Improved Air-void Quality and Rheology with Novel Amphiphilic Polycarboxylate-based Superplasticizer

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Abstract

Polycarboxylate-based superplasticizers (PCEs), invented by Nippon Shokubai Co., Ltd. over 35 years ago, have been a major innovation over other types of superplasticizers such as lignosulfonate and naphthalene sulfonate formaldehyde condensate (NSFC). PCEs are now widely utilized in the concrete industry because their molecular structure can be designed for various applications. PCEs adsorb on the cement surface resulting in significantly improved workability such as the case for self-compacting concrete. However, PCEs can also exhibit surfactant-like properties resulting in undesirable and unstable air content with poor spacing factor. In order to manage the air produced by PCEs, admixture formulators use defoamers. Air-entraining admixtures are then used to re-introduce suitable air-voids into the concrete for protection against freeze-thaw damage. This paper presents the results of an investigation on a novel Amphiphilic PCE with the capability to inherently produce stable, good quality air-voids suitable to impart freeze-thaw durability, as well as to improve the rheology of fresh concrete. The performance of the novel Amphiphilic PCE, synthesized by a highly sophisticated polymerization technology, was confirmed by air-void measurements and freeze-thaw durability testing. Furthermore, the improved rheology provided by Amphiphilic PCE allows faster placement of concrete with reduced effort. These results suggest that Amphiphilic PCE can have a novel capability compared to conventional PCEs.

1. Introduction

Polycarboxylate-based superplasticizers (PCEs), invented by Nippon Shokubai Co., Ltd.(NSCL) over 35 years ago (Figure 1, JPS5918338B2), now have been commercialized all over the world (product name: AQUALOC).

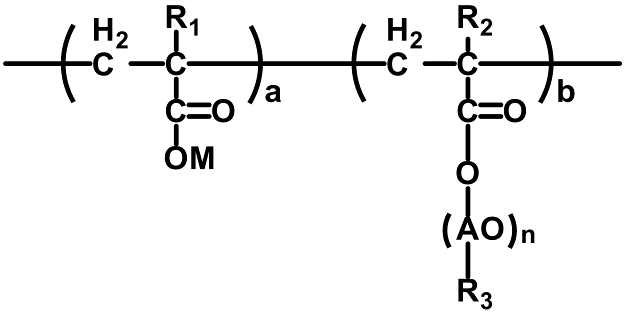

Figure 1: MPEG type PCE structure invented by NCSL, Patent JPS5918338B2

Subsequently, much effort has been made by admixture companies to introduce PCEs to the concrete industry. PCE technologies opened up novel market opportunities such as ultra-high strength concrete, self-compacting concrete, and high performance concrete with better water reduction and slump retention which cannot be realized using other water-reducing technologies such as lignosulfonate and NSFC. One of the reasons why PCEs have been a major innovation and are being used all over the world is due to their structural flexibility, whereby both the polymer chemistry and geometry can be optimized for different construction needs and applications. Also, NSCL has made a major effort develop new polyether macromonomer technologies such as IPEG, TPEG, VPEG, HPEG and APEG (Figure 2) as well as publishing patents (Table 1) to improve both manufacturing processes and polymer performance.

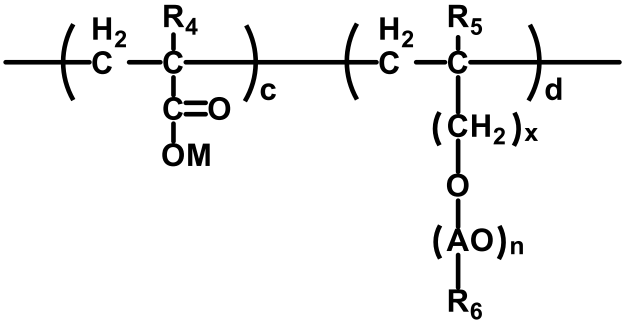

Figure 2: Structure of polycarboxylate-based ether type PCE

Table 1: Nippon Shokubai owned-PCE chemical related patents worldwide (excerpt) for the concrete industry

