Effects of Poly{Carboxylate–g–(Ethylene Glycol)Methyl Ether} on the Physical Properties of Cement Paste

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Abstract

The comb type poly{carboxylate–g–(ethylene glycol)methyl ether} (P(C–g–E)) copolymers were synthesized at different monomer ratios. The relationship between the synthetic conditions, the molecular weights (Mp, Mn, Mw, Mz and Mw/Mn) and the dispersion ability of these copolymers in cement paste has been established. The molecular weights of P(C–g–E)s were analyzed by GPC. The dispersion abilities and the dispersion stabilities of P(C–g–E)s in cement paste were tested by mini slump testing method. The optimum formulation for P(C–g–E) synthesis was found to be P23MM 17 mol.%: SMS 10 mol.%: MA 8 mol.%: SMA 65 mol.%: APS 0.2 mol.%. The key components in P(C–g–E) synthetic formulation for cement superplasticizer are SMA and P23MM. The SMA/P23MM in P(C–g–E) synthetic formulation is related to the dispersion ability and stability of P(C–g–E) in cement paste. The SMA/P23MM in P(C–g–E) synthetic formulation also influences the molecular weights and the polydispersity of P(C–g–E). The optimal range of SMA/P23MM in the formulation as a cement superplasticizer is 3.50~5.50. The dispersion ability of cement paste added with the optimum P(C–g–E) is increased more 3 times than those of the others.

Introduction

The comb type poly{carboxylate–g–(ethylene glycol) methyl ether} {P(C–g–E)} has special properties as a dispersing agent in cement materials [1,2]. In particular, the slump retention ability in cement materials of P(C–g–E) is superior to the other concrete superplasticizers. Recently the demand of P(C–g–E) in concrete industry is significantly increased in the world [3,4].

Many kinds of P(C–g–E) have been developed. In 1995, Kinoshita [5] reported that the P(C–g–E) containing carboxylic groups, ether groups, ester groups and sulfonate groups has an excellent dispersion ability in cement concrete and the optimal formulation in feed monomer for the P(C–g–E) was sodium methacrylic acid (SMA) 54 mol.%: sodium methallyl sulfonate (SMS) 7 mol.%: methyl acrylate (MA) 8 mol.%: poly(ethylene glycol) methylether methacrylate (P23MM) 31 mol.%. Yamada [6] and Sakai [7] demonstrated the effect of the chemical structure on the properties of comb type poly-carboxylates superplasticizer. Also they reported that the performance of P(C–g–E) in cement paste depended strongly on the molecular weight and the molecular weight distribution of the polymer [6-8].

However, in our preliminary study, it has been shown that the dispersion ability of the P(C–g–E) synthesized using the optimal formulation suggested by M. Kinoshita is not satisfactory [9-12]. Also, we could not find in the literature any study of the relationship between the SMA/P23MM in feed monomer for P(C–g–E) and the molecular weights (Mn, Mw, Mz, Mp and Mw/Mn) of the polymer as well as the physical properties of cement paste mixed with the polymer.

In this study, to find the optimal formulation of the P(C–g–E) for superplasticizer in cement materials, we prepared the P(C–g–E)s consisting of 4 components which were SMA, MA, SMS, P23MM by changing the molar ratios of the feed mixture. The molecular weights of P(C–g–E)s were analyzed by gel permeation chromatography (GPC). The dispersion abilities and the dispersion stabilities of P(C–g–E)s in cement paste were tested by mini slump testing method. The relationship between the syn-

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thetic conditions of the P(C–g–E)s and the physical properties of cement pastes mixed with these polymers were investigated. The relationship between the SMA/P23MM in the feed monomer mixture for P(C–g–E), the physical properties of cement pastes mixed with the superplasticizers and the molecular weights of the polymers is discussed.

Materials and Methods

Materials

Chemicals

Methacrylic acid (Macid), sodium methallyl sulfonates (SMS), methyl acrylate (MA), poly(ethylene glycol) methylether methacrylate (P23MM) were supplied by Aldrich Chemical Company, Inc. Ammonium persulfate (APS) and NaOH were purchased from Oriental Chemical, Inc.

The MA was distilled to get rid of MEHQ and stored in refrigerator. Sodium methacrylate (SMA) was prepared from Macid by neutralizing with 30% NaOH aqueous solution.

Poly(Carboxylate-g-Ethyl ether)

The P(C–g–E)s were synthesized in 4 neck round-bottom flask, at 60°C, for 8 hours [5,6]. The reaction conditions for P(C–g–E) synthesis are listed in Tables 1-3.

