- Technical Paper -

IMPROVED AIR-VOID QUALITY AND RHEOLOGY WITH NOVEL AMPHIPHILIC POLYCARBOXYLATE-BASED SUPERPLASTICIZER (AMPHIPHILIC PCE)

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ABSTRACT

PCEs have been widely utilized in the concrete industry due to the flexible molecular design for various applications because PCEs adsorb on the cement surface resulting in significantly improved workability. However, PCEs can also exhibit surfactant-like properties resulting in undesirable and unstable air. This paper presents the results of an investigation on an 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.

Keywords: Relative dynamic modulus, surface tension, SF, T-stop, Rheology

1. INTRODUCTION

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

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 naphthalene sulfonate formaldehyde condensate. 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 1) [2] as well as publishing patents about manufacturing processes [3] and compositions [4].

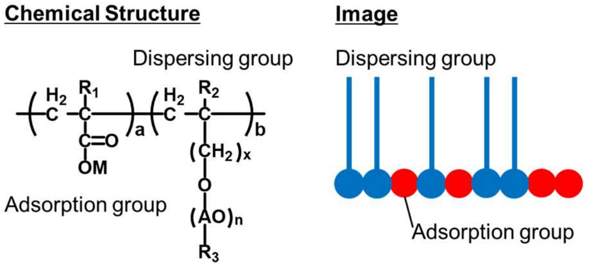

Figure 1: Structure of polycarboxylate-based ether type PCE

However, a major hurdle that PCEs have had to overcome is surfactant-like properties, which result in undesirable and unstable air contents with poor SF. The use of PCEs in air-entrained concrete with poor air quality continues to be a difficult challenge. Poor SFs can adversely impact concrete durability such as freezing-thawing resistance [5,6], 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 [7]. Air-entraining admixtures are then used to re-introduce suitable quality air-voids into the concrete for protection against freeze-thaw damage [8]. 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 [9] 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. TEST PROGRAMS

2.1 Materials

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(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 2). As for synthetic strategy of Amphiphilic PCE, different amounts of hydrophobic group replaced the dispersing group (Table 1). 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.

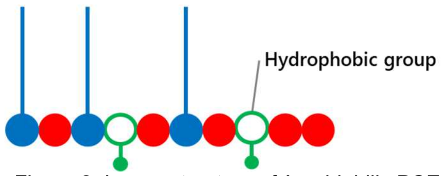

Figure 2: Image structure of Amphiphilic PCE

Table 1: The amount of hydrophobic group in Amphiphilic PCE and their notations

Sample	Hydrophobic group	notation
Coventional PCE	none	CP
Amphiphilic PCE (a)	low	AP-a
Amphiphilic PCE (b)	middle	AP-b
Amphiphilic PCE (c)	middle	AP-c
Amphiphilic PCE (d)	high	AP-d

(2) Analysis of Amphiphilic PCE

Figure 3 shows gel permeation chromatography (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 hydrophobic groups into PCE structure resulting in undesired high Mw side product, which can cause phase separation as suggested at bottom of the graph. However, an improved polymerization process for AP-d can successfully produce a homogeneous solution (Figure. 3)

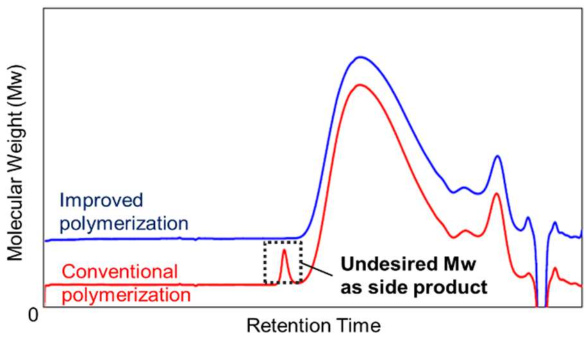

Figure 3: GPC chart of PCE polymers obtained by conventional polymerization and improved polymerization

The adsorption amounts of CP and AP-d on the surface of cement particles were measured by a total organic carbon (TOC) analyzer. 100 mL of aqueous solution with each amount of the PCEs and 100 g of cement were mixed by a magnetic stirrer for 3 hours. At each measurement time, the suspension of cement paste was rapidly centrifuged at 4000 rpm/min for 5 min. The resultant solution was filtered for TOC. The adsorption amount of PCEs on the cement surface can be calculated based on the difference between the amounts of PCEs in aqueous phase before and after mixing. AP-d had a comparable adsorption with CP. It was found that introduction of hydrophobic group did not affect adsorption behaviour even at high hydrophobic content (Figure 4).

