Korean J. Chem. Eng., **25**(6), 1553-1561 (2008)

Effects of polycarboxylate-type superplasticizer on fluidity and hydration behavior of cement paste

Jin-Yong Shin*[†], Ji-Sook Hong, Jeong-Kwon Suh**, and Young-Seak Lee*****

*Reliability Assessment Center, Korea Institute of Construction Materials, Seosan 356-874, Korea
**Korea Research Institute of Chemical Technology, Deajeon 305-600, Korea
***Dep. of Fine Chemical Engineering & Chemistry, Chungnam National University, Deajeon 305-764, Korea

(*Received 27 February 2008 • accepted 10 May 2008*)

Abstract−Polycarboxylate (PC)-type superplasticizers were synthesized with different average molecular weight of polyethylene oxide (PEO) graft groups, the molar ratios of graft group to carboxylic group, and then the chemical structure, polymerization condition, and physical and chemical properties were analyzed. In order to evaluate the effects of PC-type superplasticizers in cement paste, the adsorption, the initial plasticity and slump retention characteristics and the degree of hydration reaction were investigated. As the average molecular weight of graft group decreased and molar ratio increased, the conversion rate to copolymers, the adsorption amount of PC-type superplasticizer on cement particles improved; on the other hand, the hydration reaction was delayed.

Key words: Polycarboxylate (PC), Superplasticizer, Chemical Structure, Slump, Hydration

INTRODUCTION

Today, high-performance concrete including high durability and fluidity is developed with new superplasticizers. Because superplasticizers, such as lignosulfonate and naphthalene sulfonate, cause environmental problems, require excessive amount, and alter initial fluidity, new superplasticizers with more expansive applications have been needed [1]. In the 1,990s, the first polycarboxylate superplasticizer (PCS) for cement paste and concrete was introduced in Japan [2]. It is in the form of a graft copolymer and has greater changeability, more varieties of properties according to molecular weights and structures, more outstanding fluidity and stability, and greater effects with lesser amount compared to existing superplasticizers [3]. Therefore, various critical problems of the cement and concrete industry, such as delayed curing, limited water-reducing property, and excessive sensitivity, would probably be solved by PCS. For this purpose, it is important to understand the basic structure of PCS and recognize the effect of its molecular structure in order to apply an accurate amount of PCS to appropriate uses. However, there are not many studies or reports on this issue and most studies have only focused on the mechanical properties of cement and concrete with the addition of PCS [4-6].

Therefore, in this research we synthesized PCS copolymerized by altering the average molecular weight of polyethylene oxide (PEO) graft groups under equal ratio of carboxylic acid (AA) and the molar ratios of carboxylic acid to polyethylene glycol methyl ether methacrylate (PMEM), and then studied the effects of PCS' molecular structures on fluidity/workability and hydration behavior of cement paste.

EXPERIMENTAL

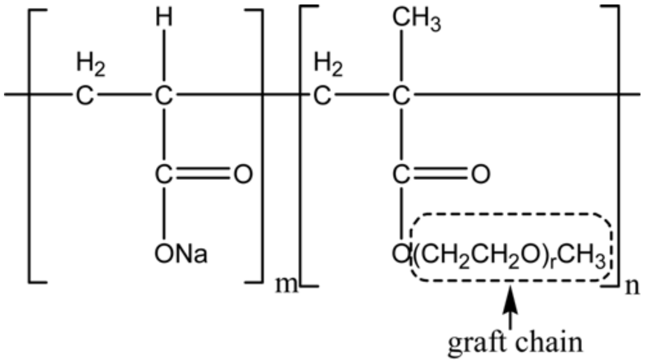
1. Materials and Synthesis

1-1. Chemicals

The three types of PMEMs (Mn=2,080, 1,100, 475), according to the repeat units of polyethylene oxide and acrylic acid (AA; 99%) were used as monomers for copolymerization. Ammonium persulfate (98%) was used as the initiator and 2-mercaptoethanol (98%) as the chain transfer to control the molecular weight.

1-2. Synthetic Procedure

In the synthetic reaction of a PC-type copolymer, the molar ratios of [AA]/[PMEM] were controlled to 2.0, 3.0, 4.0 and 0.5 wt% of initiator and 1.0 wt% of chain transfer to the amount of monomers were used. The reaction temperature was kept at 80±2 °C and a mixture of each monomer and initiator was dropped in the vessel for 4 and 5 hours, respectively. The solid content of synthetic product was 20±0.1 wt%. After the reaction was completed, 40 wt% of sodium hydroxide (NaOH) was used to set the pH to 5.5±0.1. The chemical structure of the PCS synthesized in this study and the molar ratios and physical properties of the monomers are shown in Fig. 1 and Table 1, respectively.



Molar ratio of m/n = 2, 3, 4
r = 45, 23, 9

Fig. 1. The estimated chemical structure of PCS.

[†] To whom correspondence should be addressed.
E-mail: jshong@krict.re.kr

Table 1. Molar ratio of monomers, length of PEO side chain and physical properties of synthesized PCSs

Sample name	Molar ratio of [AA]/[PMEM]	PMEM		Physical property		
		M_n	Repeat unit of EO	Solid content (wt%)	pH	Specific gravity
2080-2	2	2,080	45	20.0	5.5	1.060
2080-3	3	2,080	45	20.0	5.5	1.066
2080-4	4	2,080	45	19.8	5.5	1.080
1100-2	2	1,100	23	20.0	5.5	1.068
1100-3	3	1,100	23	20.1	5.5	1.061
1100-4	4	1,100	23	20.0	5.4	1.065
475-2	2	475	9	20.0	5.4	1.053
475-3	3	475	9	19.8	5.6	1.057
475-4	4	475	9	19.9	5.5	1.051

Table 2. Constituent oxides and physical properties of ordinary portland cement

Constituent oxide (%)								Specific surface area (cm^2/g)	Fineness (%)	
CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Free CaO	Ig. loss		44 μm	88 μm
62.95	21.77	5.32	3.52	2.13	2.42	0.78	0.66	3250	7.2	0.9

1-3. Cement

The Type I cement from Korea's H Company was used and its chemical and physical properties are shown in Table 2.