US PAT No.	US6727315B2,US6569234B2,US9212094B2,US7125944B2,US8058328B2, US7030282B2,US7026442B2,US9850378B2,US10208203B2,US6911494B2, US8859702B2,US8754264B2,US6825289B2,US7691921B2,US9079797B2, US8993656B2
EP PAT No.	EP1103570B1,EP1179517B1,EP1390317B1,EP2263984B1,EP1680377B1, EP1213315B1,EP1229005B1,EP2623528B1,EP2152771B1,EP1383805B1, EP1690877B1,EP2277932B1
CN PAT No.	CN1195785C,CN100494109C,CN1318344C,CN101054274B,CN100450958C, CN103119074B,CN102421722B,CN101657479B,CN100594195C, CN102027028B
KR PAT No.	KR100481059B1,KR100504997B1,KR100867212B1,KR100771024B1, KR100824576B1,KR100924665B1,KR101702692B1,KR100979768B1, KR101707243B1,KR101948679B1,KR101619869B1

However, a major hurdle that PCEs have had to overcome is surfactant-like properties, which result in undesirable and unstable air contents with poor spacing factor. The use of PCEs in air-entrained concrete with poor air quality continues to be a difficult challenge. Poor spacing factors can adversely impact concrete durability such as freezing-thawing resistance [1, 2], which requires a uniform distribution of very fine bubbles in the hardened concrete. In order to manage the air produced by PCEs, admixture formulators use defoamers [3]. Air-entraining admixtures are then used to re-introduce suitable quality air-voids into the concrete for protection against freeze-thaw damage [4]. Admixture formulators expend much effort to develop effective air-entraining admixture systems, especially because a recent increase in the use of supplementary cementitious materials (SCMs) to help lower concrete's carbon dioxide footprint. These SCMs often contain a carbon residue, which can cause adsorption of typically non-polar defoamers. This paper presents the results of an investigation on a novel Amphiphilic PCE with the capability to inherently produce stable, good quality air-voids suitable for freeze-thaw durability, as well as to improve the rheology of fresh concrete. The performance of the novel Amphiphilic PCE, synthesized by a highly sophisticated polymerization technology, was confirmed by air-void measurements and freeze-thaw durability testing. Furthermore, the improved rheology provided by Amphiphilic PCE can allow faster placement of concrete with reduced effort. These results suggest Amphiphilic PCE can introduce novel capabilities compared to conventional admixture systems.

2. Experiment

2-1. Structure of Amphiphilic PCE

Amphiphilic PCE was synthesized by modified aqueous free radical polymerization using a well-designed synthetic technology developed by NSCL (Figure 3). As for synthetic strategy of Amphiphilic PCE, different amounts of hydrophobic group replaced the dispersing group. The advantage of this structure is that having both hydrophobic and hydrophilic groups in the PCE polymer can provide good cement dispersion as well as fine bubbles in the concrete.

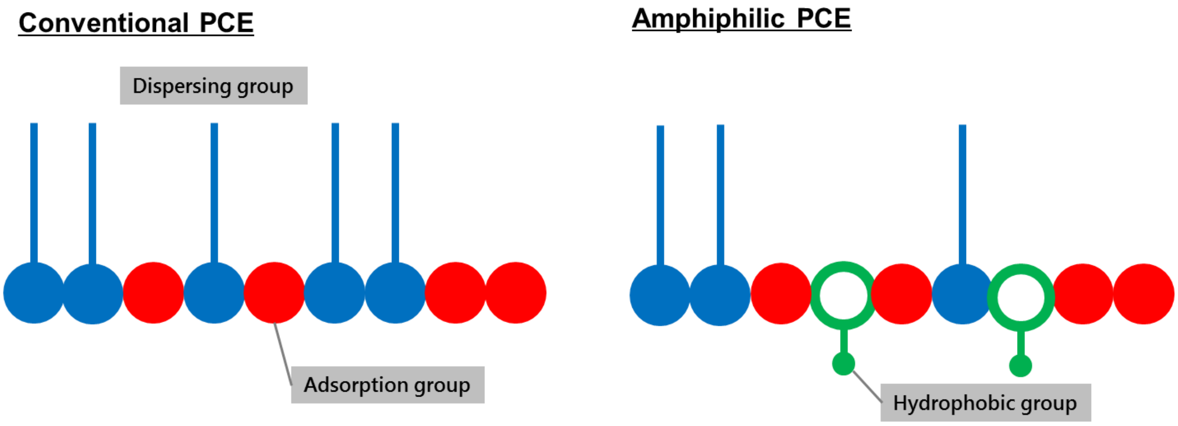

Figure 3: Structure of conventional PCE and Amphiphilic PCE

2-2. Analysis of PCE

Figure 4 shows GPC analysis of Amphiphilic PCE synthesized by both conventional and improved polymerization process. In general, conventional free-radical polymerization in aqueous phase can be difficult to introduce hydrophilic groups into PCE structure resulting in undesired high Mw by-product, which can cause phase separation as suggested at bottom of the GPC graph. However, an improved polymerization process can successfully produce a homogeneous solution (Figure. 4).

