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Cement and Concrete Research 35 (2005) 891–899

Cement and Concrete Research

Effects of the synthetic conditions of poly{carboxylate-g-(ethylene glycol) methyl ether} on the dispersibility in cement paste

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Received 10 October 2003; accepted 6 July 2004

Abstract

The objective of this study was to find the relationship between the poly{carboxylate-g-(ethylene glycol) methyl ether} [P(C-g-E)] synthetic conditions and the dispersibility in cement paste. The P(C-g-E)s, which have superior dispersion ability and stability in cement concrete, were synthesized by changing the reaction temperature (R.T.), the reaction time (R.H.) and the initiator concentration (I.C.). The molecular weights and the yields of P(C-g-E)s were analyzed by GPC. Also, the dispersion ability and dispersion stability of P(C-g-E)s in cement paste were tested by the mini slump spread testing method. The dispersibilities of P(C-g-E) in cement paste are strongly affected by the reaction temperature and the reaction time, but weakly affected by the APS dosage in the polymer synthesis. In addition, the dispersibilities of P(C-g-E) in cement paste are more affected by the heavier molecules than the lighter ones in the polymer.

Keywords: Dispersion; Admixture; Cement paste; Polymers; Stability

1. Introduction

The comb-type poly{carboxylate-g-(ethylene glycol) methyl ether} [P(C-g-E)] was developed as a cement superplasticizer at first in 1990s in Japan [1]. The P(C-g-E) is composed of polycarboxylate grafted with poly(ethylene glycol)methyl ether. The P(C-g-E) has special properties among the other cement superplasticizers, such as the easiness of molecular structure change, the various properties by controlling the molecular weight and the structure, the excellent dispersion ability and stability and the small dosage to fit dispersibility in cement paste [2–5]. In particular, the superior dispersion stability of P(C-g-E) in cement paste has clearly solved the largest problems raised by the other superplasticizers. Hence, recently, the demand of P(C-g-E) in the concrete admixture industry is sharply increased in the world [4,5].

In this research, to find the effect of P(C-g-E) synthetic conditions on the dispersibility in cement paste, the P(C-g-E)s made up four components: Sodium methacrylic acid (MAcid), methyl acrylate (MA), sodium methallyl sulfonate (SMS) and poly(ethylene glycol) methyl ether methacrylate were synthesized by changing the reaction temperature (R.T.), the reaction time (R.H.) and the initiator concentration (I.C.). The molecular weight and the yield of P(C-g-E)s were analyzed by GPC. In addition, the dispersion ability and the dispersion stability of P(C-g-E)s in cement paste were tested by the mini slump spread testing method, and the relationship between the synthesis conditions and the physical properties in cement paste of the P(C-g-E)s were investigated.

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doi:10.1016/j.cemconres.2004.07.002

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

Methacrylic acid (MAcid), sodium methallyl sulfonates (SMS), methyl acrylate (MA) and poly(ethylene glycol) methylether methacrylate (P23MM) were supplied from Aldrich Chemical.

Ammonium persulfate (APS) and NaOH were supplied from Oriental Chemical.

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

2.1.2. P(C-g-E)s

The P(C-g-E)s were synthesized in the formulation of MA/P23MM/SMS/SMA=8:13:10:69, in mol ratio [6,7]. We designed the reaction conditions for P(C-g-E) synthesis as Tables 1 and 2 by the orthogonal testing method $L_9(3^4)$ to find the effect of the polymer synthetic conditions on the cement dispersibilities.

The polymers have been synthesized in the same method as in the published papers [6–9] at pH 7.0–8.0. The estimated chemical structure of the P(C-g-E) is shown in Scheme 1.

2.1.3. Cement

The ordinary portland cement produced from S company in Korea was used. The chemical components and the physical properties of the cement were shown in Tables 3 and 4.

2.2. Methods

2.2.1. GPC analysis

GPC, model DM400 made by Vicotek, attached with column OHpak SB-803 HQ was used. The elution solvent was 0.1 N $NaNO_3$ aqueous solution, and the standard sample for calibration was PEG.