2. Evaluation

2-1. Analyses of PCS

2-1-1. Conversion

To find the conversion of PC copolymer, acetone (or methanol), a type of poor solvent, was used. The mixture of pc copolymer and acetone was left at room temperature for about two hours, and dried in a vacuum oven of 60 °C for 6-10 hours to compare the weight difference.

2-1-2. GPC Analysis

Molecular weight was performed by gel permeation chromatography (GPC) using Ultrahydrogel Liner Column and Ultrahydrogel 120 Column made by Waters. The elution solvent used was 0.1 M of $NaNO_3$ aqueous solution. The standard sample for calibration used was plotted with polyethylene glycol with the average molecular weight between 550 and 22,500 and polyethylene oxide with the average molecular weight range 42,900-53,100 dissolved in 3rd distilled water at once.

2-2. Property Tests on Cement Paste

2-2-1. Adsorption of PCS on Cement Particles

The amount of PCS adsorbed on the cement particles was measured by using total organic carbon analyzer (TOC-5000A made by Shimadzu). As results, the difference between the TOC of a blank composed of mixed water and PCS and the TOC of each cement paste after certain periods of time was determined by the amount of PCS adsorbed in the cement particles. The cement pastes for the adsorption test were made with 0.2 of PCS/cement ratio and 1.0 of water/cement ratio(W/C). The pastes were shaken at 150 rpm by using a shaker (SI-300R; JEIO Tech.) for 30 and 60 minutes, respectively. And then the pastes were filled into a centrifugal separator, rotated at 3,000 rpm for five minutes. Thereafter, the upper solution of the pastes were filtered by using a 0.45 μm syringe filter.

2-2-2. Fluidity Test of Cement Paste

The W/C of the cement paste mixed for a fluidity test was 0.3 and PCS was added into the mixing water at a given content of 0.2 wt% (solid content to cement). The fluidity test was evaluated by using a mini-slump cone (57 mm in height, 19 mm in top diameter, and 38 mm in bottom diameter) according to the Kantro's method [7]. The mini-slump test was checked up to 90 min after the first test at a temperature of 20±2 °C, measured by the variations of the mini-slump spread during the test intervals. Before the test, the paste was remixed for 1 min. Wet rags were used to protect the water content of the paste from drying out.

3. Analyses of Hardened Cement Paste

In order to examine the effects of PCS on the hydration of cement paste, 0.2 wt% of PCS was added to cement paste whose W/C was 0.3 and was mixed for two minutes. A plain sample with no addition of PCS was used as reference for comparison.

The samples of cement pastes were cured in a humidity chamber (20±2 °C, R.H. over 90%) for 1, 3, and 28 days. The samples taken at a designated period were crushed into pieces of a few millimeters and further hydration was stopped by using acetone. Then it was dried at 55±2 °C for 24 hours and was analyzed by XRD (X-Ray Diffractometer) and DSC (Differential Scanning Calorimeter).

3-1. X-Ray Diffraction

After drying, the samples were milled to go through a 200 mesh sieve. X-ray diffraction (XD-R1, Shimadzu, Japan) was carried out using Cu Kα radiation between 5° and 60° 2-theta, with step-rate of 4° min^{-1}.

3-2. Thermal Analysis

Netzsch DSC 404 calorimeter (Netzsch-Gertebau GmbH, Selb/Bavaria, Germany) was used with a computer-controlled furnace that heats the measuring head containing the sample. All analyses were conducted at a heating rate of 10 °C min^{-1} up to 700 °C in a nitrogen atmosphere.

RESULTS AND DISCUSSION

1. Conversion

Fig. 2 shows the conversion rates of PC-type copolymers accord-

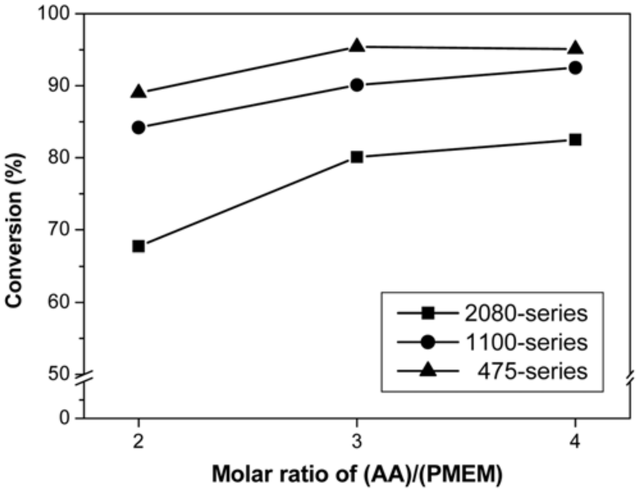


Fig. 2. Effect of molar ratio of monomers and molecular weights of PMEM on the conversion.

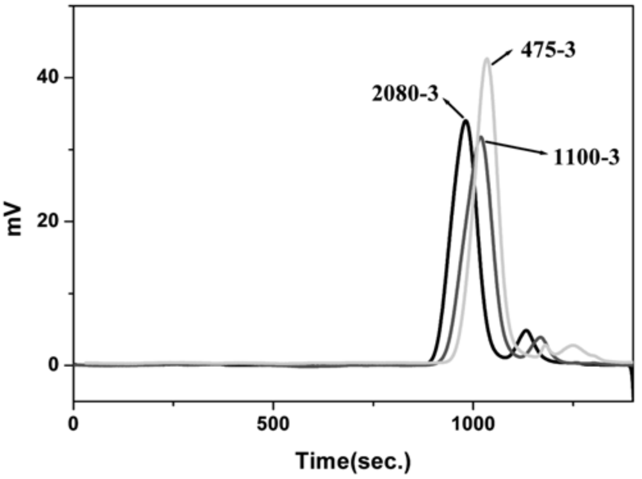


Fig. 3. Effect of average molecular weights of PMEM on molecular weight distribution.

ing to the change of PMEM's molecular weights and the molar ratios of [AA]/[PMEM]. When the molar ratio of [AA]/[PMEM] was identical, the relative density of AA, whose radical and growth reaction was relatively faster and higher, increased (density of PMEM was decreased) as the repeat units of PEO were reduced from 2,080-series to 475-series. Hence conversion to a copolymer improved (68→83%, 82→95%). At the same molecular weight of PMEM, it was confirmed that the conversion rate also tended to increase as the density of AA increased with the increase molar ratio of [AA]/[PMEM]. However, at lower molar ratio, the increase of PMEM's density decreased the conversion rate to a copolymer. It seems to have been difficult to copolymerize the monomers containing the more massive PEO graft group, which can interfere with copolymerization because of steric hinderance.

