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3rd International Conference on
Polycarboxylate Superplasticizers PCE 2019
25th, September 2019

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

Nippon Shokubai Co., Ltd.
Yuya Akao

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Introduction

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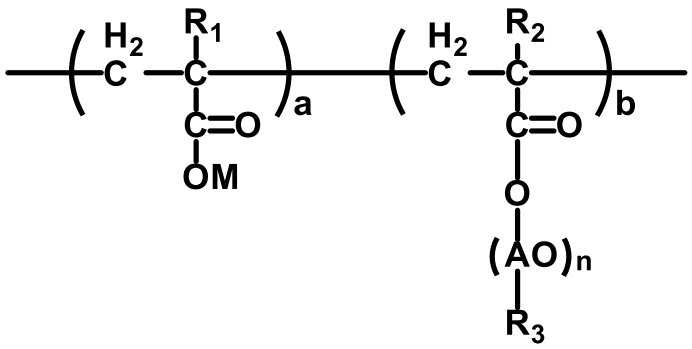
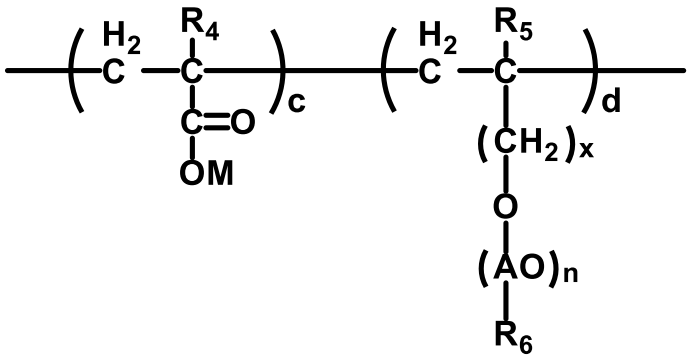
1981 The first patent application of MPEG PC-type WRA in the world

2000~ Patent application of IPEG(TPEG), HPEG, VPEG type WRA

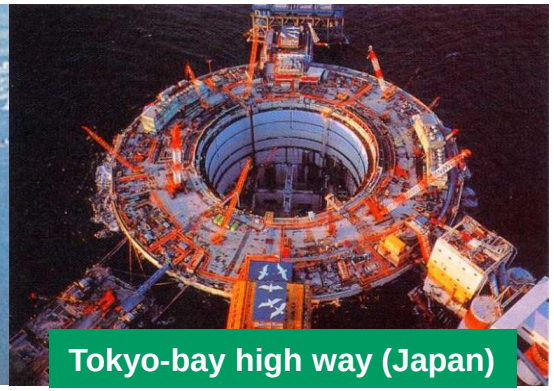


MPEG type PCE structure invented by NSCL, Patent JPS5918338B2



IPEG(TPEG), HPEG, VPEG type PCE structure invented by NSCL,

Akashi bridge pier (Japan)



Tokyo-bay high way (Japan)

Patent applications of IPEG, HPEG type PCEs

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United States Patents

US6727315B2,US6569234B2,US9212094B2,
US7125944B2,US8058328B2,US7030282B2,
US7026442B2,US9850378B2,US10208203B2,
US6911494B2,US8859702B2,US8754264B2,
US6825289B2,US7691921B2,US9079797B2,
US8993656B2

EP Patents

EP1103570B1,EP1179517B1,EP1390317B1,
EP2263984B1,EP1680377B1,EP1213315B1,
EP1229005B1,EP2623528B1,EP2152771B1,
EP1383805B1, EP1690877B1,EP2277932B1

Chinese Patents

CN1195785C,CN100494109C,CN1318344C,C
N101054274B,CN100450958C,CN103119074
B,CN102421722B,CN101657479B,CN1005941
95C,CN102027028B

Korean Patents

KR100481059B1,KR100504997B1,KR1008672
12B1,KR100771024B1,KR100824576B1,KR10
0924665B1,KR101702692B1,KR100979768B1
,KR101707243B1,KR101948679B1,KR101619
869B1

***The latest patents shall be valid until 2037**

Concept of “Amphiphilic PCE”

Concept of Amphiphilic PCE

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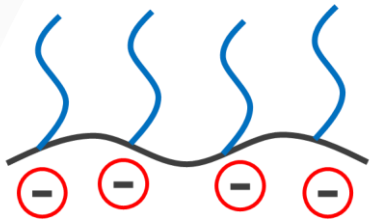
"Amphiphilic molecules" contains both hydrophilic and hydrophobic components.