2.2.2. Dispersion ability

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

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

Factors	Level		
	0	1	2
Rxn. temperature (R.T.) [°C]	50	70	90
Rxn time (R.H.) [h]	5	7	9
APS (I.C.) [%]	0.1	0.5	1.0

Table 2
The synthesis conditions and the solid contents of P(C-g-E)s

Sample number	Factor/Level			Solid content
	R.T. (°C)	R.H. (h)	I.C. (%)	(%)
1	50	5	0.1	52.59
2		7	0.5	53.27
3		9	1.0	53.41
4	70	5	1.0	54.63
5		7	0.1	54.16
6		9	0.5	54.18
7	90	5	0.5	54.80
8		7	1.0	54.11
9		9	0.1	54.03

Cement was mixed with water (w/c—30%:25%) added with 1.2% P(C-g-E) solution of the cement weight. The P(C-g-E) solutions were controlled to solid content 20% before using. The cement paste was vigorously mixed for 5 min by hand 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, and the mini slump spread of the paste was measured by the width of the spreaded paste when the mini slump cone was raised up [8,9].

2.2.3. Dispersion stability

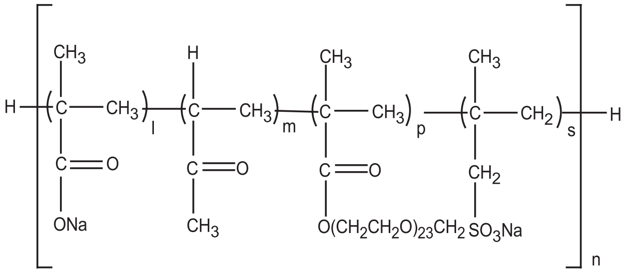
The dispersion stability of P(C-g-E) in cement paste was measured by the variations of the mini slump spread during the elapsed time. The mini slump spread testing method and the room conditions for the dispersion stability test are same with those of the dispersion ability test. But the cement paste was stored in humidity chamber controlled at 20–25 °C, with relative humidity over 90%. The mini slump spread was checked regularly (on 15, 30, 45, 60, 90 and 120 min after the first test) for 2 h. Before the test, the paste was hardly mixed for 1 min by hand [8,9].

3. Results and discussion

3.1. GPC analysis

3.1.1. Yields of P(C-g-E)s

The GPC analysis result of P(C-g-E) that has been synthesized at reaction temperature (R.T.) 50 °C, reaction



Scheme 1. The estimated chemical structure of P(C-g-E).

Table 3
Chemical composition of ordinary portland cement

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Wt.%	21.3	5.44	3.15	61.27	3.15	2.2

time (R.H.) 5 h and initiator concentration (I.C.) 0.1% is shown in Fig. 1.

In this figure, we can see the large second, third and fourth peaks at over 9.0 retention volume (R.V.). From the retention volume and the molecular weight analysis by GPC, we can confirm that the second–fourth peaks correspond to the unreacted monomers: SMS, SMA, MA. The yield of P(C-g-E) appeared to be 30.9% in this reaction condition, from the GPC analysis.

Fig. 2 is the GPC analysis result of P(C-g-E) that is synthesized at R.T. 70 °C, R.H. 9 h, I.C. 0.5%.

Comparing with Fig. 1, the P(C-g-E) synthesized with the Fig. 2 condition has less the unreacted monomers than that of the one of Fig. 1. The yield of P(C-g-E) is 92.1% in this reaction condition. Thus, we can see that the yields of P(C-g-E) is very largely changed by the synthesis conditions.

Fig. 3 is the yields of P(C-g-E)s that were synthesized by changing the reaction conditions. According to the increase of the R.T., R.H. and I.C., the yields of P(C-g-E)s are increased. In addition, in the condition of R.T. over 70 °C, R.H. over 7 h and I.C. over 0.5%, it appeared that the yields of P(C-g-E)s are reached 90–92%.

