19,1	18,7
FA45-MC21k-SC3000	18,5	19,6	19,5	**19,9**	20,1	20,7	21,2
FA45-MC17k-SC3000	16,6	17,1	17,6	**18,1**	19,0	19,2	18,3
FA45-MC40k-SC1000	16,0	16,7	16,8	**17,0**	17,2	17,4	16,3



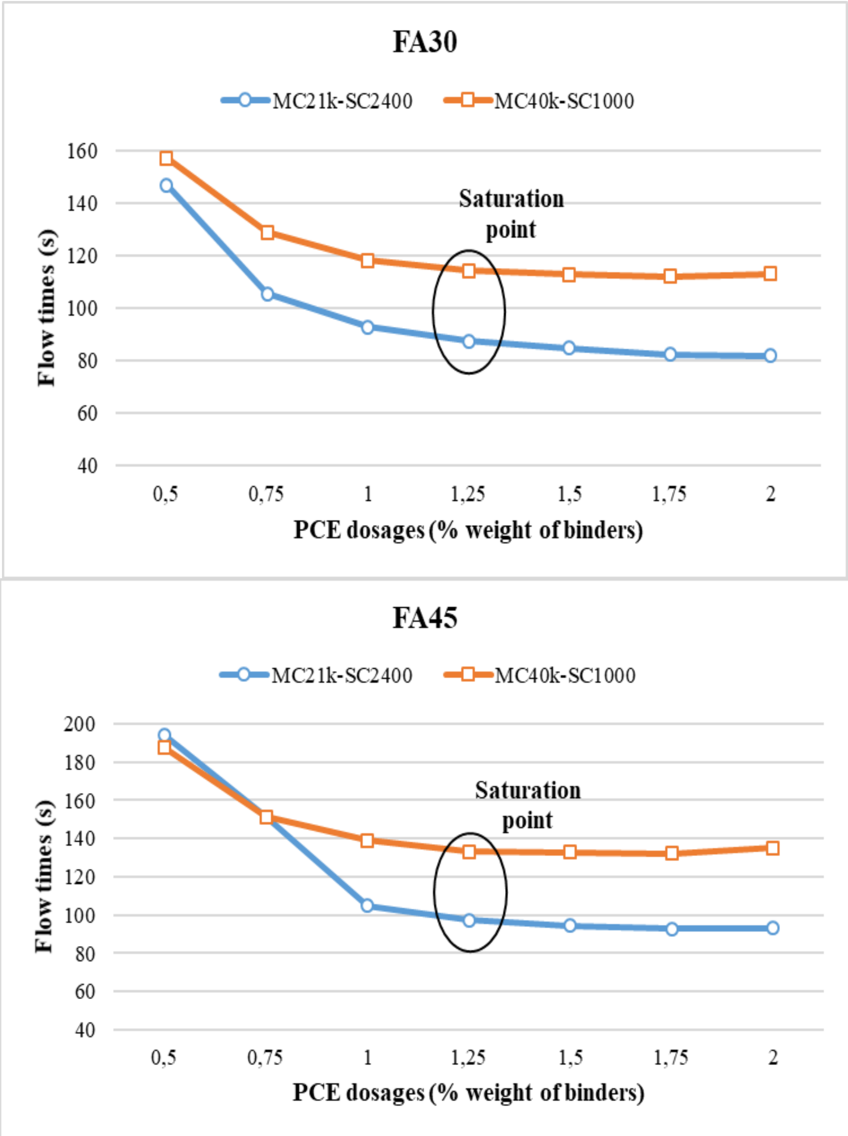


Figure 1. Marsh-funnel flow times of mixes prepared with MC21k-SC2400 and MC40k-SC1000

Figure 1 displays the graph of Marsh-funnel flow time against PCE dosage (expressed as a percentage of binder's weight) for the mixtures prepared with the MC21k-SC2400 and MC40k-SC1000. These additives represent the best and worst performing cases for each fly ash replacement rate. The flow performance at the saturation point of mixes prepared with MC21k-SC2400 exhibited a notable increase, ranging from 12% to 37%, in comparison to those prepared with MC40k-SC1000. Furthermore, this performance improvement became more pronounced as the fly ash replacement rate increased (Figure 1). When assessing the mini-slump values, it was noted that there was no substantial alteration in the mini-slump values at the saturation point, regardless of the PCE variety or the extent of fly ash replacement.

Conclusion

This study focused on assessing the compatibility between the modified molecular structure of polycarboxylate ether (PCE) and cementitious systems that incorporate fly ash substitutions. The results obtained from the experiments are summarized below:

- The Marsh-funnel flow times increased with the increment in fly ash replacement ratio.
- Mini-slump values at the saturation point remained fairly consistent across all tested mixtures, showing no significant changes irrespective of the PCE type or the extent of fly ash replacement.

- Flow performance at the saturation point was substantially improved in mixtures prepared with MC21k-SC2400 compared to those with MC40k-SC1000. This performance increase was more pronounced with higher fly ash replacement rates.

Recommendations

It is advisable to explore the compatibility of polycarboxylate ether (PCE) with cementitious systems containing fly ash substitutions by introducing variations in the molecular composition of PCE. This may include altering side chain density and adjusting the anionic/nonionic ratio. This approach allows for a comprehensive examination of how PCE interacts with different fly ash substitution scenarios.

Furthermore, it is worthwhile to investigate how PCE interacts with fly ashes of varying types and levels of fineness. This extensive investigation will contribute to a deeper understanding of the interplay between PCE and the diverse characteristics of fly ash, ultimately leading to the potential optimization of cementitious mixtures.

Scientific Ethics Declaration

The authors declare that the scientific ethical and legal responsibility of this article published in EPSTEM journal belongs to the authors.

Acknowledgements or Notes

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