Conventional PCE

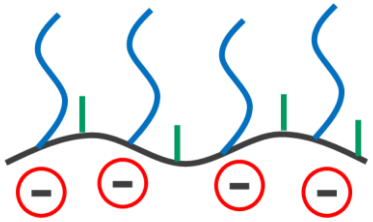


Drawbacks

Rough entrained air

Increase viscosity

Amphiphilic PCE



Improvement

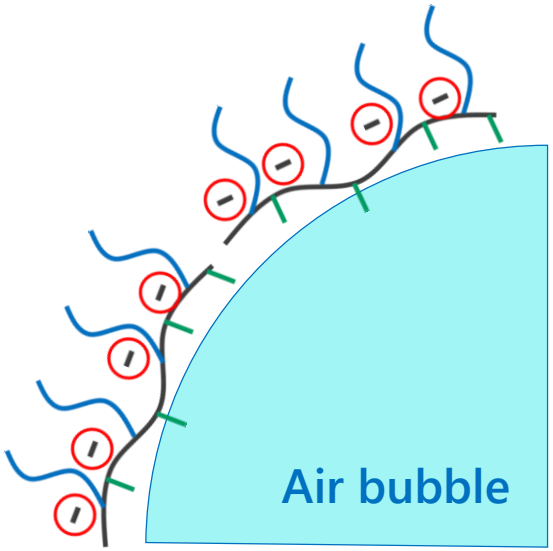
Fine entrained air

Better rheology

Estimated Mechanism

Adsorbed on cement particle and also on air bubble and refine the bubble.

Then, stabilize surfactant micelle by adding viscosity to surface water layer



Design of Amphiphilic PCEs

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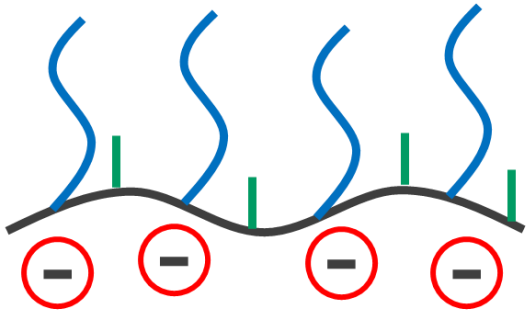
Chemical composition

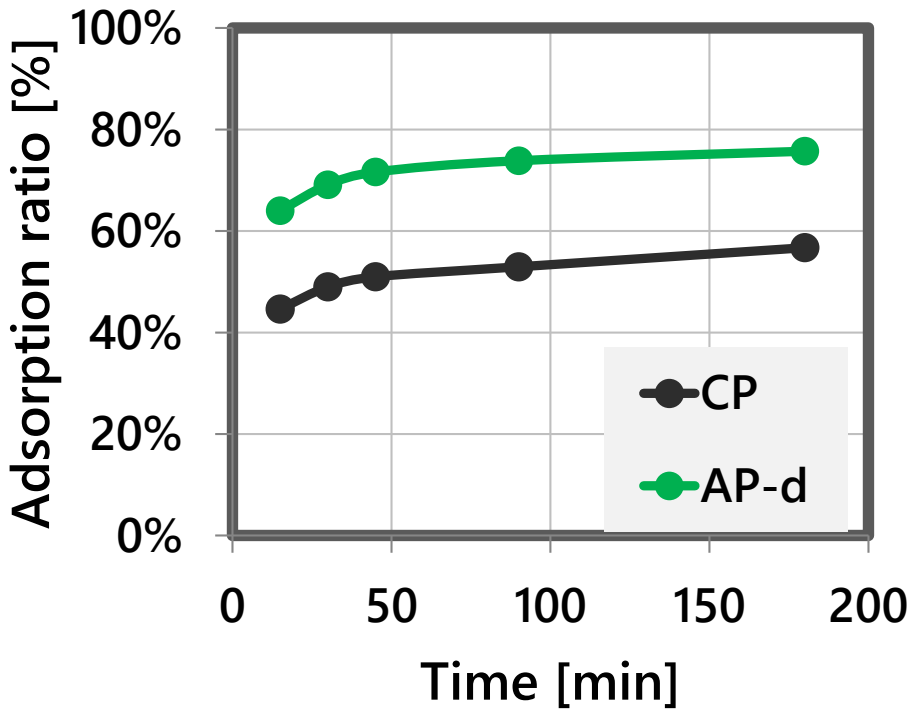


		Hydrophobic group	Dispersing group	Acid	Mw
Conventional PCE [CP]		STD	STD	STD	STD
Amphiphilic PCE [AP]	a	low	similar	Slightly high	same
	b	↓	↓		
	c	↓	↓		
	d	High	lower		