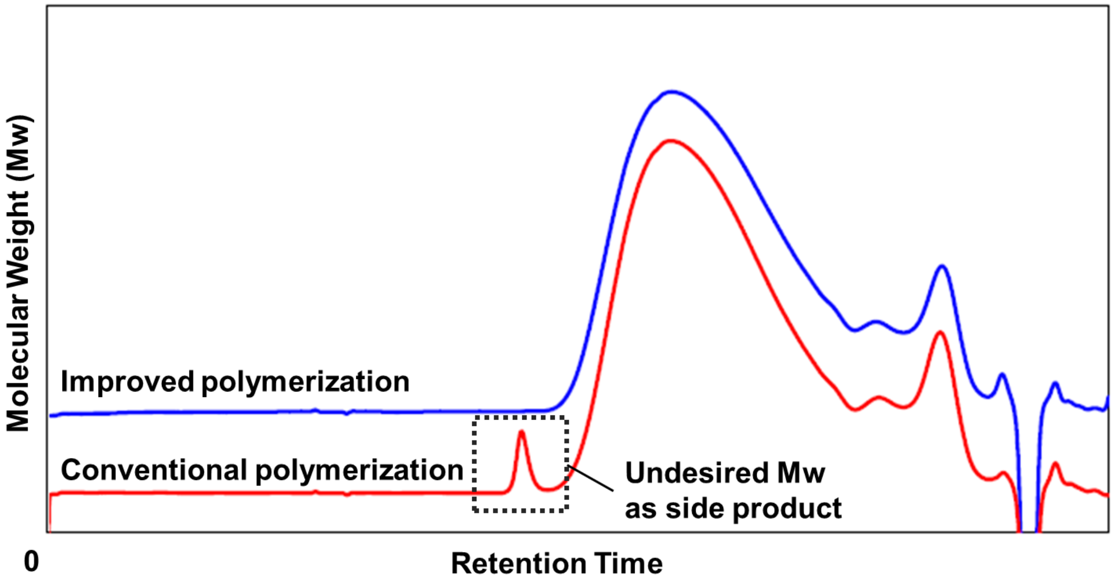

Figure 4: GPC chart of PCE polymers obtained by conventional polymerization and improved polymerization

2-3. Mortar test

Mixer type: 4.73L capacity mixer for mixing mortars as described in ASTM C305.

Volume of concrete at test: 2.2L

Mix design for mortar test is shown on the Table 2.

Table 2: Mix design for mortar test

W/C %	s/a	Water kg	Cement kg	Sand kg
40	2.5	213	535	1350

Mixing procedure: First, cement and water with superplasticizer (SP), AE agent and defoamer were added to the mixing bowl, and mixed for 30 sec at low speed. Then sand was added and mixed for 30 sec at low speed. The mortar was mixed for 30 sec at high speed and then, stopped to scrape mortar off the wall for 90 sec, following another mixing time of 1 min (according to JIS R5201).

Materials

Cement: Ordinary Portland Cement (Taiheiyo-Cement)

Fine Aggregate: Land sand, saturated surface-dry condition

2-4. J-funnel flow time

J-funnel, which has steeper angle than other funnels, was employed to prevent flow stoppage by mortar blocking. Mortar flow speed was measured according to Japanese Standard JSCE-F5411.

Apparatus: Brass material. Upper diameter 70mm, bottom diameter 14mm, height 392 mm and thickness 3mm. Total volume of J-funnel is 630ml.

2-5. Concrete test method

Mixer type: 50L capacity dual axles revolving-paddle mixer

Volume of concrete at test: 30L

Mix design for concrete test is shown on the Table 3.