The 1-st synthesis of P(C–g–E)s has been performed by orthogonal array testing method {L₉(3⁴)}

Table 1
Experimental factors and levels for P(C–g–E) synthesis

Factors	Level, mol.%		
	0	1	2
MA	20	14	8
P23MM	30	17	5
SMS	15	10	5
APS	1.0	0.5	0.2

Table 2
The 1-st synthesis plan of P(C–g–E)

Sample No.	MA, mol.%	P23MM, mol.%	SMS, mol.%	SMA, mol.%	APS, %	SMA/P23MM
1-1	20	30	15	35	1.0	1.2
1-2	20	17	10	53	0.5	3.1
1-3	20	5	5	70	0.2	14.0
1-4	14	30	10	46	0.2	1.5
1-5	14	17	5	64	1.0	3.8
1-6	14	0.5	15	66	0.5	13.2
1-7	8	30	5	57	0.5	1.9
1-8	8	17	15	60	0.2	3.5
1-9	8	5	10	77	1.0	15.4

Table 3
The 2-nd synthesis plan of P(C–g–E)

Sample No.	MA, mol.%	P23MM, mol.%	SMS, mol.%	SMA, mol.%	APS, %	SMA/P23MM
2-1	8	21	10	61	0.2	2.90
2-2	8	17	10	65	0.2	3.82
2-3	8	13	10	69	0.2	5.31
2-4	8	9	10	73	0.2	8.11
2-5	8	5	10	77	0.2	15.4

[13] to find out the optimum formulation of the polymer as a dispersing agent in a cement paste (Table 2).

The 2-nd synthesis of P(C–g–E)s has been performed to find out the optimum SMA/P23MM ratio in P(C–g–E) synthetic formulations as a cement superplasticizer (Table 3).

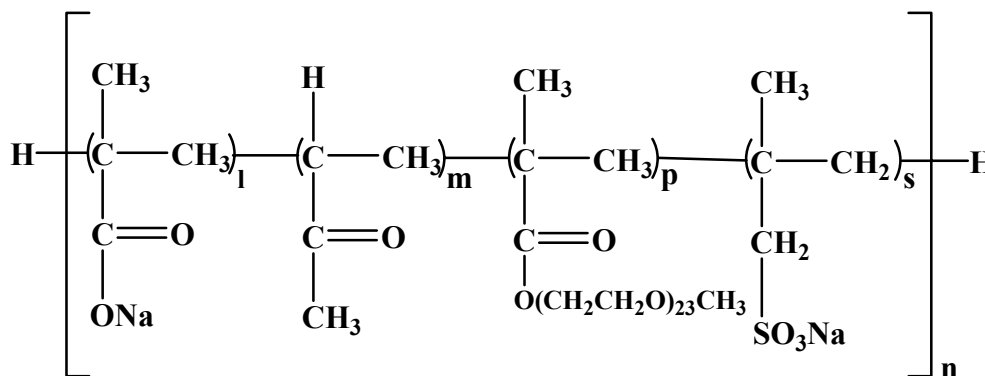The estimated chemical structure of the P(C–g–E) is shown in Fig. 1.

Fig. 1. The estimated chemical structure of P(C–g–E).

Cement

The ordinary portland cement produced from S company in Korea was used. The chemical composition and the physical properties of the cement are shown in Tables 4 and 5.

Methods

GPC analysis

The molecular weights (Mn, Mw, Mz, Mp and Mw/Mn) of P(C–g–E)s were analyzed by GPC, model DM400 made by Vicotek Co., using the column OHpak SB-803 HQ. The elution solvent was $0.1N$ $NaNO_3$ aqueous solution and PEG was used as a standard for the instrument calibration.

Dispersion ability

The dispersion ability of P(C–g–E) in cement paste was measured by mini slump test. The mini slump test was conducted at 20~25°C, relative humidity over 50%.

Cement was mixed with water (W/C: 30%) admixed with 1.2% P(C–g–E) solution (solid content: 20%) of the cement weight. The cement paste was shaken manually for 5 min and poured to the mini slump cone. The mini slump cone was made with PVC in lower diameter 38.1 mm, upper diameter 19.1 mm and height 57.2 mm. The mini slump spread of

Table 4
Chemical composition of ordinary portland cement

Composition, wt.%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
	21.3	5.44	3.15	61.27	3.15	2.2
C_3S	C_2S	C_3A	C_4AF	H.M.	L.S.F.	I.M.	S.M.
41	31	9	10	2.03	87.8	1.58	2.44

Table 5
Physical properties of ordinary portland cement

Specific gravity	Fineness, cm²/g	Sieve residue, %		Setting time		Compressive strength, kgf/cm²		
		44 μm	88 μm	Initial (min)	Final (hr:min)	3 days	7 days	28 days
3.15	3.260	9.7	1.1	241	08:19	217	296	372

the paste was measured by the width of the paste when the mini slump cone was raised up.

Dispersion stability

The dispersion stability of P(C–g–E) in cement paste was measured by the variations of mini slump spread during the elapsed time. The mini slump testing method and the room conditions for the dispersion stability test are the same as those of the disper-

sion ability test. However the cement paste was stored in humidity chamber controlled at 20~25°C, relative humidity over 90%, during the elapsed time. The mini slump spread was checked regularly (15, 30, 45, 60, 90, 120 minutes after the 1-st test) for 2 hours. Before the test, the paste was fiercely shaken manually again for 1 minute.