Fundamental results

Adsorption ratio on cement

W/C=100, OPC(JP)=100g, W=100g, Dosage of PCE 0.05wt%/C,
Analyzed by TOC



AP-d has moderate adsorption rate

MD simulation

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Modeling conditions

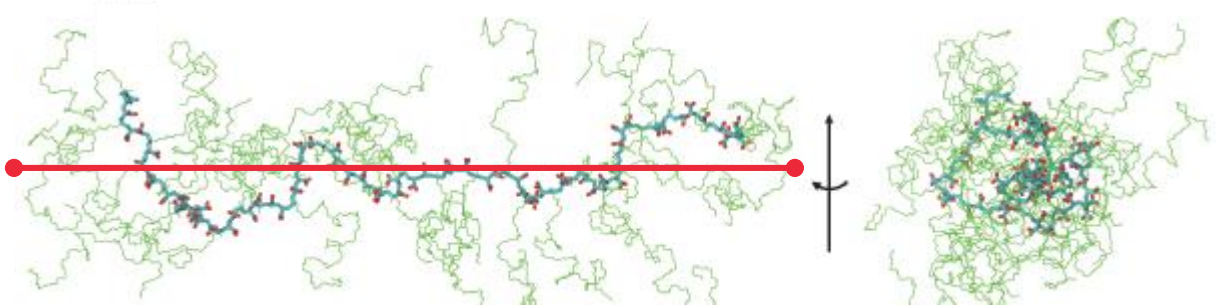
[1] *Scientific Reports* , **7**, 16599 (2017)

- MD simulations: Gromacs package[1]
- Cement pore solution[1]:
  1.72 g/L $CaSO_4$ $2H_2O$, 6.959 g/L Na_2SO_4, 4.757 g/L K_2SO_4 and 7.12 g/L KOH

* Replace “acid” to “hydrophobic group”