Table3: Mix design for concrete test

W/C %	s/a	Water kg	Cement kg	Rock kg	Sand kg	air L
45	47	172	382	930	821	45

Mixing procedure: First, cement, fine aggregate and coarse aggregate were dry-mixed for 10 sec. Then, water with superplasticizer (SP), AE agent, defoamer were added and mixed for 1min, and stopped to scrape mortar off the wall, following another mixing for 1 min

(Materials)

Cement: Ordinary Portland Cement (Taiheiyo-Cement)

Fine Aggregate: Land sand (were used in the saturated surface-dry condition)

Coarse Aggregate: Crashed Stone (were used in the saturated surface-dry condition)

Superplasticizer (SP): polycarboxylate ether type superplasticizer

AE agent: modified alkyl carboxylic acid anionic surfactant

Defoamer: polyalkylene glycol-based nonionic surfactant

2-6. Air Void Analysis

Measurement of spacing factor (SF) in hardened concrete was conducted using ASTM C457 Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete. ASTM C 457 requires that the surface of the concrete specimen be ground and polished to obtain an acceptably smooth, plane surface for microscopical observation.

2-7. Freezing Thawing test

Freezing and thawing durability was performed using ASTM C666 Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing. Size of test specimen is 100 x 100 x 400mm. After concrete specimens were placed inside the molds, they were stored for 24 hours at 20℃. Then, the specimens were de-molded and stored again in water for 27 days at 20℃. Freezing and thawing cycles were conducted over a temperature range from 5℃ to -18℃. The time for 1 cycle of freezing and thawing was about 3 to 4 hours.

3. Results and Discussion

3-1. Dosage and Flowability

PCE dosages to obtain moderate flow without AEA are shown in Table 4. Increasing hydrophobic group content causes a slightly higher amount of PCE to get proper flowability because of a less amount of dispersing group compared to conventional PCE. Also, slightly more defoamer is required to decrease entrained air by Amphiphilic PCE due to the effect of more surfactancy caused by the increased hydrophobicity of the Amphiphilic PCE than conventional PCE.

Table 4: Dosage and flowability of non-AE concrete with both conventional PCE and Amphiphilic PCE

	Hydrophobic group	Dosage %/C			Flow	air
		PCE	Defoamer	AEA	mm	%
Coventional PCE	none	0.125	0.001	-	420	1.7
Amphiphilic PCE (a)	low	0.135	0.001	-	463	1.7
Amphiphilic PCE (b)	middle	0.150	0.002	-	450	1.8
Amphiphilic PCE (c)	middle	0.150	0.002	-	490	1.3
Amphiphilic PCE (d)	high	0.140	0.004	-	380	2.2

As for the performance of AE concrete with Amphiphilic PCEs, the defoamer dosage of Amphiphilic PCE was almost similar trend to non-AE concrete (Table 5). However, PCE dosage was relatively comparable to conventional PCE.

Table 5: Dosage and flowability of AE concrete with both conventional PCE and Amphiphilic PCE

	Hydrophobic group	Dosage %/C			Flow	air
		PCE	Defoamer	AEA	mm	%
Coventional PCE	none	0.112	0.004	0.016	425	4.5
Amphiphilic PCE (a)	low	0.110	0.001	0.012	400	5.2
Amphiphilic PCE (b)	middle	0.125	0.002	0.012	450	5.5
Amphiphilic PCE (c)	middle	0.121	0.002	0.006	450	5.2
Amphiphilic PCE (d)	high	0.123	0.003	0.013	388	5.1

3-2. Effect of the amount of hydrophobic group on spacing factor

The amount of introduced hydrophobic group had an impact on the spacing factor (SF) of hardened concrete (W/C 0.45). Under the conditions of concrete with defoamer (Figure 5, air < 2%), PCEs including low amount of hydrophobic group had similar spacing factor to conventional PCE. On the other hand, the spacing factor of concrete, admixed with PCEs having higher amount of hydrophobic group, have dramatically better SF, SF from 800 μ m to 550 μ m. Under the conditions of concrete with defoamer and AE agent (Figure 5, air 5-

6%), spacing factor of AE concrete was even better, SF from 400 to 280 μm) which showed that there was a better air void system compared to conventional PCE system. These results demonstrate that Amphiphilic PCE is able to improve the bubble size and spacing factor of the hardened concrete.