2. Molecular Weight

The above PC-type copolymer's average molecular weight (M_w), polydispersity (PDI), and molecular weight distribution results are shown in Table 3 and Fig. 3. We could see that a monodispersed copolymers were synthesized, based on the results in Table 3 (28,000-37,000 for M_w and 2.1-3.0. for PDI). The M_w of the copolymers tended to decrease as the PMEM's molecular weight decreased. Because the ratio of AA in a monomers increases as PMEM's molecular weight decreases in consistent molar ratio of [AA]/[PMEM], the density of AA increases in the copolymer created after a radical reaction and the density of more massive PMEM decreases; thus, the M_w decreased relatively. However, the degree of polymerization of each unit in the copolymer increased as the molecular weight of PMEM decreased. Based on the average molecular weight, if PC coploymer were alternating copolymer, the degree of polymerization of 2080-2, 1100-2, and 475-2 was about 16-17, 27-28, and 60-61, respectively and increased greatly as the repeat units of PEO reduced.

In the case of same PMEM (i.e., same repeat unit of PEO), The M_w of the copolymers decreased as the molar ratio of [AA]/[PMEM] increased. There are two major reasons: the first, the growth of a copolymer stops after it reaches a certain growth level and enters a chain transfer reaction with non-reacted monomers to create new lower copolymers and polydispersed copolymers [8]. This was proven by the increasing PDI value. The second, the molecular weights of carboxylic acid and PMEM are greatly different (about 7-27 times). Because the ratio of more massive PMEM reduced and the density

Table 3. Weight average molecular weights and polydispersity of PCS

Sample name	Mw	PDI (M_w/M_n)
2080-2	37,100	2.8
2080-3	35,300	3.0
2080-4	35,700	2.9
1100-2	35,300	2.5
1100-3	30,100	2.7
1100-4	28,100	2.8
475-2	28,700	2.1
475-3	28,100	2.1
475-4	28,100	2.4

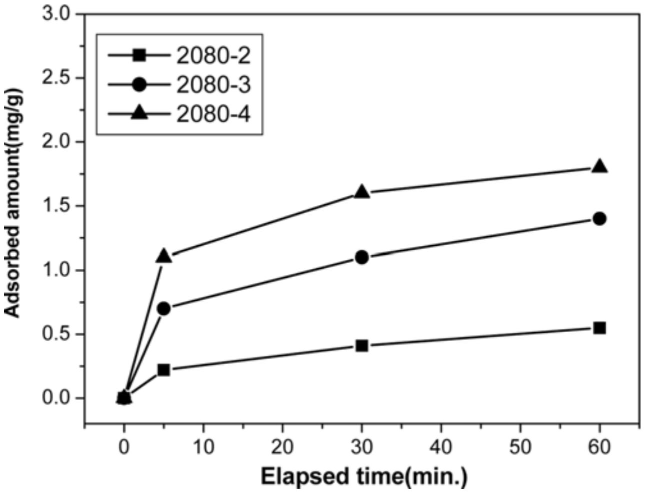


Fig. 4. Effect of molar ratios of [AA]/[PMEM] on adsorption behavior.

of AA with lower molecular weight became greater in a fully grown copolymer structure, Mw showed a trend of decreasing at higher molar ratios.

3. Absorption Amount of PCS on Cement Particles

Fig. 4 shows the adsorbed amounts of PCS with time for dosage of 0.2 wt% and W/C of 1.0 when the molar ratio of [AA]/[PMEM] increases from 2.0 to 4.0. As mentioned above, the conversion rate increased as the molar ratio increased (Fig. 2) and the carboxyl group in the PCS structure also increased. Therefore, its negative (–) charge increased in density and reacted with the positive (+) charge of the calcium ions on cement particles to increase the adsorbed amount in hydration. The adsorbed amount increased with time. Because super-sized high molecules in the early molecular structure had entangled structural property, the adsorption rate on the cement particles was lated at the early stage. Also, the PEO chain of PMEM with higher molecular weight took time to expand in water and the slow-releasing reaction to create the 2nd carboxylic acid which was formed by decomposition of PMEM in alkali condition (i.e., in cement solution) increased the adsorbed amount with time [9].

The absorption amount increased as PMEM's molecular weight decreased (Fig. 5). As the average molecular weight of PMEM de-

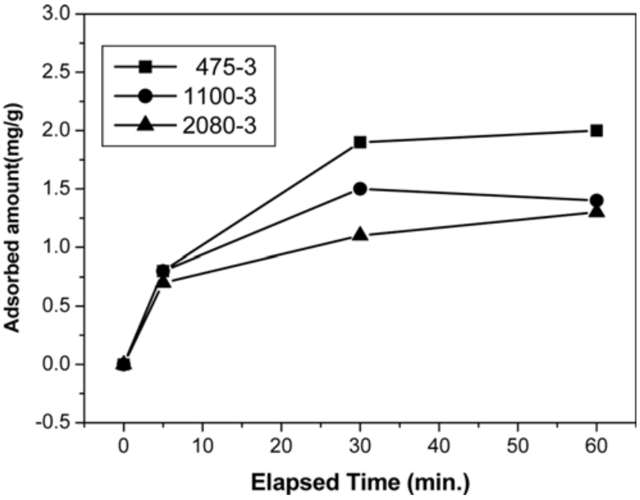


Fig. 5. Effect of average molecular weights of PMEM on adsorption behavior.