3.1.2. Molecular weights of P(C-g-E)s

3.1.2.1. Number average molecular weight (Mn). Mn is the simple counting average in which the mass of the sample, expressed in atomic mass unit or daltons, is divided by the number of molecules that it contains [10]. The Mn is defined by

$$Mn = \Sigma N_i M_i / \Sigma N_i \quad (1)$$

In here, N_i is the number of molecules of the ith kind. M_i is the molecular weight of the ith kind.

The Mn variations of P(C-g-E)s by changing the reaction conditions are shown in Fig. 4. By changing the reaction temperature from 50 to 90 °C, the Mn values of P(C-g-E)s are continuously decreased from 12,400 to 10,100 Da. This means that when the reaction temperature in P(C-g-E) synthesis is heated up, the number of lighter weight molecules is increased. This trend is different to the general trend of polymer synthesis. Ordinarily, the Mn of the polymer is increased by the increase of the reaction temperature.

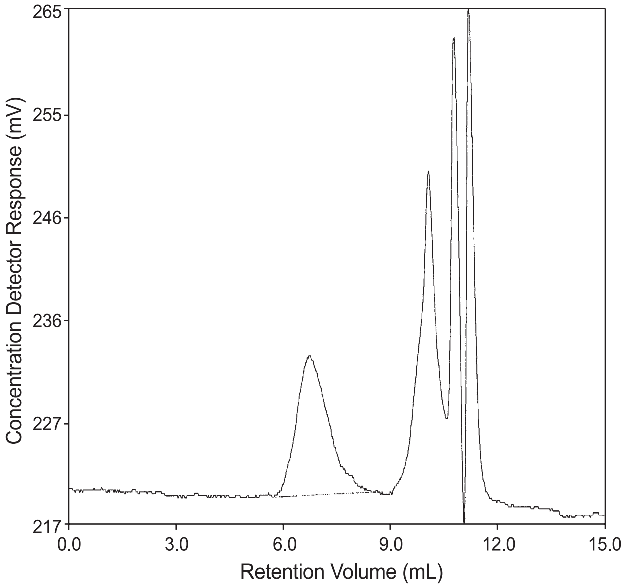


Fig. 1. GPC result of P(C-g-E) (R.T.: 50 °C; R.H.: 5 h; I.C.: 0.1%).

In addition, by increasing the reaction time from 5 to 9 h, the Mn of P(C-g-E)s are slowly decreased. But when the initiator concentration in the reaction condition is increased from 0.1% to 1.0%, the Mn of P(C-g-E) is a little increased.

From these results, we can see that the Mn of P(C-g-E) is strongly affected by the reaction temperature but weakly affected by the reaction time and the initiator content in the P(C-g-E) synthesis.

3.1.2.2. Weight average molecular weight (Mw). The Mw is defined by

$$Mw = \Sigma w_i M_i / \Sigma w_i = \Sigma N_i M_i^2 / \Sigma N_i M_i \quad (2)$$

As we can see from Eq. (2), the Mw is focused more on the heavier molecules than on the lighter ones. Hence, the Mw is greater than the Mn in polydisperse polymer [10,11].

The Fig. 5 is the Mw analysis results of P(C-g-E)s by GPC. In contrast to Mn, the Mw values of P(C-g-E)s are a little increased by warming up the reaction temperature from 50 to 70 °C, but when the reaction temperature in P(C-g-E) synthesis is heated up more than 70 °C, the Mw of the polymer is deeply decreased.

In addition, when the reaction time in P(C-g-E) synthesis is extended from 5 to 7 h, the Mw of the polymer is a little increased, but when the time is longer than 7 h, Mw of the one is a little decreased. When the initiator concentration is

Table 4
Physical properties of ordinary portland cement

Specific gravity	Fineness (cm^2/g)	Setting time		Compressive strength (kgf/cm^2)		
		Initial (min)	Final (h/min)	3 days	7 days	28 days
3.15	3260	241	08:19	217	296	372