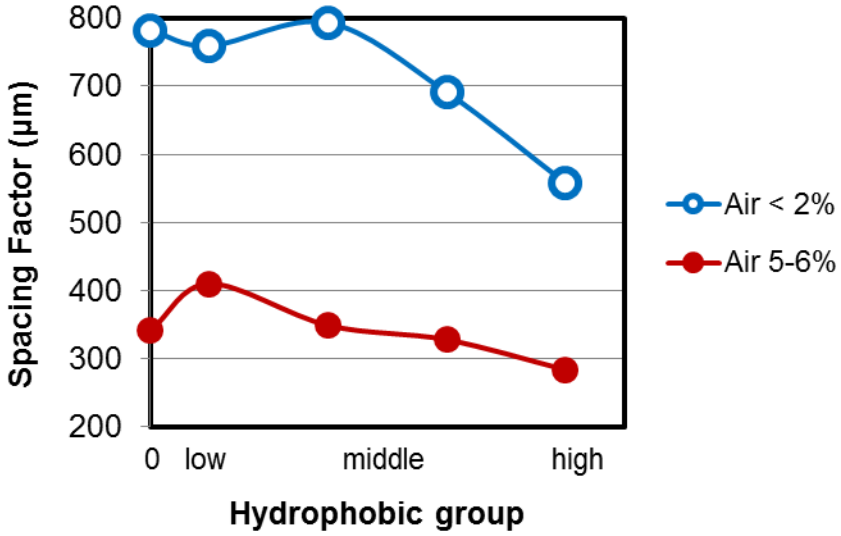

Figure 5: Spacing factor vs the amount of hydrophobic group

3-3. Freezing Thawing test

Freezing thawing test was performed using ASTM standard C666. Concrete specimens using two types of Amphiphilic PCE system were prepared in order to evaluate whether superior spacing factor of Amphiphilic PCE gave some effect on freezing thawing resistance. One is the conventional PCE system where air content with Amphiphilic PCE was decreased with defoamer, and then air was re-introduced to 5.0% by AEA. The other is the new system where air content with Amphiphilic PCE was decreased to 5.4% with only defoamer (Table 6).

Table 6: Concrete test conditions for freezing thawing resistance test.

sample	hydrophobic group	Dosage %/C			SL	FL (ave.)	air
		PCE	Defoamer	AEA	mm	mm	%
Conventional PCE	none	0.11	0.004	0.01	23	410	5.2
Amphiphilic PCE (c)	middle	0.12	0.004	0.01	23	385	5.0
Amphiphilic PCE (c)	middle	0.12	0.001	**none**	23	400	5.4

Changes in the dynamic modulus of elasticity of concrete specimens when exposed to freezing-thawing cycling in water are shown in Figure 6. The relative dynamic modulus of elasticity is the ratio of the dynamic modulus of elasticity measured at certain freeze-thaw cycles to that measured before the freeze-thaw cycling. The conventional AE system with both conventional PCE and Amphiphilic PCE (c) maintained a 100% of relative dynamic modulus of elasticity. To be surprised, it is suggested that Amphiphilic PCE (c) without AEA could meet the ASTM standard although the relative dynamic modulus of elasticity with Amphiphilic PCE (c) had slightly dropped after 200 freezing-thawing cycles.