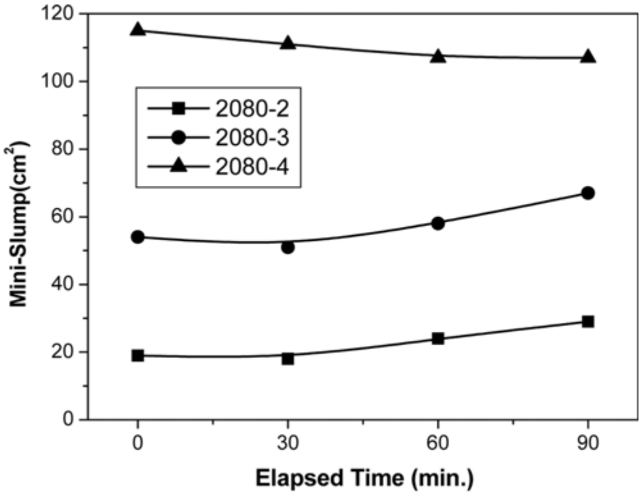
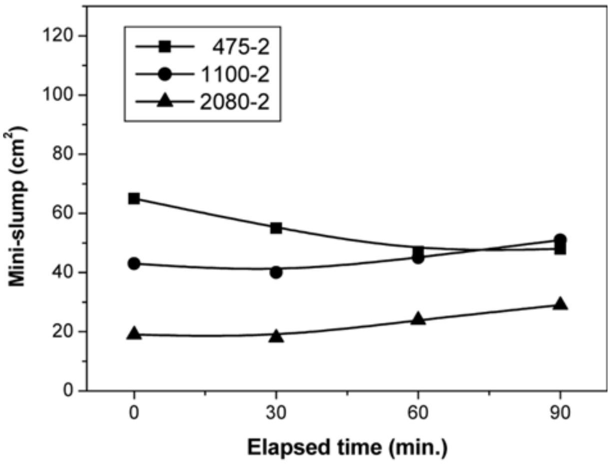
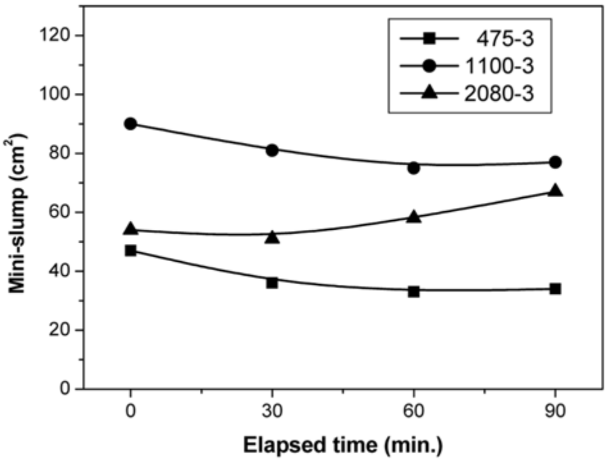


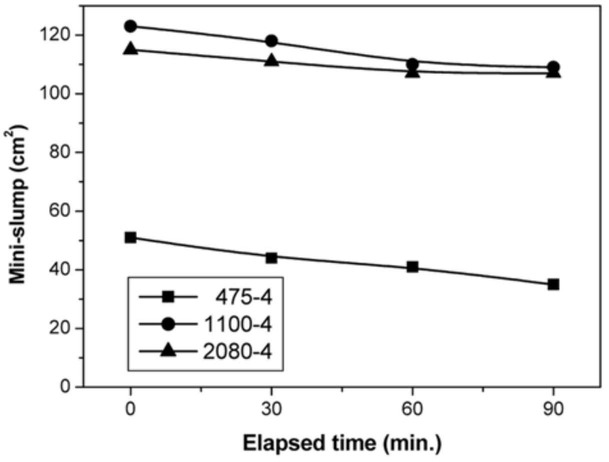
Fig. 6. Comparison of fluidity and slump-retaining ability of cement pastes with different molar ratios of [AA]/[PMEM].



(A) Molar ratio = 2



(B) Molar ratio = 3



(C) Molar ratio = 4

Fig. 7. Comparison of fluidity and slump-retaining ability of cement pastes with various average molecular weights of PMEM. (A) Molar ratio=2, (B) 3, and (C) 4.

creased, the content of AA increased in the copolymer structure to multiply the density of carboxyl which is the adsorption agent. Also, because the lower molecular weight of PC-type copolymer moves more freely in the medium, the adsorbing ability was improved.

4. Effect of PCS on Fluidity and Slump-retaining Ability

Figs. 6 and 7 compare the fluidity of cement paste with PCS. As shown in Fig. 6, initial flow was enhanced largely as the density of the carboxyl group increased in higher molar ratio. It was indicated by the results that electrostatic repulsive force and steric hinderance greatly improved inter particles, as the amount adsorbed on cement particles increased and the adsorption speed accelerated to easily expand the loop/tail/train backbone and the repeating graft group into the paste. The backbone's degree of polymerization decreased as the molar ratio of AA increased to correspond to the results of Yamada [10,11] and Tanaka [12] who said that the fluidity after the addition of PCS increases as the main chain's degree of polymerization decreases.

Fig. 7 compares the synthetic PCS' fluidity with the change of PMEM's molecular weight. The early fluidity of (A) whose AA/PMEM ratio was 2 was better when PMEM's repeat unit was shorter, but longer repeat units of PMEM (1,110 and 2,080) achieved better slump-retaining ability with time. The early fluidity was better when the PCS copolymer in 475-series was applied in the above AA/PMEM ratio, because the carboxylic acid content in the copolymer structure was high (about 24%) and its degree of polymerization was low to make faster and denser absorption and to easily expand the PEO group after absorption. The early fluidity was improved better when the molecular weight of repeat units was 1,100, not 2,080.

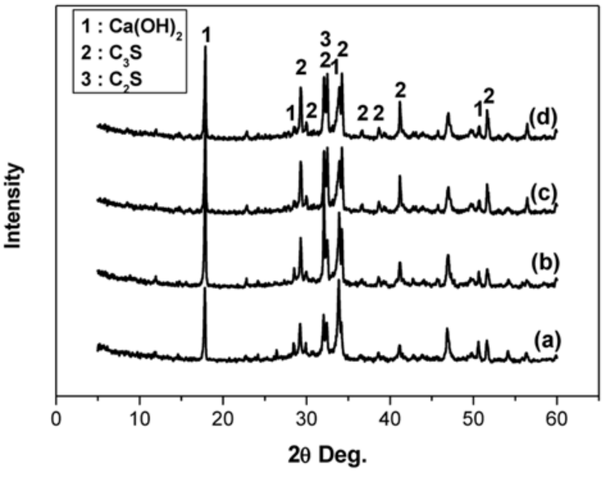
When the AA/PMEM ratio was 3 and 4 as shown in (B) and (C), the lowest early fluidity and slump-retaining ability were achieved when the PMEM's molecular weight was 475. In this case, the carboxyl content in the copolymer molecular structure increased greatly to 32 and 40%; thus the fluidity is expected to see a great improvement. However, a high density of negative charges converted the zetapotential on the surface of PCS on cement particles from positive to negative. Therefore, it was determined that other cement particles with positive charges approach to free PCS to quickly lower the fluidity. Another cause of low fluidity was that there was a high probability for PEO groups to anchor together because of the expanded PEO group's low density and short length even though the carboxylic ions of cement particles were densely covering the particle [13].