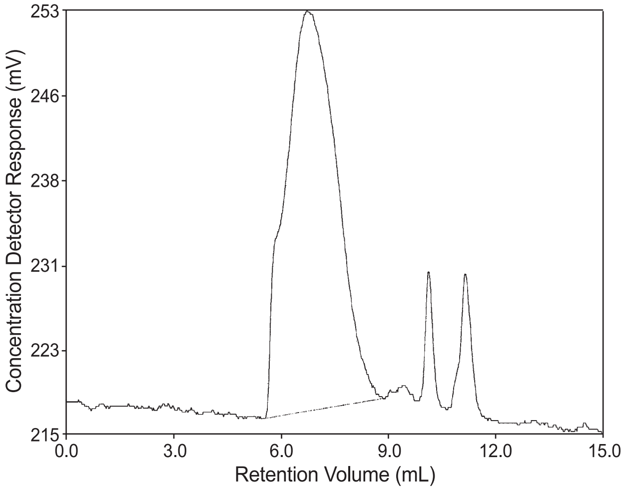


Fig. 2. GPC result of P(C-g-E) (R.T.: 70 °C; R.H.: 7 h; I.C.: 1.0%).

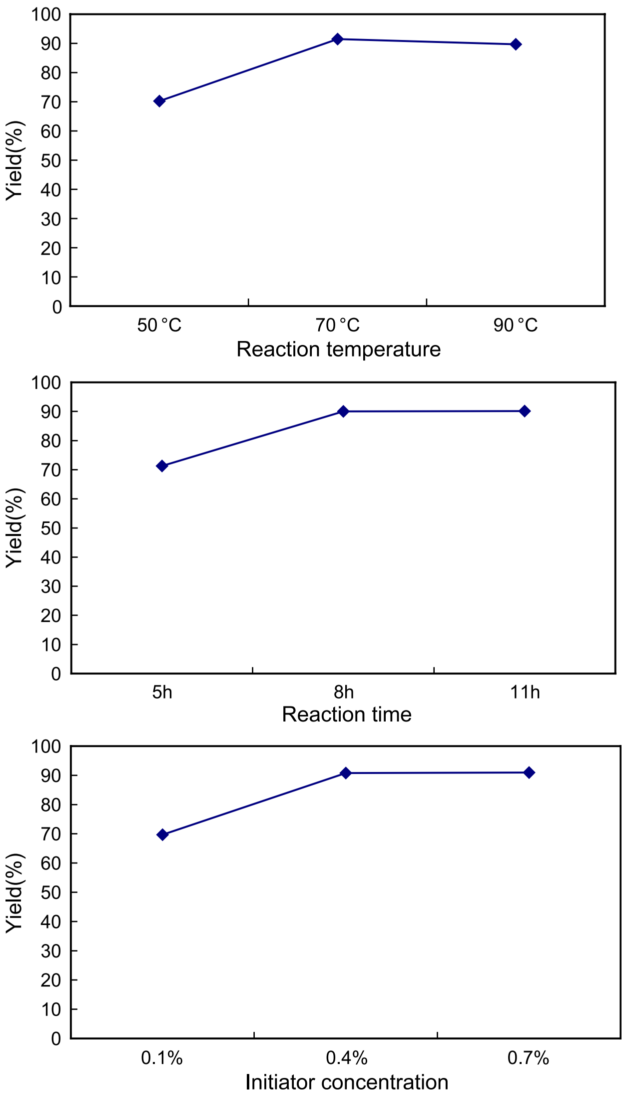


Fig. 3. The yields of P(C-g-E)s by changing the reaction conditions.