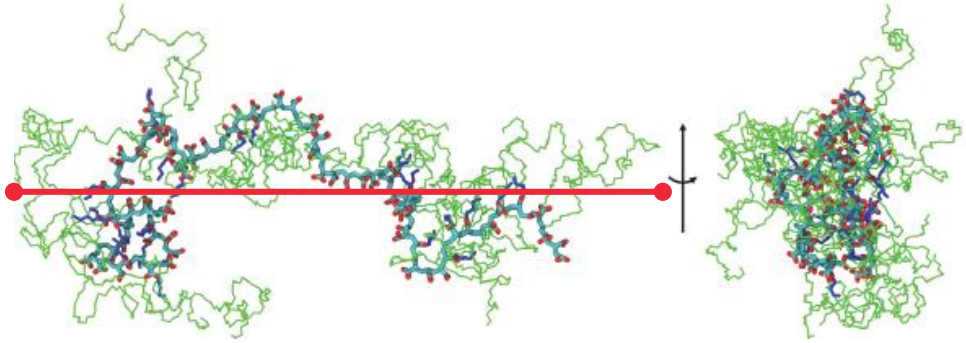
CP-model

Rg (all) = 4.2 nm



AP-model

Rg (all) = 3.71 nm



Lower Rg value indicated lower cement dispersibility by Amphiphilic PCE

Polymer analysis

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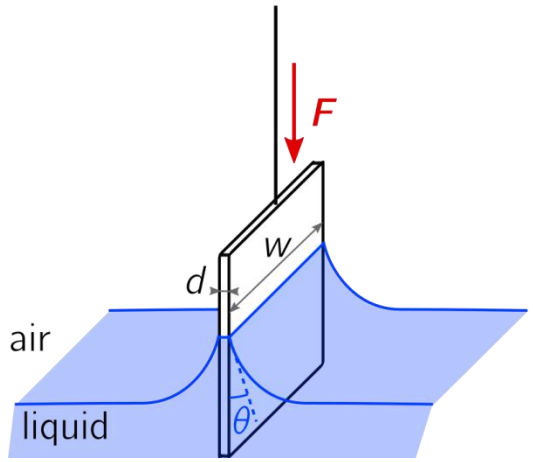
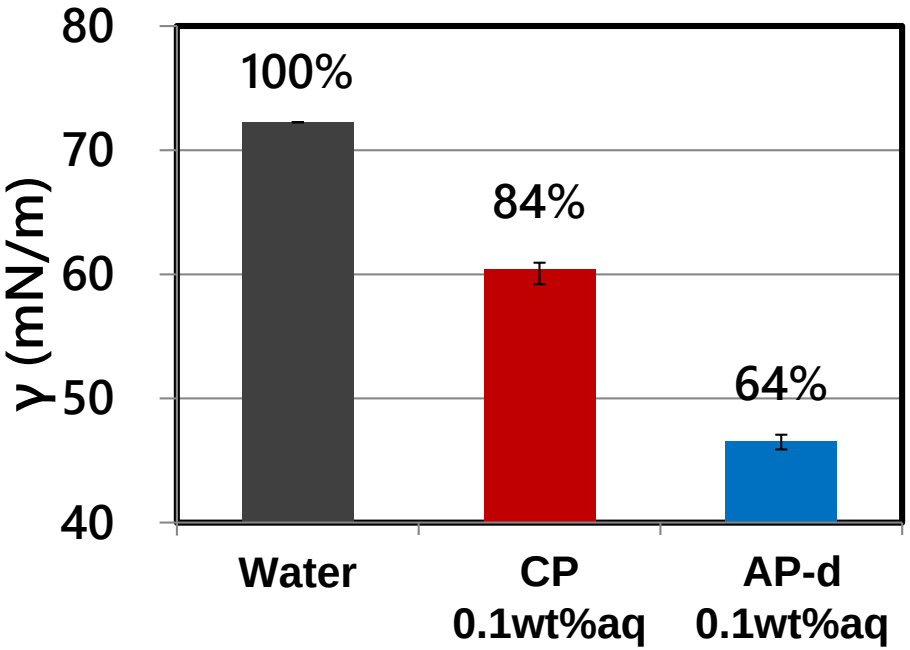
Wilhelmy method



γ：Statistic surface tension
L：2d + 2W

$$\gamma = \frac{F}{L * cos\theta}$$

Result



AP-d is stronger to foam than CP

Dosage efficiency

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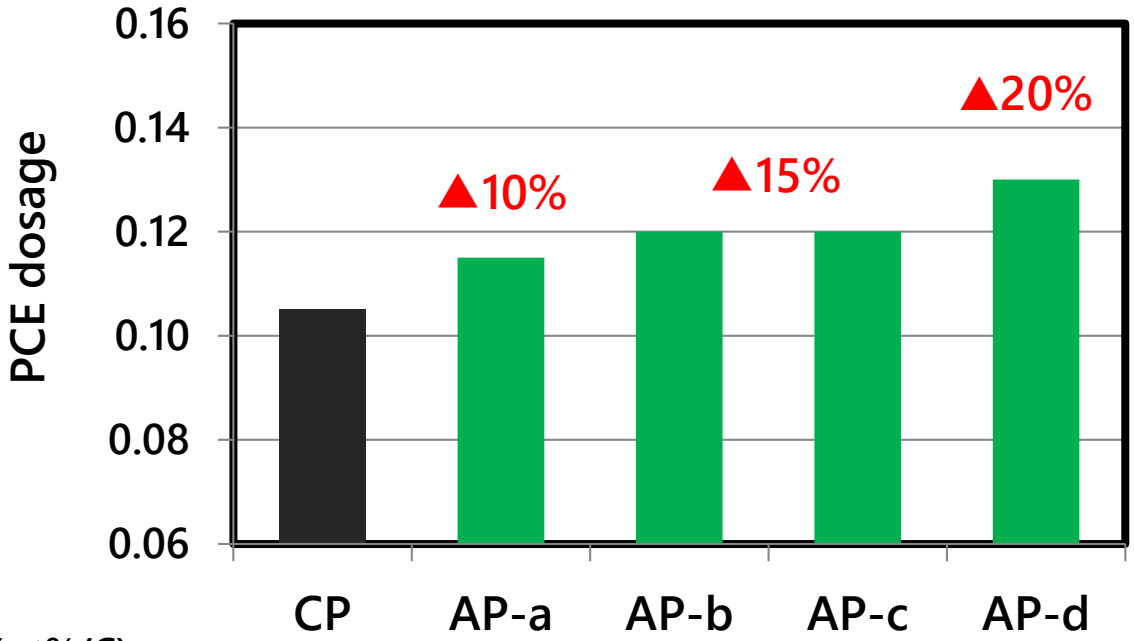
Concrete Test

Mix design: W/C=0.45 s/a=0.47 OPC(JP)=382.2kg/m3, Slump 22±1, Air<2.0%

Mixing protcol : C+W+S+G ⇒90sec (60rpm.)