The effects of PMEM's molecular weight on fluidity and slump-retaining ability revealed that the early fluidity was excellent when PMEM's molecular weight was 1,100, and the slump-retaining ability was excellent when the length of a repeat unit was longest at 2,080. Therefore, it was determined that the repeat unit's multidimensional interference is the most important factor to improve the slump-retaining ability. Better fluidity was achieved when the molar ratio of AA/PMEM was decreased with low molecular weight of PMEM and when the ratio was increased with high molecular weight of PMEM.

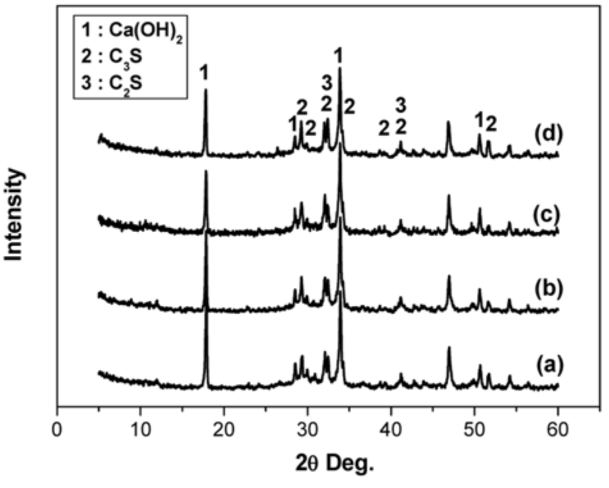
5. Effect of PCS on Hydration Reaction of Hardened Cement

5-1. Degree of Hydration (XRD)

Figs. 8, 9, and 10 indicate the analysis of PMEM's molecular weight, changes in AA/PMEM ratio, and the product of hydration and non-hydrated cement through XRD.



(A) 1 day

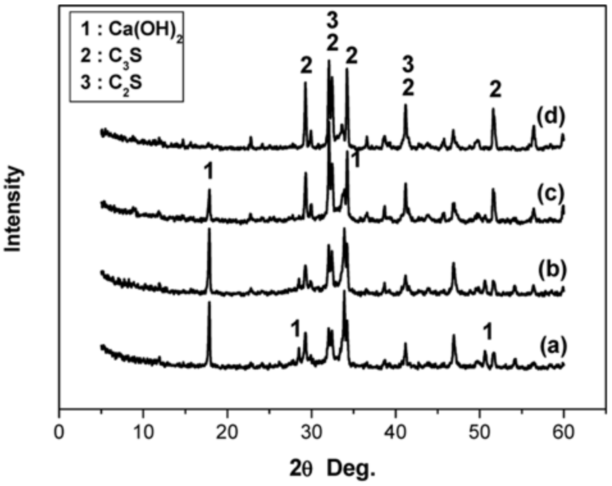


(B) 3 day

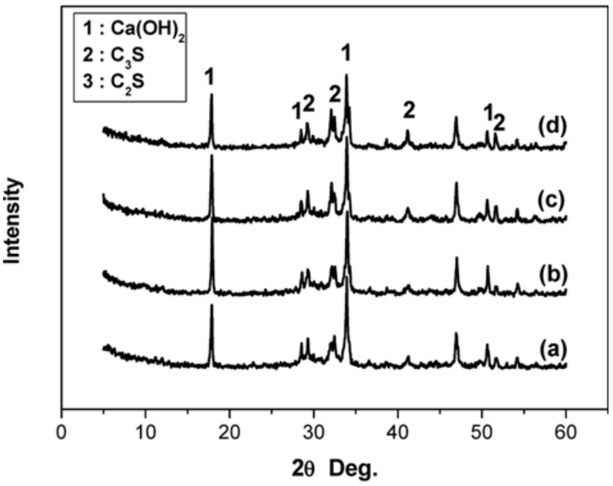
Fig. 8. XRD patterns of Plain and cement pastes hydrated with 2,080-series for (A) 1, (B) 3 day.
(a) Plain, (b) 2080-2, (c) 2080-3, (d) 2080-4

Considering that the relative durability of 18^{o} and 34^{o} (2θ deg.) decreased in higher AA/PMEM ratio on Day 1 regardless of the length of repeat units and that the relative peak durability of non-reacted cement paste (C_3S, C_2S) was higher than that of plain cement paste, it was revealed that the hydration reaction was delayed. It was because the hydration of calcium silicate (C_3S and C_2S), which creates a great amount of calcium hydroxide in cement, was delayed. Cement cures and hardens by the hydration of intermediates (C_3A and C_4AF) and alite (C_3S) and fewer calcium hydroxide crystals indicate that early hydration was delayed by the high absorption rate of alite on cement particles [14,15]. However, the hydration behavior of cement was mostly recovered as time passed, except for in the 475-series.