Normal consistency(W/C)

The normal consistency of cement pastes admixed with P(C–g–E)s were tested by KS L 5102[testing method for normal consistency of hydraulic cement].

Setting time

The initial and the final setting time of cement pastes mixed with P(C–g–E)s were tested by KS L 5103 [testing method for setting time of hydraulic cement by Gilmour needles].

Results and discussion

Dispersion ability and stability by change of P(C–g–E) synthetic condition

Dispersion ability and stability of P(C–g–E)s in cement paste

The dispersion abilities of P(C–g–E)s which have been synthesized in different formulations in cement paste were measured by mini slump testing method (Fig. 2). From these results, we can see that 1-2, 1-5 and 1-8 samples have better dispersion ability in cement paste than the others.

So, the dispersion stabilities of P(C–g–E)s in cement paste were measured for only three samples (Fig. 3). The three P(C–g–E)s samples have a good dispersion stability in cement paste for 120 minutes after adding water. From this result, we can conclude that the P(C–g–E) having a good dispersion ability has a good stability also.

Significance of the P(C–g–E) synthetic factors

In order to assess the significance of P(C–g–E) synthetic factors on the dispersion ability in cement paste, the mini slump data of cement paste mixed with P(C–g–E)s were analyzed as a function of the monomer molar ratios and the initiator concentration by orthogonal array testing method {$L_9(3^4)$}. As we can see from the results listed in Table 6, the most
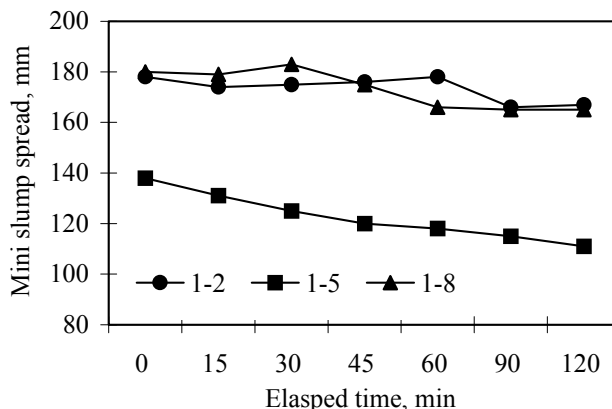

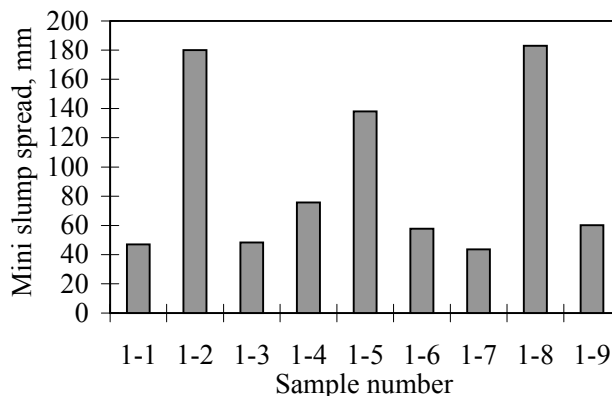Fig. 2. The dispersion abilities of P(C–g–E)s in cement paste.

Fig. 3. The dispersion stabilities of P(C–g–E)s in cement paste.

significant factor of the P(C–g–E) synthetic conditions affecting the dispersion ability in cement paste is P23MM which has the main chain of polyethyl ether, the second one is SMS which has sulfonate groups and the third one is APS which is used as an initiator. But the formulation change of MA which has ester groups has a little significance on the dispersion ability in cement paste.

Table 6
Variance analysis of orthogonal array testing for the effects of components

Factors	Sum	Freedom	Significance
MA	41.47	2	0.006
P23MM	24946.34	2	3.708
SMS	1281.34	2	0.190
APS	642.55	2	0.096

*Confidence: a = 0.10, F(1-a) = 3.11

From the data shown on Figure 4 we can conclude that the optimum P(C–g–E) formulation for cement superplasticizer is P23MM 17 mol.%: SMS 10 mol%: MA 8 mol.%: SMA 65 mol.%: APS 0.2%. Table 2 shows that the optimal range of SMA/P23MM in P(C–g–E) synthetic formulation is 3.1~3.8.
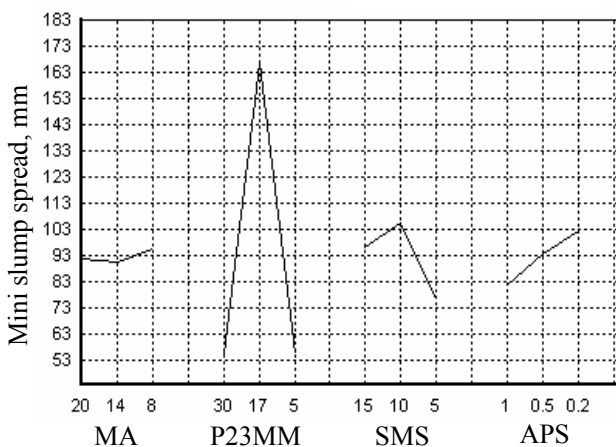

Fig. 4. Effect of the P(C–g–E) formulations on the dispersion ability in cement paste.