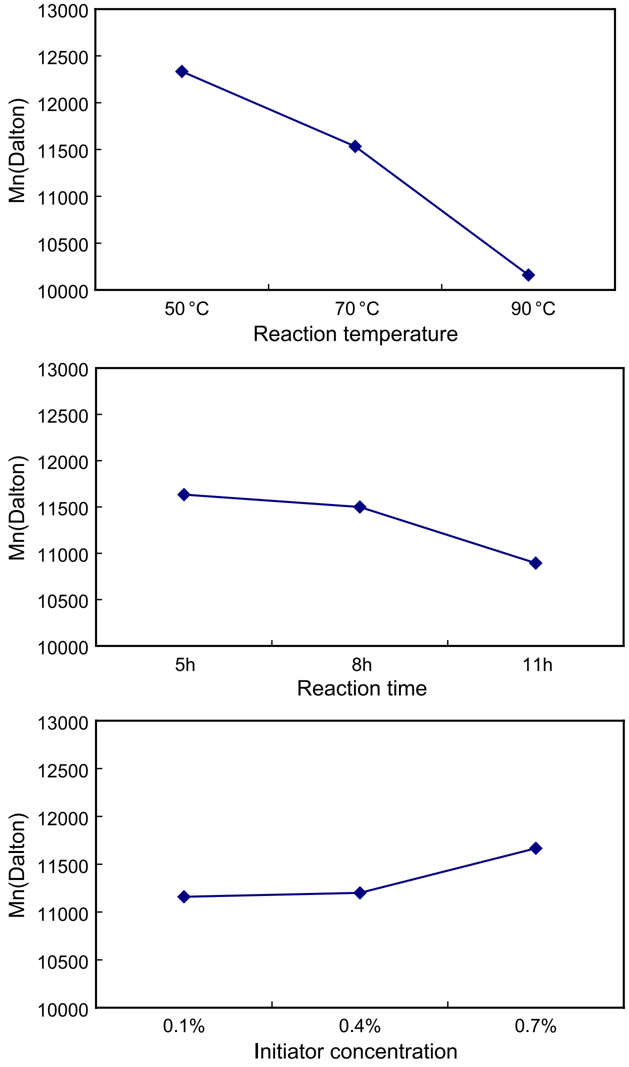


Fig. 4. The Mn of P(C-g-E) by changing the reaction conditions.

increased in P(C-g-E) synthesis from 0.1% up to 1.0%, the Mw of the polymer is increased from 16,100 to 18,600 Da. This means that the heavier molecules more than the lighter ones are increased in the P(C-g-E) synthesis condition at R.T. 70 °C, R.H. 7 h and I.C. 1.0%.

The trend that the Mw of P(C-g-E) is increased according to the increase of APS concentration is in contrast to the general trend that the Mw of polymer is decreased when the initiator concentration is increased in polymer synthesis. Hence, we need to study more about this in the future.

3.1.2.3. Z average molecular weight (Mz). The Mz is defined by

$$\mathrm{Mz} = \Sigma N_i M_i^3 / \Sigma N_i M_i^2 \tag{3}$$

As we can see from the Mz definition, Mz is focused more on the heavier molecules than at the Mw. Hence, the relationship of Mn<Mw<Mz exists in polydisperse polymer. And the difference among these three molecular weights are