On Day 1, it was found that the durability of hydrated cement was 9% (1100-3; 152) and 21% (475-3; 169) higher than the relative durability of non-hydrated minerals in 2080-3 (140) to reveal that the early hydration behavior was greatly delayed as the length of repeat unit decreased. In addition, the cement paste samples with



(A) 1 day



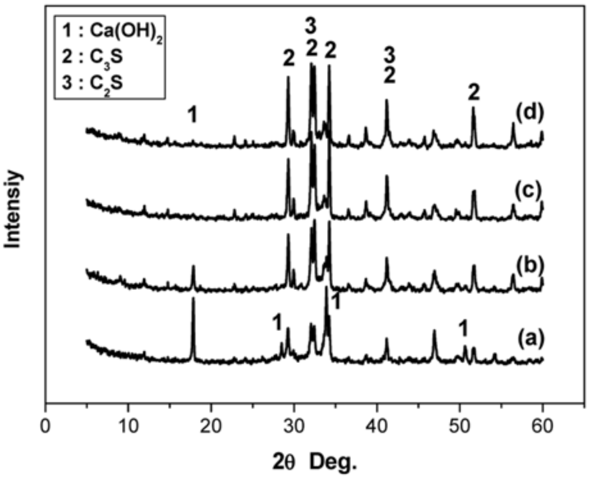
(B) 3 day

Fig. 9. XRD patterns of Plain and cement pastes hydrated with 1,100-series for (A) 1, (B) 3 day.
(a) Plain, (b) 1100-2, (c) 1100-3, (d) 1100-4

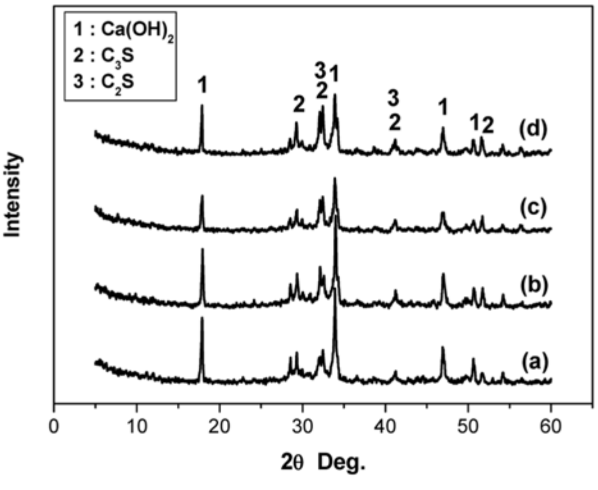
1100-4, 475-3, and 475-4 PCS created almost no calcium hydroxide crystals on Day 1 to reveal that the early hydration is greatly delayed by chelation with Ca^{2+} ions created by the hydration of cement particles in high carboxylic content.

5-2. Thermal Decomposition of Cement Hydrates (DSC)

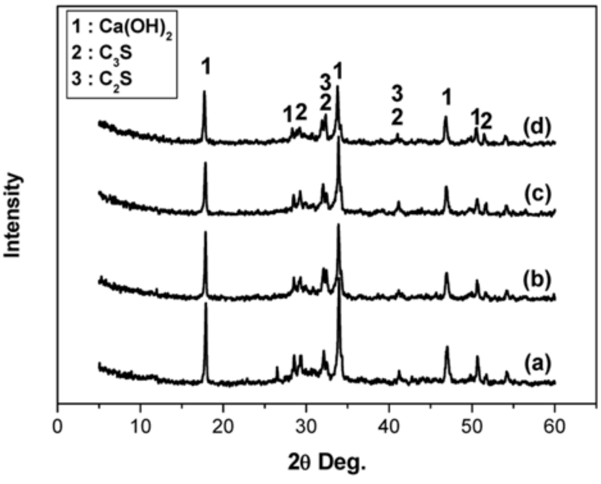
Figs. 11 and 12 show the DCS results of cement paste samples with synthetic PCS with different lengths of repeat units and AA/PMEM ratios on Day 1 and Day 28. On Day 1, all cement paste samples, except for the one with the copolymer PCS with the shortest repeat unit at 475, did not considerably delay the hydration reaction when the AA/PMEM ratio was 2. However, the samples with 1,100- and 475-series showed considerable hydration when the ration increased to 3 and 4. Compared to the plain sample, the sample with 1100-3 greatly reduced the calcium hydroxide's area of peak thermal absorption and no peak thermal absorption was seen in the sample with 475-3. Such tendency is more clearly shown in Fig. 11(C). Considering that the peak thermal absorption was greatly decreased and the length of repeat unit and carboxylic density increased even when the molecular weight of PMEM was 1,100, it was found that the thermal absorption directly influenced the hydration of cement