Statistic surface tension was measured in order to check the stability of air bubble using Wilhelmy method as shown in Figure 5. Water itself had 72 mN/m. CP has 60 mN/m at 15% lower than water. Surprisingly, AP-d had 47 mN/m rather lower surface tension. These results indicate AP-d might be stronger to foam in the aqueous solution.

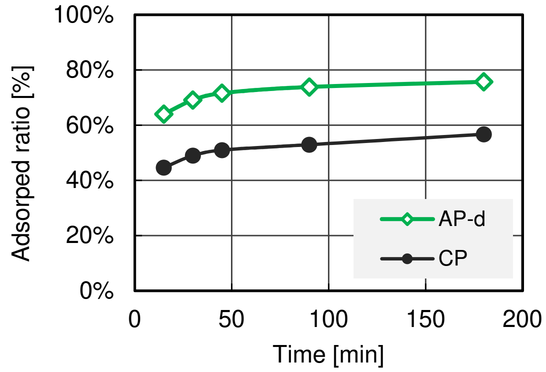

Figure 4: Adsorption test with CP and AP-d

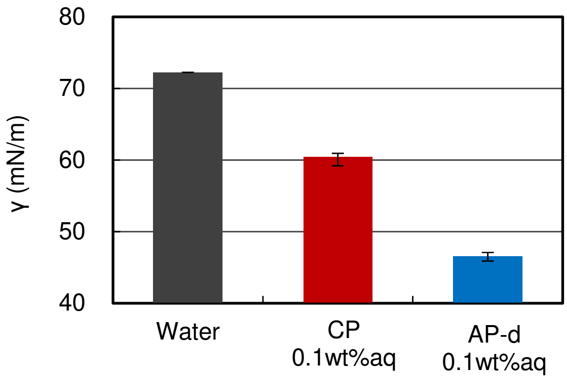

Figure 5: Measurement of surface tension with each water, CP and AP-d

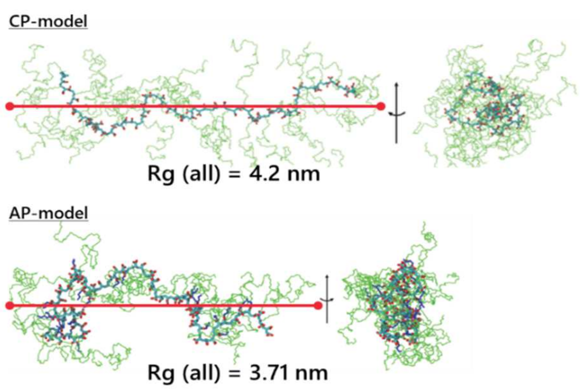

Figure 6: MD simulation of CP-model and AP-model using Gromacs package. For simulation purposes, the molar concentrations are converted to volumetric concentrations: Ca^{2+}: 6.087 × 10^{-3}/nm^3, Na^+: 5.901 × 10^{-2}/nm^3, K^+: 0.109/nm^3, SO_4^{2-}: 5.203 × 10^{-2}/nm^3, and OH^-: 7.642 × 10^{-2}/nm^3.

Molecular dynamics simulation of both CP-model and AP-model was performed in the using Gromacs package, which was shown in the previous work [10]. In this study, Hydrophobic group was replaced with acid moiety for simulation model. Importantly, molecular dynamics simulation gave a radius of two polymers in the cement pore solution environment.

CP-model had 4.2 nm radius, on the other hand AP-model had much smaller radius 3.71 nm in the cement pore solution of MD simulation (Figure 6). This result indicated AP-model is agglomerated by intramolecular hydrophobic effect.