Dispersion ability and stability by the change of SMA/P23MM

Dispersion ability by SMA/P23MM

In order to investigate the effect of SMA/P23MM in P(C–g–E) synthesis on the dispersion ability and stability in cement paste in details, the SMA/P23MM in the same formulation has been changed from 2.90 to 15.40 (Table 3). The testing results of the dispersion abilities and stabilities of cement pastes mixed with those are shown in Figs. 5, 6. The dispersion abilities of P(C–g–E)s in cement paste did not much decrease by the change in SMA/P23MM from 2.90 to 5.31. However when the SMA/P23MM is increased to more than 8.11, the dispersion ability of P(C–g–E)s is decreased significantly.

Dispersion stabilities by SMA/P23MM

The dispersion stabilities of P(C–g–E)s synthesized with SMA/P23MM = 2.90~5.31(sample: 2-1, 2-2, 2-3) in cement paste were good for 120 minutes (Fig. 6). But the stability of P(C–g–E) which was synthesized with SMA/P23MM = 8.11 (sample: 2-4) decreased gradually according to the elapsed time.

To clarify the dispersion stabilities of P(C–g–E)s in cement paste, the widths of mini slump change
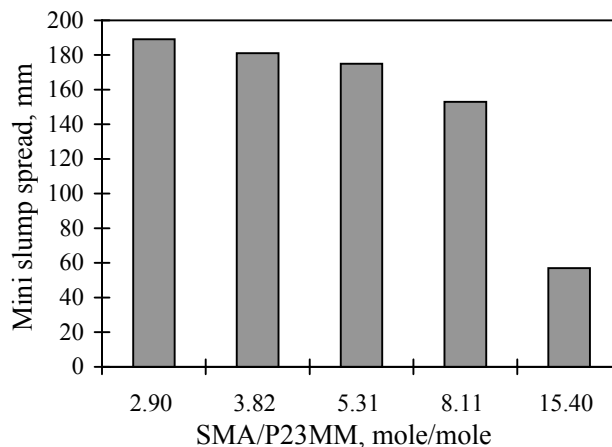

Fig. 5. Mini slumps of cement pastes admixed with P(C–g–E)s different in SMA/P23MM.
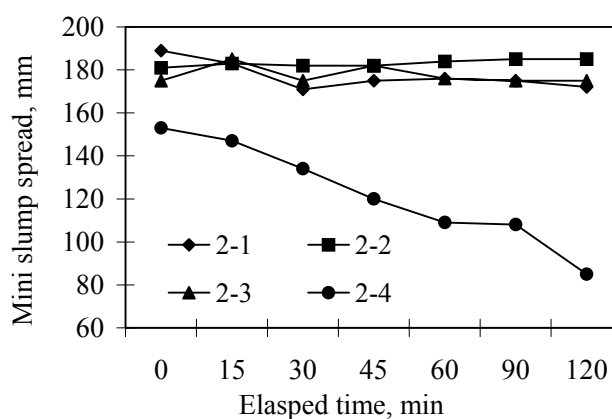

Fig. 6. Dispersion stabilities of cement paste admixed with P(C–g–E)s different from SMA/P23MM.

from the initial mini slumps according to the elapsed time are plotted as Fig. 7.
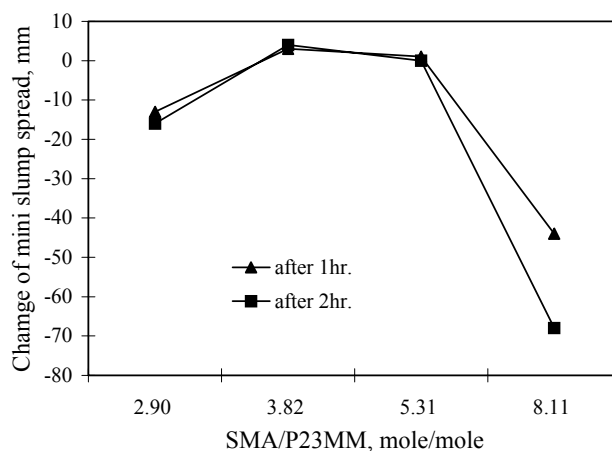

Fig. 7. The mini slump spread changes of cement pastes admixed with P(C–g–E)s different from SMA/P23MM.

The mini slump of P(C–g–E) which is synthesized with SMA/P23MM = 2.90 has a little decrease in 1 hour after adding water. The mini slumps of P(C–g–E)s which are synthesized with SMA/P23MM = 3.82~5.31 increased slightly for 2 hours. But the mini slump of P(C–g–E) synthesized with SMA/P23MM = 8.11 has a large reduction in 1 and 2 hours.