(A) 1 day

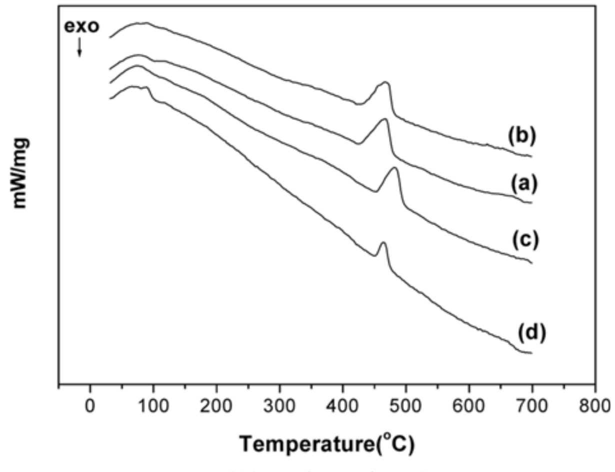


(B) 3 day

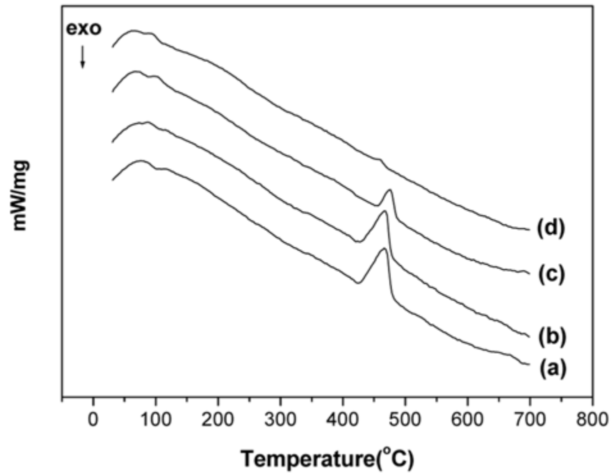


(C) 28 day

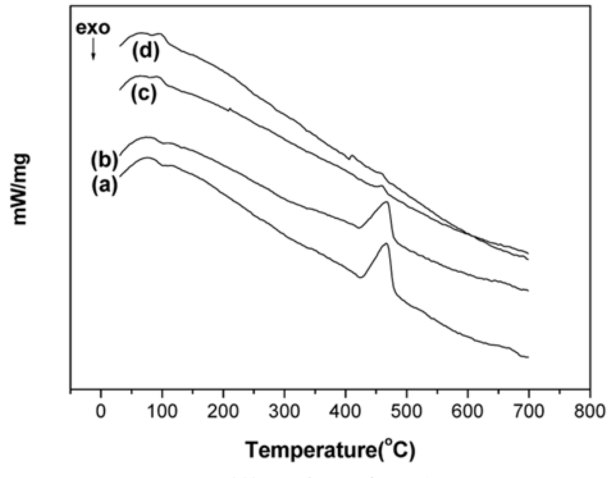
Fig. 10. XRD patterns of Plain and cement pastes hydrated with 475-series for (A) 1, (B) 3, (C) 28d.
(a) Plain, (b) 475-2, (c) 475-3, (d) 475-4



(A) Molar ratio = 2



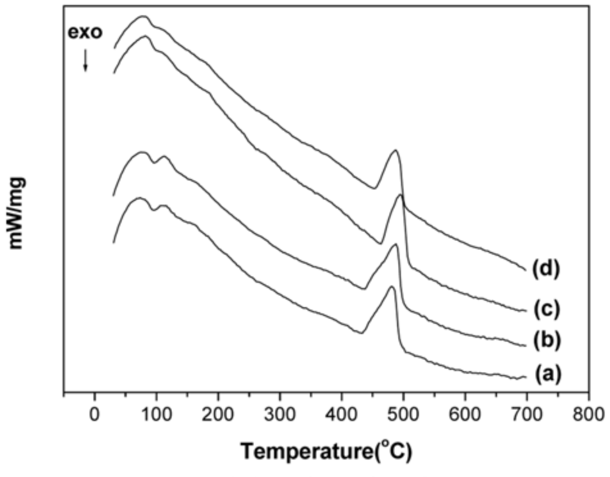
(B) Molar ratio = 3



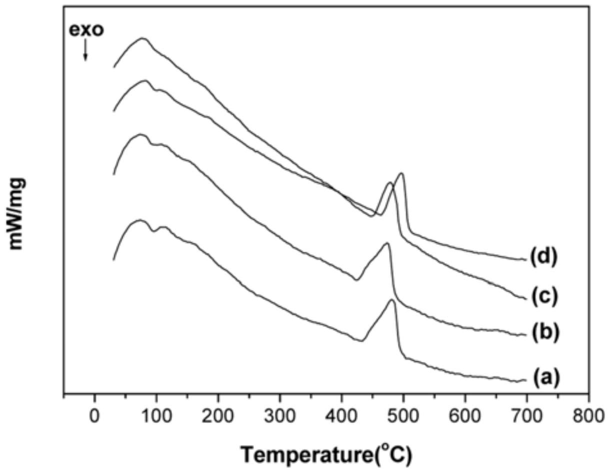
(C) Molar ratio = 4

Fig. 11. DSC curves of Plain and cement pastes hydrated with (A) Molar ratio=2, (B) 3, and (C) 4 type PCS for 1 day.
(a) Plain, (b) 2080-, (c) 1100-, (d) 475-

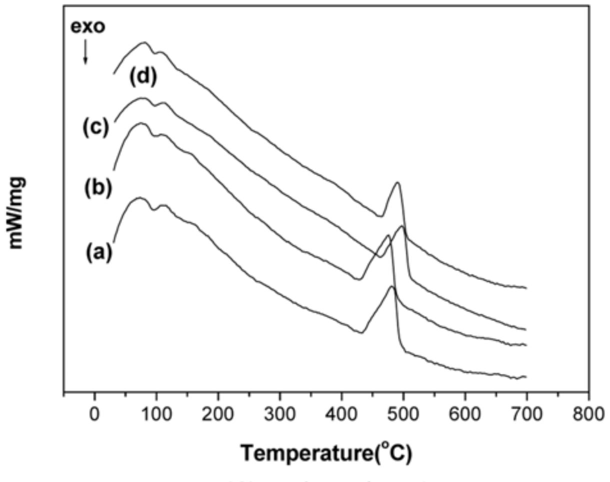
paste. Such tendency disappeared as time passed, but the degree of hydration of the plain sample was not as high as that of cement paste samples with 2080-3 and 2080-4 PCS by Day 28.



(A) Molar ratio = 2



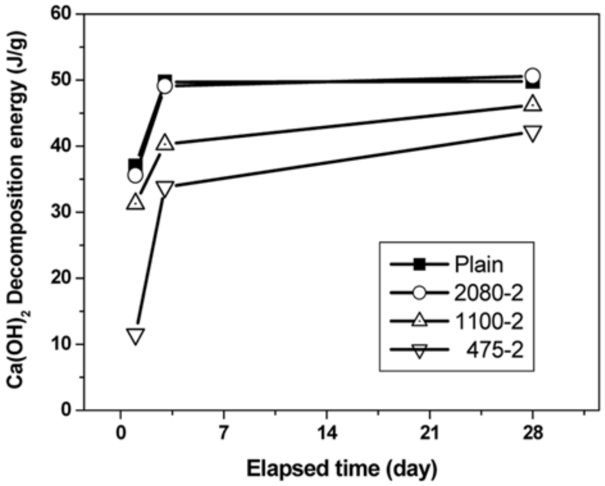
(B) Molar ratio = 3



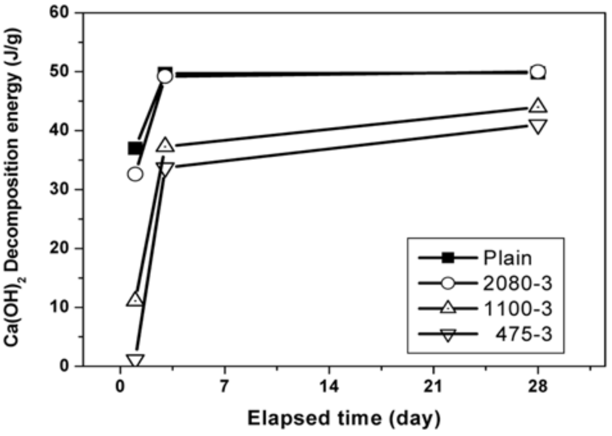
(C) Molar ratio = 4

Fig. 12. DSC curves of Plain and cement pastes hydrated with (A) Molar ratio=2, (B) 3, (C) 4 type PCS for 28 day.
(a) Plain, (b) 2080-, (c) 1100-, (d) 475-