(wt%/C)

	CP	AP-a	AP-b	AP-c	AP-d
PCE	0.105	0.115	0.120	0.120	0.130
Defoamer	0.0	0.0	0.0012	0.0024	0.0051

More hydrophilic group, Higher dosage of PCE and more foaming

Results of mortar/concrete test

Features of Amphiphilic PCE①

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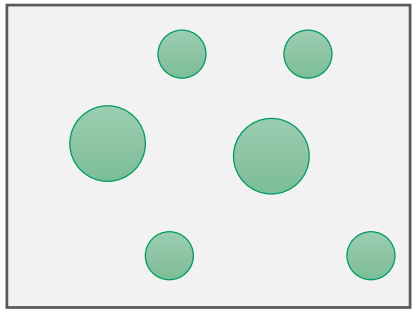
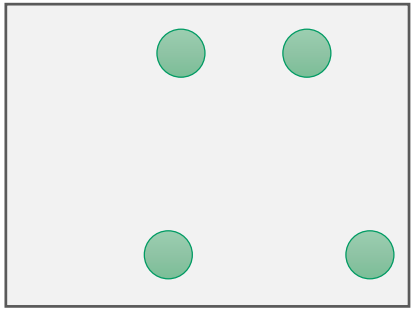
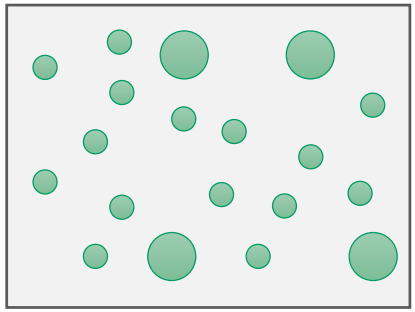
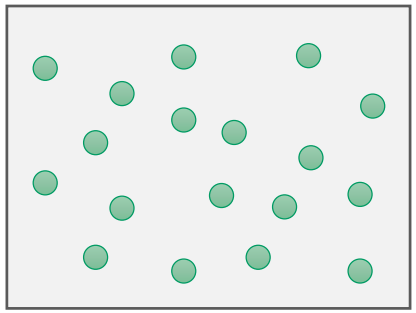
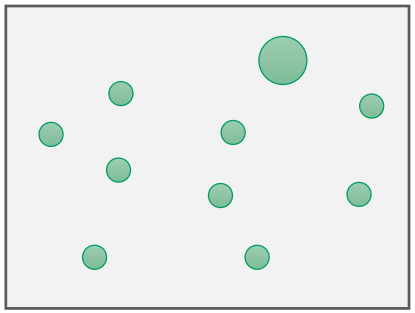
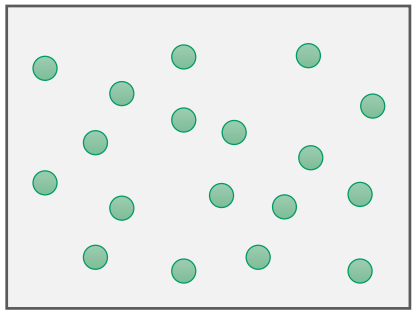
Images in hardened concrete

	PCE as is	With Defoamer	With Defoamer (& AEA)
Air	~ 10 vol%	~2 vol%	~5 vol%
Conventional PCE			
Amphipilic PCE			

Entrained air property

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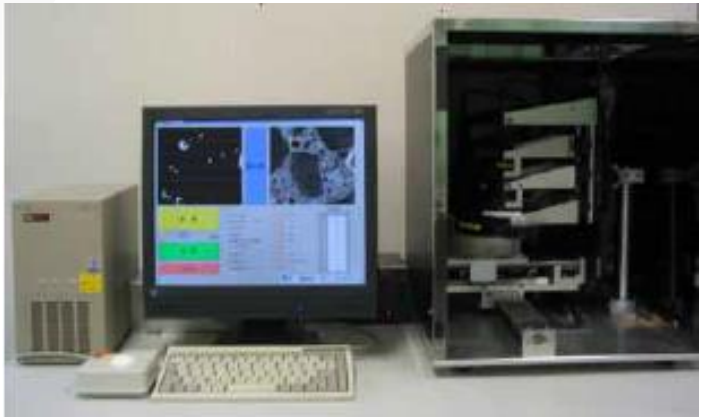
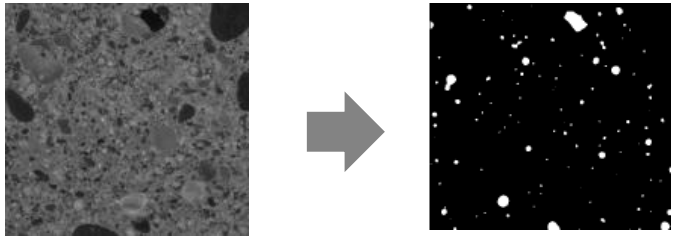
Air Void Measurement