The relationship between SMA/ P23MM and mini slump

To investigate how much the SMA/P23MM in P(C–g–E) synthetic condition affects the mini slump of cement paste, the mini slump data of the cement pastes mixed with P(C–g–E)s which are prepared according to Table 2 and 3 are plotted against SMA/P23MM (Fig. 8).

From the results, we can conclude that the mini slump of paste is related to the SMA/P23MM in P(C–g–E) synthesis formulations and the optimum SMA/P23MM in P(C–g–E) is 3.50~5.50. The reason of this relationship is discussed in a separate paper [14].

The relationship between SMA/P23MM and molecular weights of P(C–g–E)s

Apex molecular weight (Mp)

The Mp of P(C–g–E)s according to the SMA/P23MM in P(C–g–E) synthetic formulations are shown in Fig. 9. The Mp of P(C–g–E)s are monotonously decreased from 25,000 Da to 17,000 Da by the change in SMA/P23MM from 2.90 to 15.40.

Number average molecular weight (Mn)

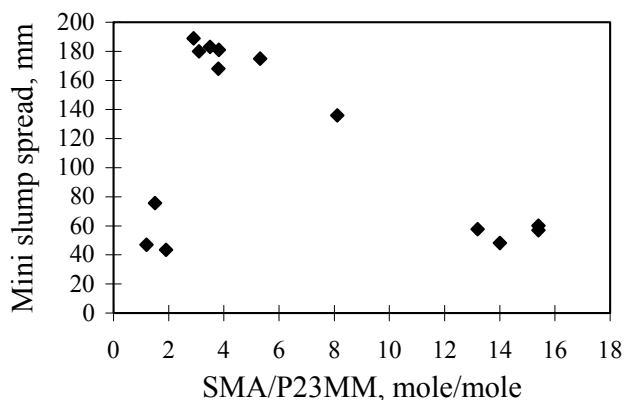The Mn of P(C–g–E)s according to the SMA/P23MM in P(C–g–E) synthetic formulations are

Fig. 8. The mini slump spreads of cement pastes admixed with P(C–g–E).
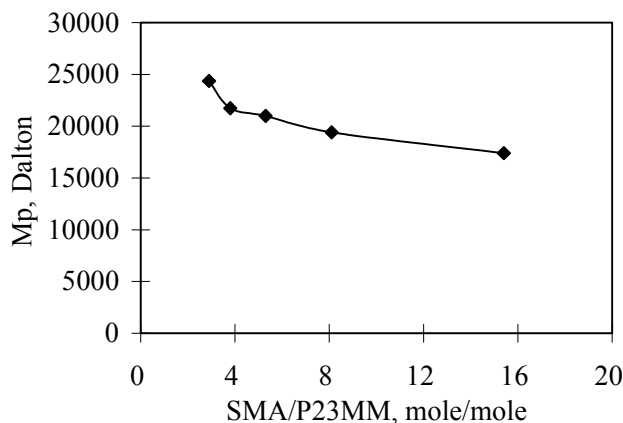

Fig. 9. Effect of SMA/P23MM on the Mp of P(C–g–E)s.

shown in Fig. 10. There is a small deflection around SMA/P23MM = 4.00, but the Mn of P(C–g–E)s are monotonously decreased from 21,000 Da to 16,000 Da by the change in SMA/P23MM from 2.90 to 15.40.
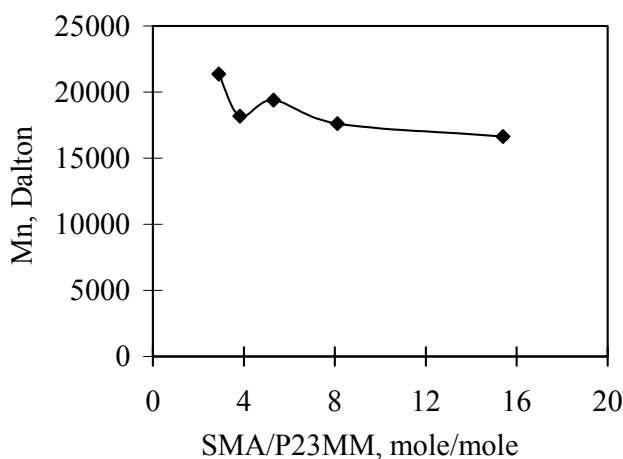

Fig. 10. Effect of SMA/P23MM on the Mn of the P(C–g–E)s.

Weight average molecular weight (Mw)

The Mw of P(C–g–E)s according to the SMA/P23MM in P(C–g–E) synthetic formulations are shown in Fig. 11. There is a little large point of deflection around SMA/P23MM = 4.00, but the Mw of P(C–g–E)s are very slightly decreased by the change in SMA/P23MM from 5.31 to 15.40.