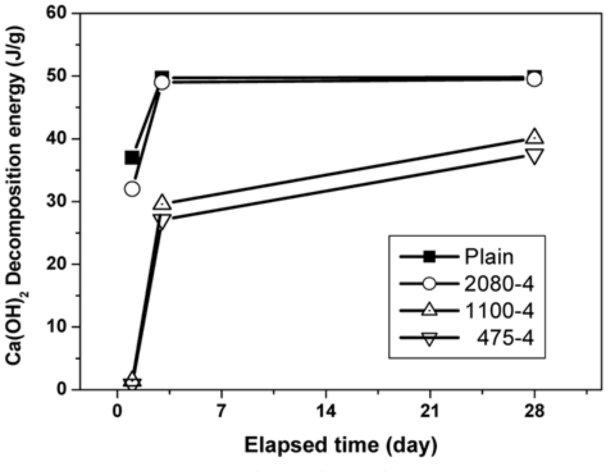
Fig. 13 compares the peak thermal absorption calories generated by the decomposition of calcium hydroxide in around 425-500 as shown in the DSC analysis, and it helps make an accurate observa-



(A) Molar ratio = 2



(B) Molar ratio = 3



(C) Molar ratio = 4

Fig. 13. Heat energies calculated from endothermic peaks of Ca(OH)$_2$ of hardened cement pastes containing PCS synthesized with average molecular weights of PMEM.
(A) Molar ratio=2, (B) 3, (C) 4 type PCS

tion of PCS' effects on cement's hydration behavior. On Day 1, the degree of hydration of cement paste with 2,080-series was not influenced when the AA/PMEM ratio was low as shown in Fig. 11 (A) and showed a degree of hydration about 86% higher than that of the plain sample even when the ratio was increased (Fig. 11(B) and (C)). On the other hand, the relative degree of hydration of the sample with 1,100-series to the plain sample was lower than the sample with 2,080-series, but showed a similar tendency. The degree of hydration decreased as the ratio of main chain/repeat unit, but recovered by 85-4% on Day 1, 81-60% on Day 3, and 93-80% on Day 28. The sample with 475-series showed a result similar to the above results, but its relative degree of hydration was lower. Its degree of hydration was 31-2% on Day 1, 68-55% on Day 3, and 85-75% on Day 28 and the effects of PCS on the early hydration delayed the early hydration for a long time as its thick layer of absorbed PCS interfered with the diffusion of ions. However, as the Ca^{2+} ions were saturated on the surface with time, the creation and growth of $Ca(OH)_2$ core eliminated the double layer of electricity and diffused the silicate-rich layer on the surface to the solution (inside the paste) to cover the hydration behavior with time [14].

CONCLUSION

The following are the results from the study of the properties of synthetic PCS with different lengths of repeat units and AA/PMEM ratios and the effects of PCS on the fluidity and hydration behavior of cement paste:

1. As the repeat units of PEO shortened and molar ratio of AA/PMEM increased, the conversion rate to copolymers improved, whereas the average molecular weight of the copolymers decreased.
2. As the repeat units of PEO shortened and molar ratio of AA/PMEM increased, the absorption amount of PCS on cement particles increased and the PCS' slow-releasing reaction constantly increased the absorption amount with time.
3. The early fluidity was excellent when PMEM's molecular weight was 1,100 and the slump-retaining ability was excellent with 2,080-series. Better fluidity was achieved when the molar ratio of AA/PMEM was decreased with low molecular weight of PMEM and when the ratio was increased with high molecular weight of PMEM.
4. The hydration reaction was delayed as the length of repeat unit decreased and molar ratio of AA/PMEM increased. The cement paste sample with 475-series PCS particularly saw the longest delay of hydration. Regardless of time frame, the hydration behavior of samples of PCS became similar to that of the plain sample as the repeat unit was longer and the carboxylic content inside the molecular structure was lower.

REFERENCES

1. S. Hanehara and K. Yamada, *Cement and Concrete Research*, **29**, 1159 (1999).
2. M. Kinoshita, T. Yonezawa and Y. Yuki, *Semento, Konkurito Ronbunshu*, **47**, 196 (1993).
3. H. Y. Cho and J. M. Suh, *Cement and Concrete Research*, **35**, 891 (2005).
4. I. Papayianni, G. Tsohos, N. Oikonomou and P. Mavria, *Cement and Concrete Composites*, **27**, 217 (2005).
5. Y. C. Tseng, W. L. Wu, L. Huang, C. T. Wang and K. C. Hsu, *Superplasticizers and other chemical admixtures in concrete SP-195*, 401 (2000).

6. J. Gołaszewski and J. Szwabowski, *Cement and Concrete Research*, **34**, 235 (2004).
7. D. L. Kantro, *Cement Concrete Aggregate*, **2**, 56 (1980).
8. G. Odian, *Principles of polymerization*, Wiley Interscience, 34-39 (2004).
9. J. March, *Advanced organic chemistry*, John Wiley & Sons, Inc., New York, 667-689 (1992).
10. K. Yamada, S. Ogawa and S. Hanehara, *Cement and Concrete Research*, **31**, 375 (2001).
11. K. Yamada, T. Takahashi, S. Hanehara and M. Matsuhisa, *Cement and Concrete Research*, **30**, 197 (2000).
12. T. Yoshio, *Chemical structure and dispersion mechanism of air entraining high-range water reducing agents*, NMB Research Transactions 9, 5-11 (1992).
13. D. J. Shaw, *Introduction to colloid and surface chemistry*, Butterworth-Heinemann, London, 174-209 (1992).
14. H. F. W. Taylor, *Cement chemistry*, Academic Press, London, 128-133 (1990).
15. S. S. Park and H. Y. Kang, *Korean J. Chem. Eng.*, **23**, 367 (2006).