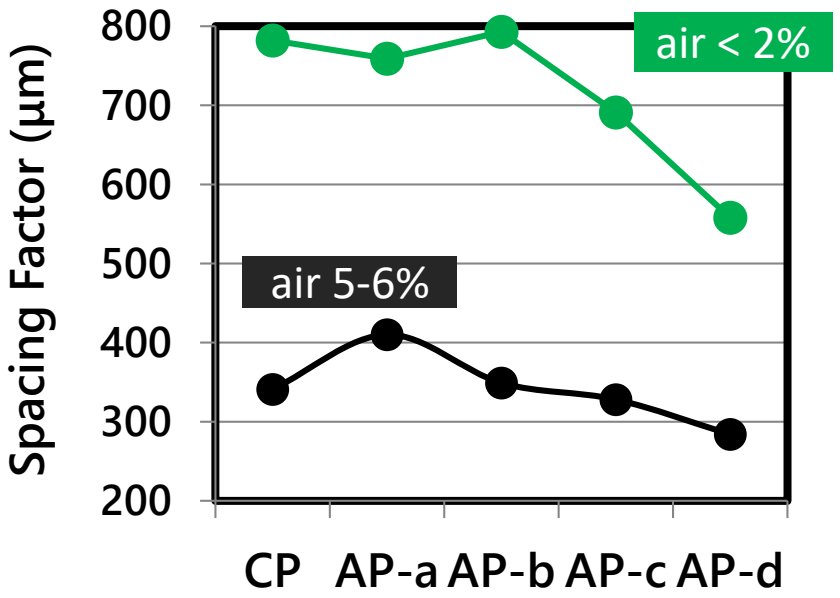
Refer to ASTM C457-98.





Concrete Test

Mix design: W/C=0.45, s/a=0.47, OPC(JP)=382.2kg/m3
Mixing protocol: C+W+S+G ⇒90sec (60rpm.)



More hydrophobic group,
smaller spacing factor

Entrained air property

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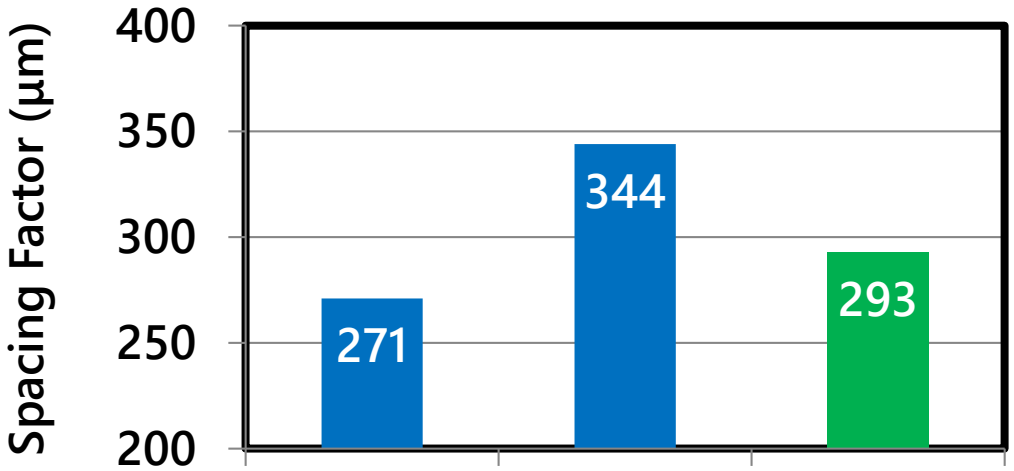
Concrete Test

W/C=0.45, s/a=0.47, OPC(JP)=382.2kg/m3, Slump=23±1cm, Air=5-6%

C+W+S+G ⇒90sec (60rpm.)



(wt%/C)	CP	CP	AP-d
PCE	0.115	0.12	0.135
Defoamer	0.0017	none	0.0016
AEA	0.0041	0.0023	none
Air	5.3%	5.5%	5.1%