Z average molecular weight(Mz)

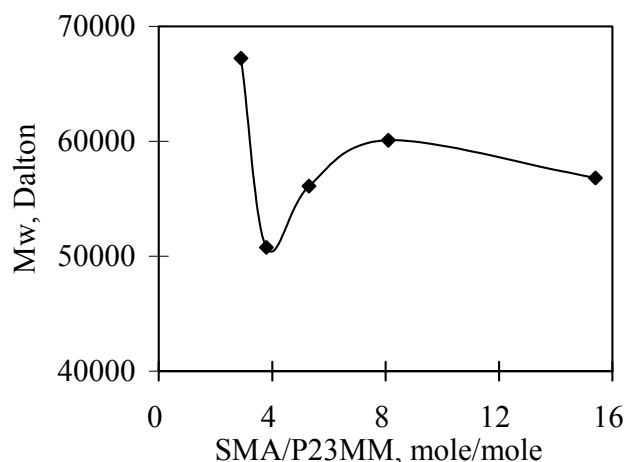The Mz of P(C–g–E)s according to the SMA/P23MM in P(C–g–E) synthetic formulations are shown in Fig. 12.

Fig. 11. Effect of SMA/P23MM on the Mw of P(C–g–E).

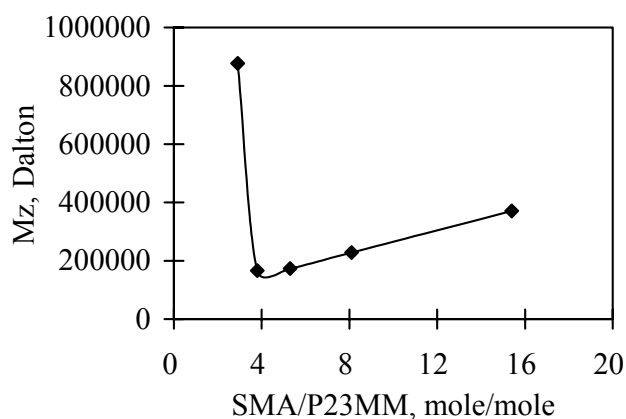Fig. 13. Effect of SMA/P23MM on the Mw/Mn of P(C–g–E)s.

Fig. 12. Effect of SMA/P23MM on the Mz of P(C–g–E).

The Mz of P(C–g–E)s are steeply decreased by the change in SMA/P23MM from 2.90 to 3.82. But the Mz of P(C–g–E)s are monotonously increased from 200,000 Da to 400,000 Da by the change in SMA/P23MM from 5.31 to 15.40.

Polydispersity(Mw/Mn)

The polydispersity of copolymers is calculated as Mw/Mn ratio [14]. Mw is more focused on the heavier molecules than on the lighter ones. So, the Mw is greater than the Mn in a polydisperse polymer. Also, Mz is more focused on the heavier molecules than Mw. In general, the relationship of Mn<Mw<Mz exists in a polydisperse polymer [14].

The Mw/Mn of P(C–g–E)s according to the SMA/P23MM in P(C–g–E) synthetic formulations are shown Fig. 13. The Mw/ Mn of P(C–g–E) decreased by the change in SMA/P23MM from 2.90 to 5.31. But the Mw/Mn of P(C–g–E)s are not affected by the change in SMA/P23MM from 8.11 to 15.40.
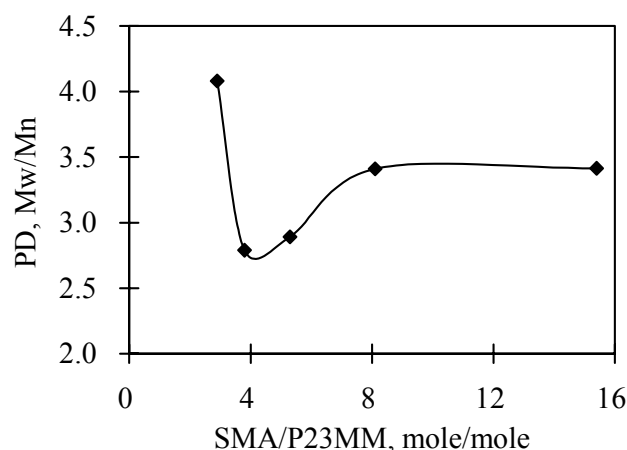
We can conclude that the change in SMA/P23MM in P(C–g–E) synthetic formulations has greater influence on the heavier molecules than on the lighter ones. Also, when P23MM which has polyethylene-glycol group {–(CH₂ CH₂–O)₂₃–} adjacent to SMA which has carboxylic group{–COONa} is relatively increased, the heavier molecules in P(C–g–E) are largely increased. But when SMA adjacent to P23MM is increased, the Mw and the Mz are slowly increased.

Meanwhile, for many addition polymers, Mw/Mn lies in the range 1.5~5.0. Typical range of Mw/Mn in grafted polymer is 20~50 [11]. From this rule and the molecular structures of monomers, we can conclude that the P(C–g–E) is polymerized by addition reaction.