2.2 Testing Method

(1) 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	C g	W g	FA g
40	2.5	213	59	1320

*C: Ordinary plotland cement, density 3.16g/cm^3
*Fine Aggregate (FA): Land Sand, saturated surface-dry condition, density 2.64g/cm^3
*Superplasticizer: polycarboxylate ether type superplasticizer (PCE)
*Defoamer: polyalkylene glycol-based nonionic surfactant

Mixing procedure: First, cement and water with superplasticizer (SP) 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).

(2) 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-F 541.
Apparatus: Brass material. Upper diameter 70mm, bottom diameter 14mm, height 392 mm and thickness 3mm. Total volume of J-funnel is 630ml (Figure 7).

(3) Plastic viscosity

RST Coaxial Cylinder Rheometer with four axis vanes manufactured by BROOKFIELD was used for the plastic viscosity measurement (Figure 8). The vane-cup geometry shows high resemblance to the measuring mechanism of the concentric cylinders. In principle, the vane replaces the inner cylinder and is expected to collect paste in between its blades so that a virtual cylinder of paste rotates alongside the paste volume in the gap [11].

(4) Concrete test method

30L concrete was prepared by using 50L capacity dual axles revolving-paddle mixer was used. Mix design for concrete test is shown on the Table 3.

Figure 7 J-funnel

Figure 8 Rheometer

Table 3: Mix design for concrete test

W/C %	S/C	W kg/m^3	C kg/m^3	CA kg/m^3	FA kg/m^3	Air L
45	47	172	382	930	821	45

*C: Ordinary plotland cement, density 3.16g/cm^3
*Fine Aggregate (FA): Land sand (were used in the saturated surface-dry condition), density 2.64g/cm^3
*Coarse Aggregate (CA): Crashed Stone (were used in the saturated surface-dry condition), density 2.65g/cm^3, F.M 2.90
*Superplasticizer: polycarboxylate ether type superplasticizer (PCE)
*Air Entrained Agent (AEA): modified alkyl carboxylic acid anionic surfactant
*Defoamer: polyalkylene glycol-based nonionic surfactant

(5) Air Void Analysis

Measurement of SF (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.

(6) 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 with 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 CP. Also, slightly more defoamer is required to decrease entrained air by Amphiphilic PCEs due to the effect of more surfactancy caused by the increased hydrophobicity of the Amphiphilic PCEs than CP.

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

PCE	Dosage %/C			Flow	air
	PCE	Defoamer	AEA	mm	%
CP	0.112	0.004	0.016	425	4.5
AP-a	0.110	0.001	0.012	400	5.2
AP-b	0.125	0.002	0.012	450	5.5
AP-c	0.121	0.002	0.006	450	5.2
AP-d	0.123	0.003	0.013	388	5.1

As for the performance of AE concrete with APs, the defoamer dosage of AP was almost similar trend to that of non-AE concrete (Table 5). However, PCE dosage of APs slightly increased compared to that of CP.

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

PCE	Dosage %/C			Flow	air
	PCE	Defoamer	AEA	mm	%
CP	0.125	0.001	-	420	1.7
AP-a	0.135	0.001	-	463	1.7
AP-b	0.150	0.002	-	450	1.8
AP-c	0.150	0.002	-	490	1.3
AP-d	0.140	0.004	-	380	2.2

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 9, air 1.5-2.5%), PCEs including low amount of hydrophobic group had similar SF to CP. On the other hand, the SF of concrete, admixed with PCEs having higher amount of hydrophobic group, have better SF, SF from 800μm to 550μm. Under the conditions of concrete with defoamer and AE agent (Figure 9, air 4-6%), SF of AE concrete was even better, SF from 388 to 280μm which showed that there was a better air void system compared to CP system. These results demonstrated that AP was able to improve the bubble size and SF of the hardened concrete.