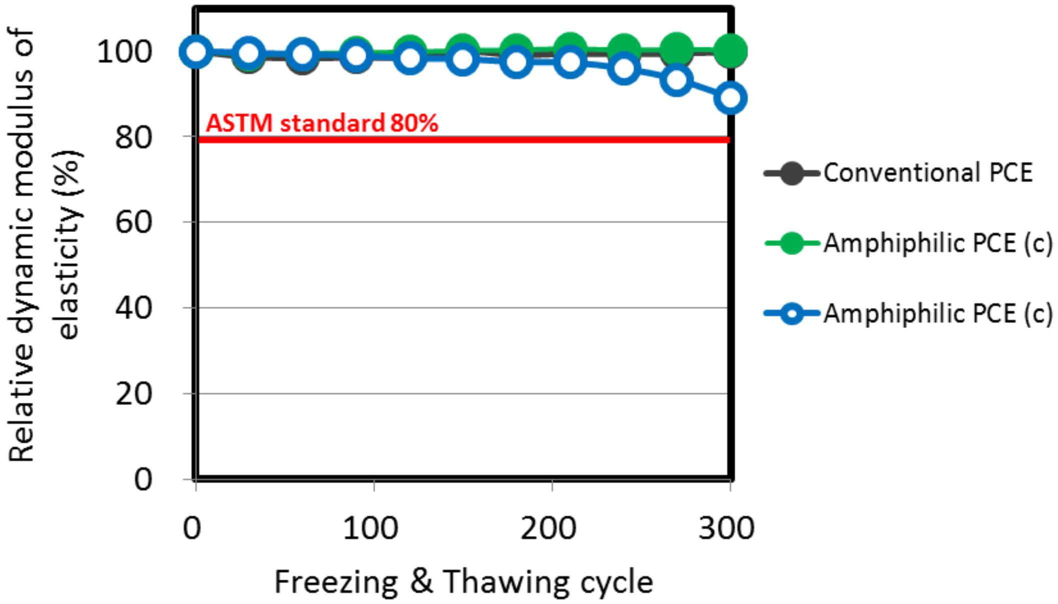

Figure 6: Relative dynamic modulus of elasticity

3-4. Rheological property

Amphiphilic PCE has also been found to improve rheological properties of concrete based on better flowability compared to conventional PCE. This finding is based on mortar J-funnel flow time and T-stop of concrete test.

3-4-1. J-funnel flow time

J-funnel flow time was measured at each condition, such as low air content to high air content (W/C 0.40, Table 7).

Table 7: Results of mortar flow test and J-funnel flow speed

Sample	PCE wt%/C	Defoamer wt%/PCE	Flow mm	air %	J-funnel time sec
Conventional PCE	0.130	0.8	187	3.2	60.0
Conventional PCE	0.125	0.6	182	4.0	53.0
Conventional PCE	0.113	0.5	181	5.3	38.4
Amphiphilic PCE (d)	0.145	1.1	182	3.1	51.2
Amphiphilic PCE (d)	0.135	0.4	178	3.8	44.8
Amphiphilic PCE (d)	0.133	0.3	183	4.0	41.9
Amphiphilic PCE (d)	0.130	0.2	178	5.1	35.2

The results indicate that Amphiphilic PCE (d) provides better flow speed at any mortar condition. At low air content, Amphiphilic PCE (d) could especially improve funnel flow speed by about 15% (Figure 7). This result means that concrete using Amphiphilic PCE has lower viscosity, which can reduce the effort to pump concrete compared to conventional PCE.

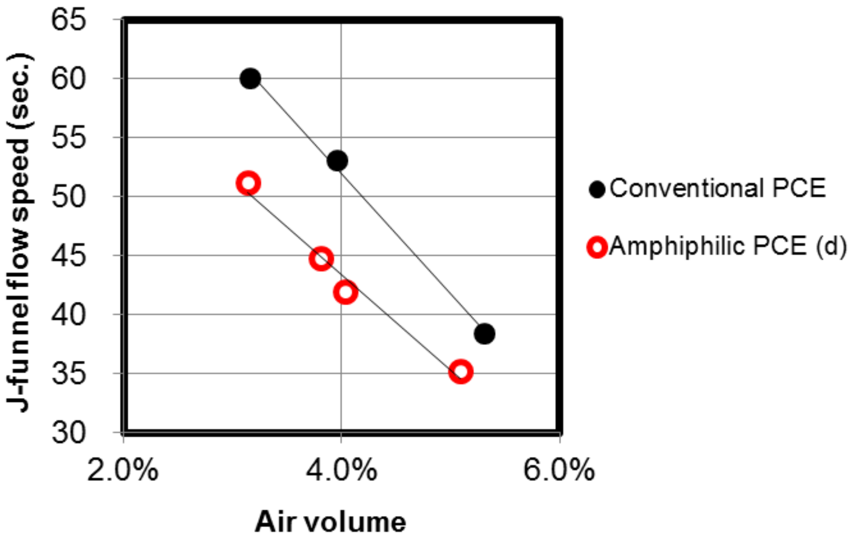

Figure 7: J-funnel flow speed measurement at several air volume contents

3-4-1. T-stop measurement

T-stop which means time from flow start to flow stop was measured at concrete condition (W/C 0.45, Table 8). Compared to conventional PCE, Amphiphilic PCE (d) showed better flowability.