From these results, we can conclude that when the SMA/P23MM in P(C–g–E) synthetic formulations is below 3.82, the P(C–g–E) may be mainly polymerized by addition of P23MM. But when the SMA/P23MM in P(C–g–E) synthetic formulations is more than 5.31, the P(C–g–E) may be mainly polymerized by addition of SMA.

Also, considering the data shown on Fig. 8 to Fig. 13, we can see that the dispersion ability and stability of P(C–g–E) in cement paste has a strong relationship with the molecular weights of the polymer. Therefore, in order to use P(C–g–E) as a superplasiticizer in cement, the SMA/P23MM in P(C–g–E) synthetic formulation has to be adjusted to 3.50~5.50. In this range of SMA/P23MM, the P(C–g–E) may be balanced with the poly(ethyleneglycol) groups and the carboxylic groups. So the P(C–g–E) acts as a good dispersing agent in a cement paste [6,7].

The physical properties of cement by the change of SMA/P23MM

Consistency (W/C)

The normal consistencies (W/C) of cement pastes mixed with P(C–g–E)s are plotted against the change in SMA/P23MM ratio in P(C–g–E) synthetic conditions (Fig. 14). When the SMA/ P23MM in P(C–g–E) is changed from 2.90 to 3.82, the W/C is decreased from 22.00 to 20.45. But when the SMA/ P23MM in P(C–g–E) is changed from 3.82 to 8.11, the W/C is increased from 20.45 to 23.56. When the SMA/ P23MM in P(C–g–E) is changed from 8.11 to 15.40, the W/C is not changed. From this result, we can also conclude that an excessive increase of SMA or P23MM in P(C–g–E) synthetic conditions drops down the dispersion ability of P(C–g–E) in cement paste.
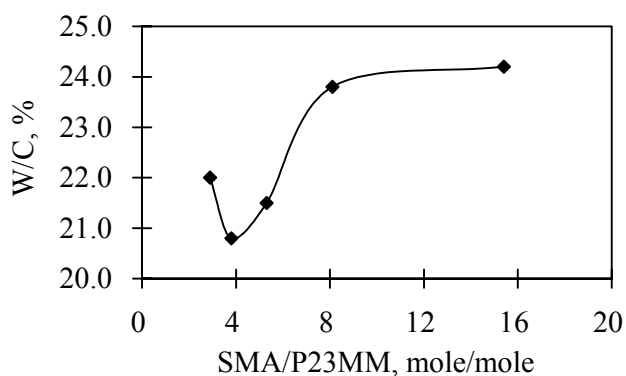

Fig. 14. The normal consistencies of cement pastes by changing SMA/P23MM in P(C–g–E).

Setting time

The variations of the initial and the final setting times of cement pastes mixed with P(C–g–E)s by changing the SMA/P23MM in P(C–g–E) synthetic conditions are shown in Figs. 15 and 16. When the SMA/ P23MM in P(C–g–E) synthetic condition is increased from 2.90 to 5.31, the initial and the final setting times of cement pastes are shorten down. But when the SMA/ P23MM in P(C–g–E) synthetic condition is increased to more than 5.31, the setting times of paste are not shorten down any more.

Conclusions

The comb type P(C–g–E)s were synthesized with different feed monomer formulations with SMA,
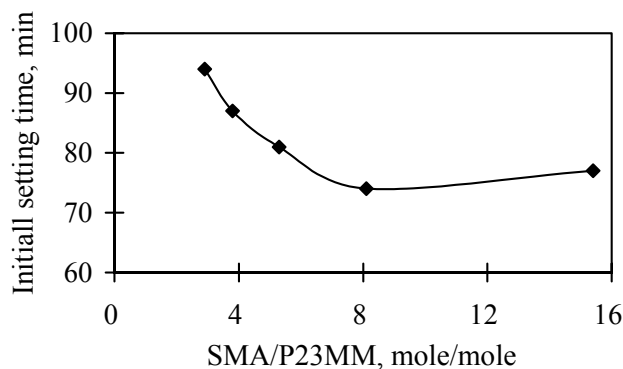

Fig. 15. The initial setting times of cement pastes admixed with P(C–g–E)s.
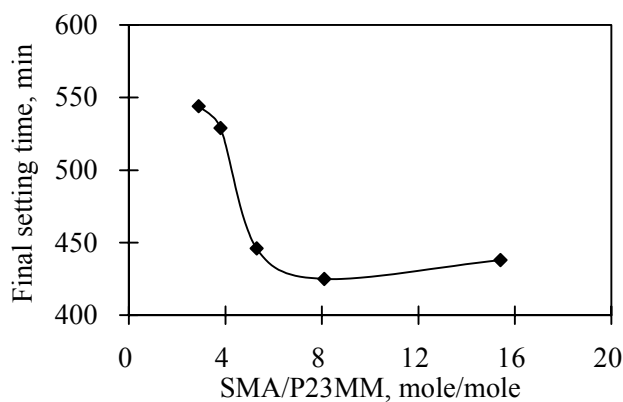

Fig. 16. The final setting times of cement pastes admixed with P(C–g–E)s.