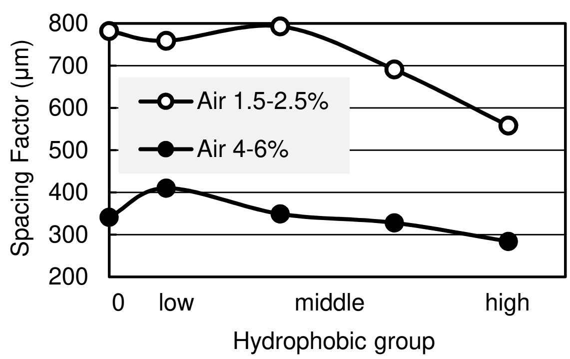

Figure 9: SF vs the amount of hydrophobic group

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 SF of Amphiphilic PCE gave some effect on freezing thawing resistance.

One is the CP system where air content with AP-d was decreased with defoamer, and then air was re-introduced to 5.2% by AEA. The other is the new system where air content with AP-d was decreased to 5.5% with only defoamer (Table 6).

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

PCE	Dosage %/C			Slump	air	SF
	PCE	Defoamer	AEA	cm	%	μm
CP	0.115	0.002	0.0041	24	4.5	271
AP-d	0.135	0.004	0.0037	24	5.2	252
AP-d	0.135	0.002	**none**	24	5.5	293

Changes in the dynamic modulus of elasticity of concrete specimens when exposed to freezing thawing cycling in water are shown in Figure 10. 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 freezing thawing cycling. The conventional AE system with both CP and AP-d maintained a 100% of relative dynamic modulus of elasticity. To be surprised, it is suggested that AP-d without AEA could meet the ASTM standard although the relative dynamic modulus of elasticity with AP-d had slightly dropped after 200 freezing thawing cycles.

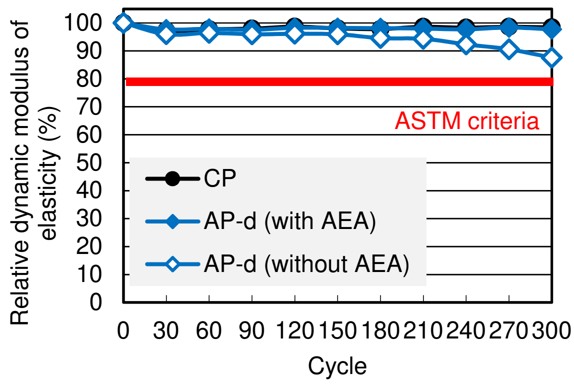

Figure 10: Relative dynamic modulus of elasticity

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 rheometer, J-funnel flow time of mortar test and T-stop of concrete test.

(1) Rheometer measurement

The steady flow properties of cement pastes refer to viscosity and yield stress by means of so-called flow curves, as seen in Figure 9. The test was performed in steps with a couple of seconds for shear rate increment. The downward branch was applied to calculate the plastic viscosity μ_p. μ_p is a function of share rate (Δx [1/s]) and share stress (Δy [Pa]) (eq. 1).

$\mu_p = \Delta y / \Delta x$ (1)

Mortar test was conducted for the rheometer measurement as shown in Table 7. Then results with two PCE were plotted in Figure 11. The first maximum point is said to be an apparent yield stress based on thixotropic material model. The apparent yield stress of AP-d was much higher than that of CP. This result might indicate that AP-d can add segregation resistance of concrete matrix. And the μ_p of AP-d (18.8 Pa*s) was much lower than the μ_p of CP (24.9 Pa*s) at same mortar conditions. This means concrete prepared by AP-d might afford a better pumpability at a casting site.

Table 7: Results of mortar flow test for rheometer measurement

PCE	Dosage wt%/C		Slump	Flow	air
	PCE	Defoamer	mm	mm	%
CP	0.128	0.051	120	204	2.7
AP-d	0.172	0.069	186	206	2.5

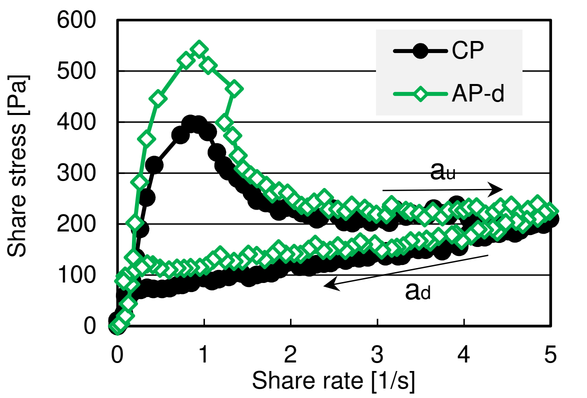

Figure 11: Shear stress versus shear rate hysteresis cycles with CP and AP-d showing the ascending a_u and descending a_d branches and a linear approximation of the descending branch to determine the Bingham parameters plastic viscosity μ_p.