・All met ASTM freezing thawing resistance criteria

・AP-d + DE had better spacing factor that CP + AEA

Features of Amphiphilic PCE②

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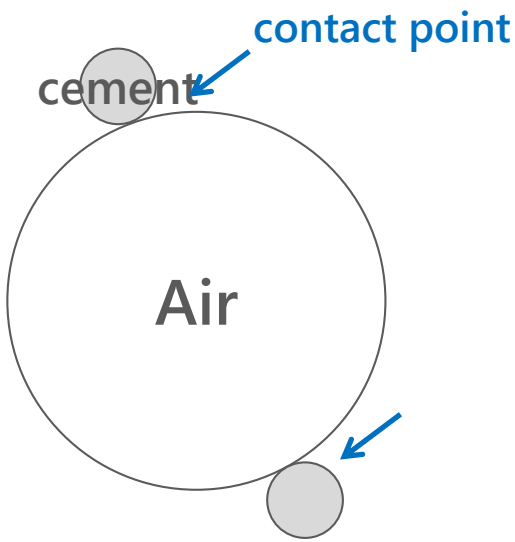
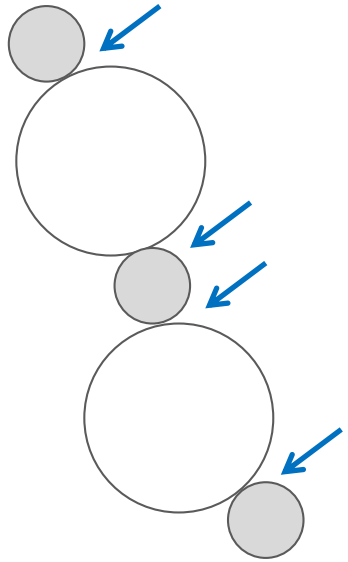
Fresh concrete

Conventional PCE



Amphiphilic PCE



- Stronger bubble may show stronger bearing effect.
- More of contact points to cement particles may increase yield point.

Rheological property

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RST Rheometer (BROOKFIELD)