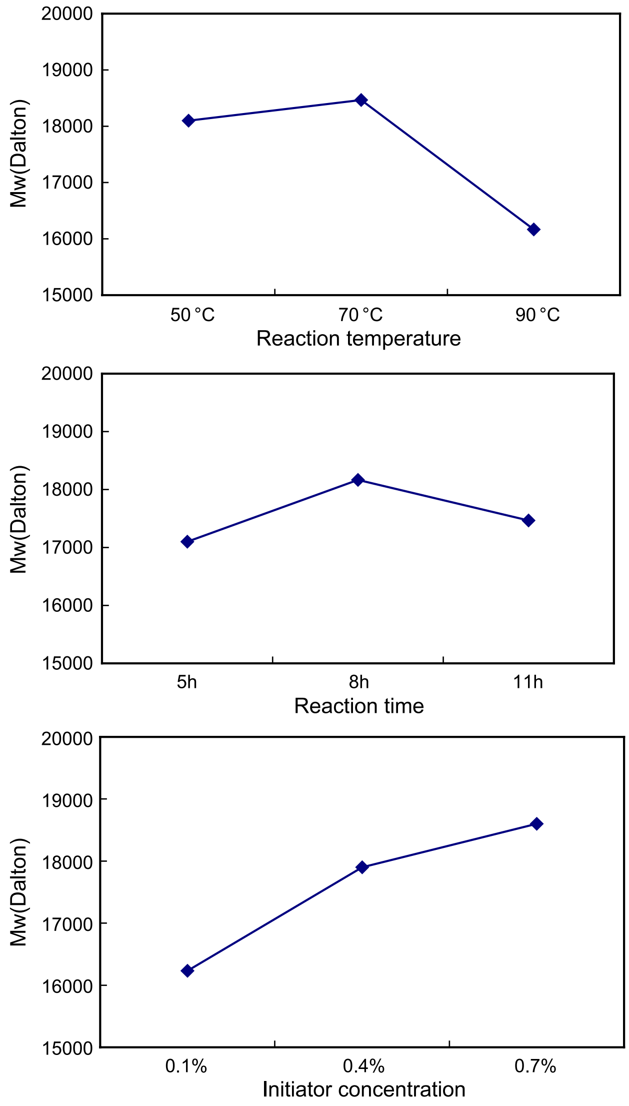


Fig. 5. The Mw of P(C-g-E) by changing the reaction conditions.

representative of the degree of inhomogeneity in polymer [11].

From Fig. 6, which is the Mz analysis results of P(C-g-E)s by changing the reaction conditions, we can see that the trends in the Fig. 6 are same as the ones of the Fig. 5.

3.1.2.4. Polydispersity index (P.I.=Mw/Mn). For many addition polymers, P.I. lies in the range 1.5–2.0. The P.I. is 1.0 for a monodisperse polymer. Typical range of P.I. in grafted polymer is 20–50 [11].

In this syntheses, the P.I. of P(C-g-E)s appeared to lie in the range 1.27–1.64. Thus, the reason that the P.I. of those polymers are very low compare with that of the typical branched polymer is explained as follows. The P(C-g-E) is synthesized by the addition polymerization of P23MM, which has an acryl group in the poly(ethylene glycol) methyl ether with the other acryl groups (SMA, MA) and allyl group (SMS).

The P.I. values of P(C-g-E)s synthesized in different reaction conditions are shown in Fig. 7. The P.I. values of the polymers increased according to the increase of reaction temperature from 50 to 70 °C, but when the R.T. is increased up to 90 °C, the P.I. is a little decreased. The P.I. values of P(C-g-E)s are increased by the increase of R.H. or I.C. in the reaction condition.

From those molecular weight results, we can conclude that the P(C-g-E)s have more much heavier molecules than do lighter ones when the polymers are synthesized at R.T. 70 °C, R.H. 9 h and I. C. 0.5%.

3.2. Dispersion abilities of P(C-g-E)s in cement paste

To investigate the dispersion abilities of P(C-g-E)s that were synthesized in different reaction conditions in cement paste, the mini slump spreads of the cement paste added with 1.2% P(C-g-E)s of cement weight were tested. The mini slump spread results are shown in Fig. 8.

As a whole, the mini slump spreads of the cement pastes made with w/c 30% are larger, about 40 mm, than the those of the pastes made with w/c 25%. The dispersion ability of