(2) 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 8).

Table 8: Results of mortar flow test and J-funnel flow speed

PCE	Dosage wt%/C		Flow	air	J-funnel time
	PCE	Defoamer	mm	%	sec
CP	0.130	0.0010	187	3.2	60
	0.125	0.0008	182	4.0	53
	0.113	0.0006	181	5.3	38
AP-d	0.145	0.0016	182	3.1	51
	0.135	0.0005	178	3.8	45
	0.133	0.0004	183	4.0	42
	0.130	0.0003	178	5.1	35

The results indicate that AP-d provides better flow speed at any mortar condition. At low air content, AP-d could especially improve funnel flow speed by about 15% (Figure 12). This result means that concrete using AP-d has lower viscosity, which could reduce the effort to pump concrete compared to CP.

(4) T-stop measurement

T-stop which means time from flow start to flow stop was measured at concrete condition (W/C 0.45, Table 9). Compared to CP, AP-d showed better flow speed at same flow.

T-stop with AP-d could be improved by about 35% (Figure 13). 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.

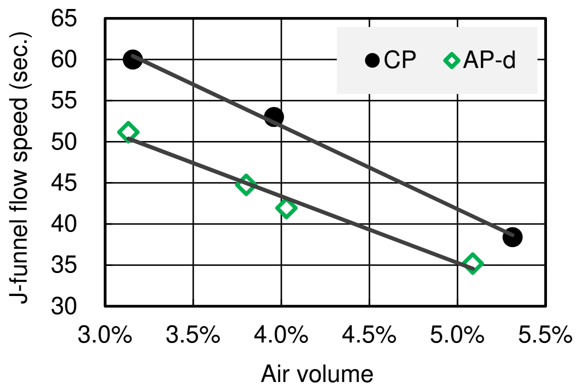

Figure 12: J-funnel flow time measurement in mortar test

Table 9: Results of concrete flow test and T-stop measurement

PCE	Dosage wt%/C		Flow	air	T-stop
	PCE	Defoamer	mm	%	sec
CP	0.190	0.004	625	0.7	47
	0.170	0.004	578	0.7	35
	0.150	0.004	470	0.9	28
AP-d	0.190	0.008	598	0.9	26
	0.170	0.008	508	0.9	20
	0.170	0.008	520	0.9	20

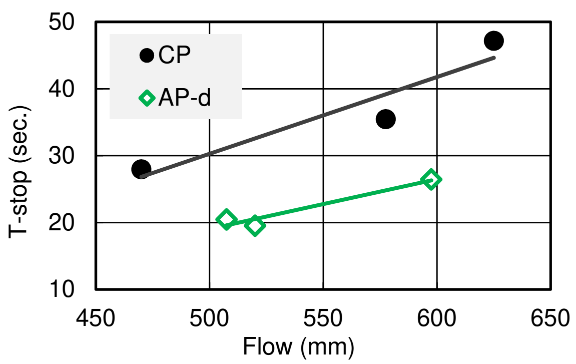

Figure 13: T-stop measurement in concrete test

4. CONCLUSIONS

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 PCEs 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:

(1) Amphiphilic PCE incorporating higher hydrophobic group dramatically improves SF of hardened concrete.
(2) Freezing thawing durability of Amphiphilic PCE without air-entraining agent meets ASTM C666 criteria, although a slight decrease occurs after 200 cycles.
(3) Rheometer analysis showed Amphiphilic PCE was able to decrease plastic viscosity and increase apparent yield stress.
(4) Both J-funnel flow time measurement at mortar test and T-stop measurement at concrete test demonstrated that Amphiphilic PCE gave better plastic viscosity to improve pumpability at placing concrete.

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 although there is a room to improve the performance of Amphiphilic PCE. 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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