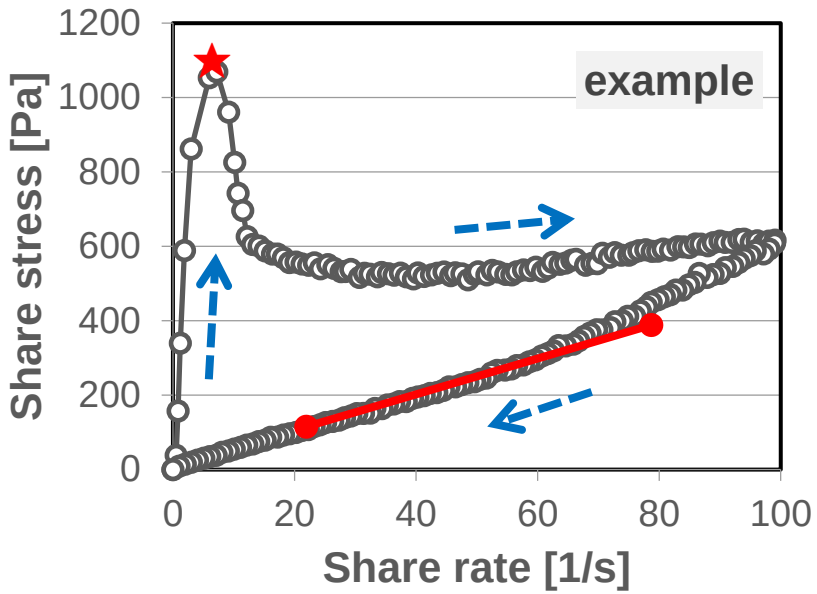
Hysteresis curve

★ $Yield\ point = Maximum\ Y_i\ [Pa]$

● $Plastic\ viscosity = \frac{Y_m - Y_l}{X_m - X_l}\ [Pa * S]$

$X\ axis = Share\ rate\ [1/s]$

$Y\ axis = Share\ Stress\ [Pa]$



Rheological property

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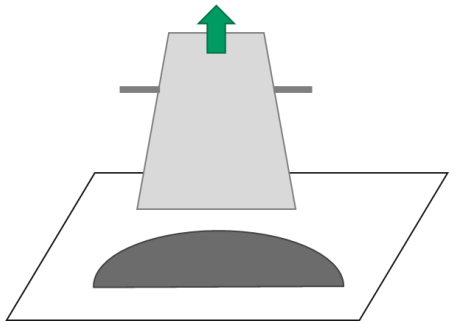
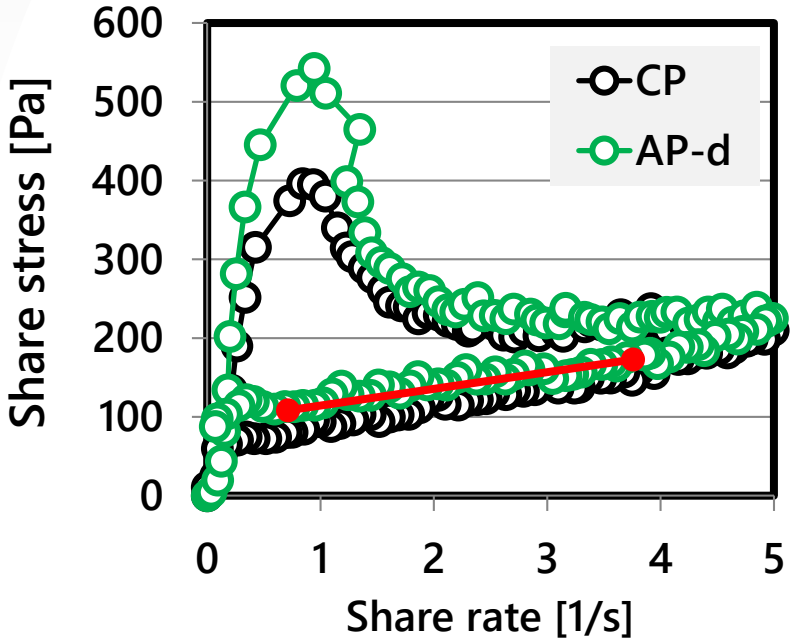
Mortar conditions

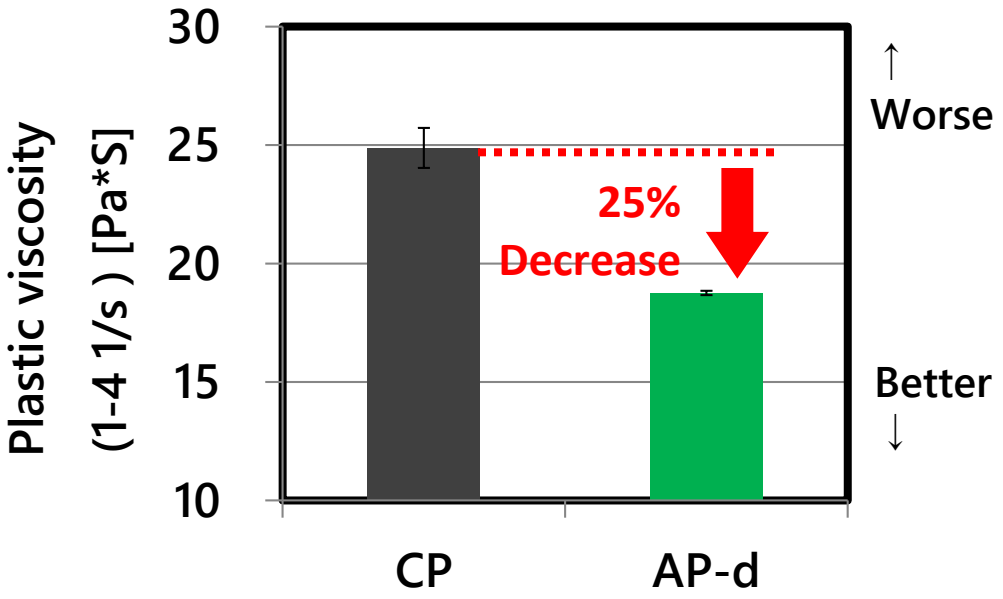
W/C=0.45, OPC(JP)=525g, Sand=1350g, W=188.8g,

Temp.=20℃, Flow 190±10mm, air 3±0.5%

Mixing procedure ：S+C+W (9min), Hobart mixer (speed 1)







Better plastic viscosity & yield point

Summary

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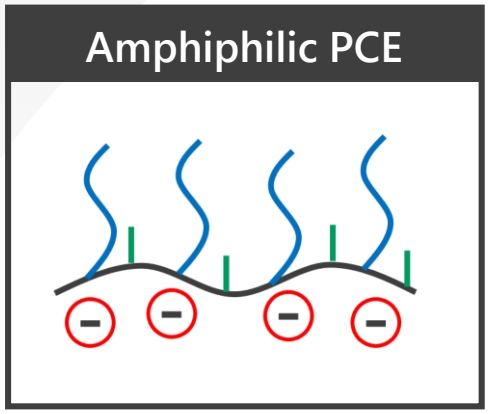

Features

Smaller spacing factor

Adapted freezing thawing criteria

Better plastic viscosity & yield point

Prospective applications

- Contribute to better pumpability with Lower plastic viscosity
- Simplify admixture system
  ex) Amphiphilic PCE with defoamer instead of conventional AEA system
- Improve segregation resistance with higher yield point

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Thank you for your kind attention

- NSCL are ready for supplying sample
- It is possible to provide this PPT file