Table 8: Results of concrete flow test and T-stop measurement

Sample	Dosage wt%/C		Flow	air	T-stop
	PCE	Defoamer	mm	%	sec
Conventional PCE	0.190	0.0	625	0.7	47.2
Conventional PCE	0.170	0.0	578	0.7	35.5
Conventional PCE	0.150	0.0	470	0.9	28.0
Amphiphilic PCE (d)	0.190	0.0	598	0.9	26.5
Amphiphilic PCE (d)	0.170	0.0	508	0.9	20.5
Amphiphilic PCE (d)	0.170	0.0	520	0.9	19.5

T-stop with Amphiphilic PCE (d) could be improved by about 35% (Figure 8). This means that in the case of placing fresh concrete, workers could expend less effort because the concrete not only flows faster but also comes to rest more quickly.

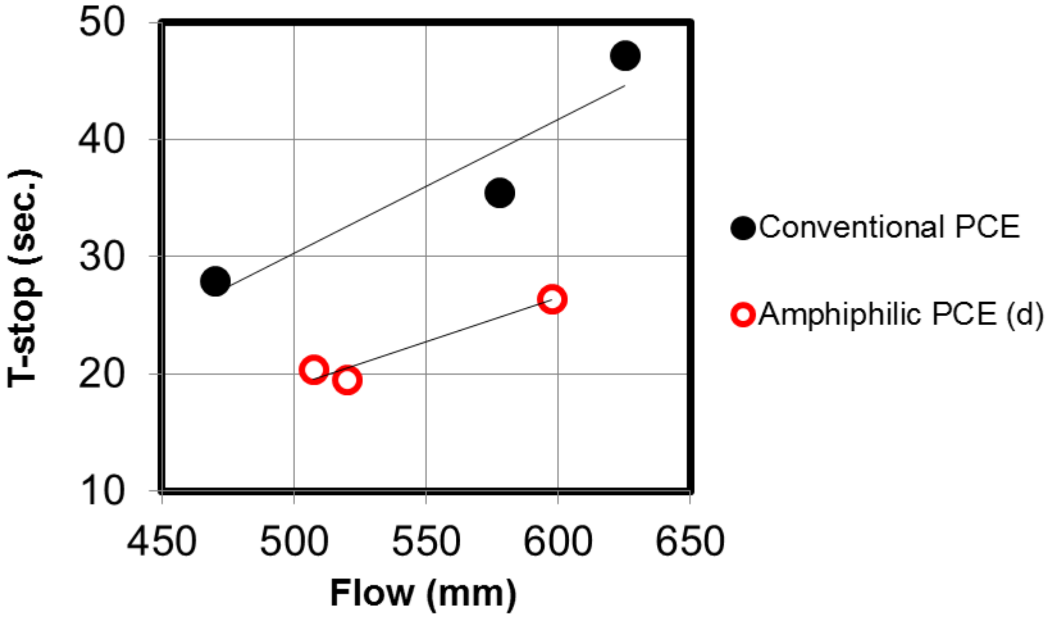

Figure 8: T-stop measurement in concrete test

4. Conclusion

Amphiphilic PCEs containing hydrophobic groups were successfully synthesized and their performance were investigated. Compared to conventional free-radical aqueous phase polymerization, hydrophobic group has been incorporated into hydrophilic PCE structure using our improved synthetic technology, resulting in certain improved properties of concrete. The use of Amphiphilic PCE in a concrete has the capability to obtain a finer air void system resulting in better freezing thawing resistance and improvement of rheological property compared to conventional PCE. A summary of the differences between Amphiphilic PCE versus conventional PCE is as follows:

- Amphiphilic PCE incorporating higher hydrophobic group dramatically improves spacing factor of hardened concrete.
- Freezing thawing durability of Amphiphilic PCE (c) without air-entraining agent meets ASTM C666 criteria, although a slight decrease occurs after 200 cycles.
- J-funnel flow speed with Amphiphilic PCE (d) is 30% faster than conventional PCE.
- T-stop measurement indicate that Amphiphilic PCE (d) has better plastic viscosity and thixotropic property.

The concrete industry has always made great effort to control the air content of concrete with defoamer and AEA not only because of conventional PCE, but also due to variable properties of concrete materials. However, the Amphiphilic PCE system could be one of the solutions to simplify the control and quality of air content in concrete. This is because of the use of only PCE and defoamer. Furthermore, Amphiphilic PCE has the potential to place concrete more easily due to better rheological properties. NSCL is will strive to improve this unique technology to serve the current and future needs of the concrete industry.

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