SMS, MA, P23MM. The relationship between the synthetic formulation of the P(C–g–E) and the molecular weights (Mp, Mn, Mw, Mz and Mw/Mn) of the polymer and the dispersion ability and stability of the admixtures in cement paste were analyzed. From those results we can draw the following conclusions:

- The optimal formulation of P(C–g–E) synthesis for cement concrete admixture was found to be P23MM 17 mol.%: SMS 10 mol.%: MA 8 mol.%: SMA 65 mol.%: APS 0.2%.
- The SMA/P23MM in P(C–g–E) synthetic formulation is related to the performance of P(C–g–E) in cement paste. The optimal range of the SMA/ P23MM in the formulation as a cement superplasticizer is 3.50~5.50.
- The SMA/P23MM in P(C–g–E) synthetic formulation is related to the molecular weights of P(C–g–E). The SMA/P23MM in the formulation is more related to the Mz and the Mw than the Mn and the Mp of P(C–g–E).

References

1. Mitsuo Kinoshita, Toshio Yonezawa and Yasuo Yuki, Chemical structure and performance of a new type high-range water-reducing agent for ultra high strength concrete, Cement/Concrete Ronbunshu 47 (1993) 196-201 (in Japanese).
2. Kazuo Yamada, Tomoo Takahashi and Masato Matsuhisa, Effect of chemical structure and water cement ratio on the fluidity of cement paste added with polycar-boxylate type dispersant, Cement/Concrete Ronbunshu 52 (1998) 158-164 (in Japanese).
3. A. Ohta, T. Sugiyama and Y. Tanaka, Fludizing mechanism and application of polycarboxylate based super- plasticizers, V.M. Malhotra ed. 5th CANMET/ACI Int'l conf. on super-plasticizer and other chemical admixture in concrete (1997) 359-378.
4. Kazuo Yamada, Shoichi Ogawa, Shunsuke Hanehara, Controlling of the adsorption and dispersing force of polycarboxylate type super-plasticizer by sulfate ion con-centration in aqueous phase, Cem Concr Res 31 (2001) 375-383.
5. Mitsuo Kinoshita, Yasuo Yuki, Kazuhide Saitou, and Tomoo Takahashi, Methacrylic type water soluble polymer as high-range water reducing agent for ultra high-strength concrete, Kobunshi Ronbunshu 52 (6) (1995) 357-363 (in Japanese).
6. Kazuo Yamada, Tomoe Takahashi, Shunsuke Hanehara, Makoto Matsuhisa, Effects of the chemical structure on the properties of poly-carboxylate type superplasticizer, Cem Concr Res 30 (2000) 197-207.
7. Mitsuo Kinoshita, Yasuo Yuki, Yoshimasa Miura, and Tomoo Takahashi, Synthesis of methacrylic water soluble polymer using sodium methallylsulfonate as molecular weight control agent - Properties as cement dispersing agent-, Kobunshi Ronbunshu 52 (1) (1995) 33-38 (in Japanese).
8. Etsuo Sakai, Kazuo Yamada and Akira Ohta, Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan, Journal of Advanced Concrete Technology 1 (1) (2003) 18-25.
9. Heon-young Cho, Oh-jin Kim, Jung-mok Suh, Physical properties and characteristics of a cement admixture of poly(carboxylate-g-ethylene oxide) by changing the mole ratio of ester group, carboxyl group and ethyleneoxide group, The 15-th Symposium on CHEMICAL ENGINEERING Kyushu(Japan)-Taejon/Chungnam (Korea) (2002) 407-408.
10. Heon-young Cho, Tae-sook Park Jung-mok Suh, Physical properties and characteristics of a cement admixture of poly(carboxylate-g-ethyleneoxide) by changing the reaction temperature, the reaction time and the initiator concentration, The 15-th Symposium on CHEMICAL ENGINEERING Kyushu(Japan)-Taejon/Chungnam(Korea) (2002) 90-91.
11. Xia-yong Mei, Heon-young Cho, Tae-sook Park, Jung-mok Suh, Fang Yun, Effects of structures of polycarboxylates grafted polyethylene oxide on their performance as cement additives, The 14-th Symposium on CHEMICAL ENGINEERING Kyushu(Japan)-Taejon/ Chungnam (Korea) (2001) 217-218.
12. Yong-mei Xia, Heon-young Cho, Jung-mok Suh, Xiao-ya Liou,Yun Fang, Relationship between structure and performance of polyacrylates used as chelator in detergents, J. Ind. Eng. Chem. 8(2) (2002) 108-113.
13. Park, S.H., A statistical process optimization technique, 35-th Annual Quality Congress Transactions, Internal Conference for Quality Control, Sanfrancisco, May(1981) 26-29.
14. Heon-young Cho, Jung-mok Suh, Effects of the synthetic conditions of poly{carboxylate-g-(ethylene glycol) methyl ether} on the dispersibility in cement paste, Cem Concr Res, 35(203) 891-899.