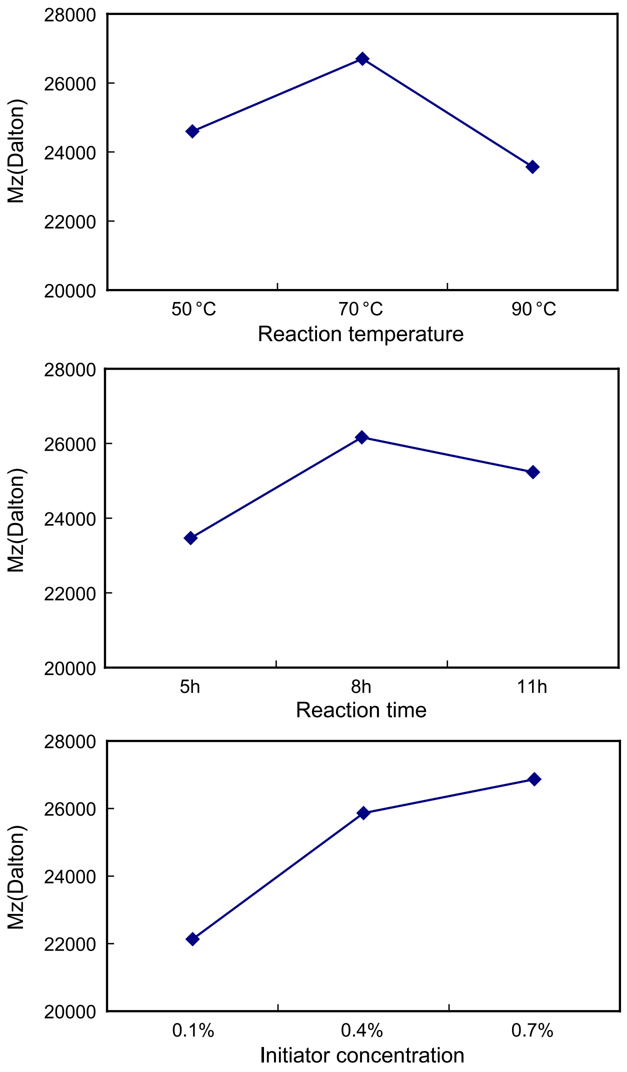


Fig. 6. The Mz of P(C-g-E) by changing the reaction conditions.

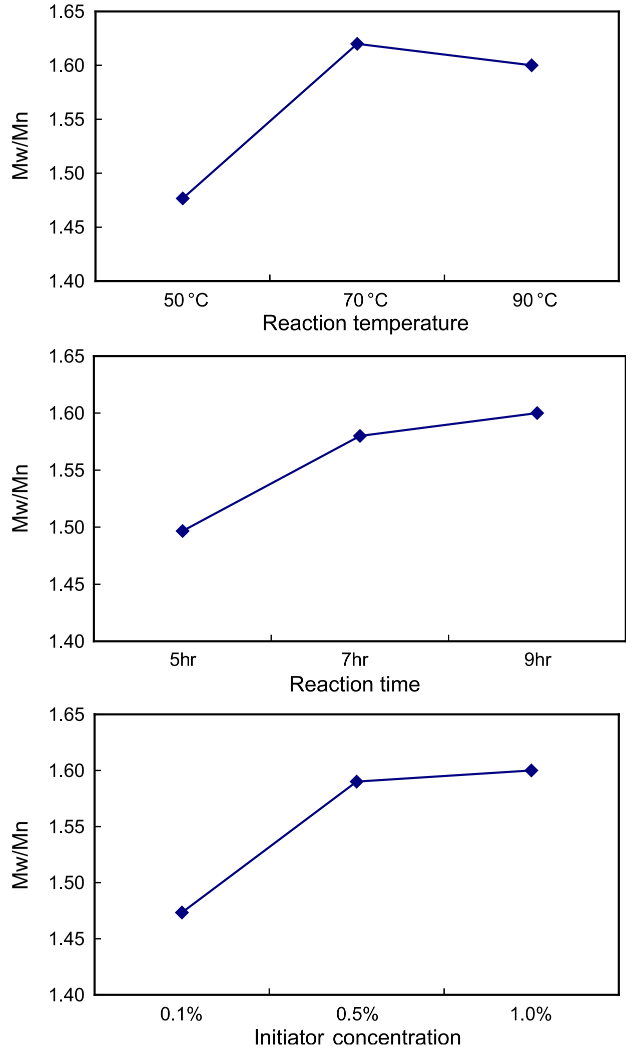


Fig. 7. The Mw/Mn of P(C-g-E) by changing the reaction conditions.

P(C-g-E) in the cement paste is increased when the polymer is synthesized at above 70 °C. When the reaction time in the P(C-g-E) synthesis is increased, the dispersion ability of P(C-g-E) in cement paste is also increased. But the change of initiator concentration in P(C-g-E) synthesis has nearly no effect on the dispersion ability of the polymer in cement paste[8,9].

3.3. Dispersion stabilities of P(C-g-E)s in cement paste

3.3.1. Dispersion stabilities of P(C-g-E)s in w/c 30% cement paste

To investigate the dispersion stabilities of P(C-g-E)s that are synthesized in different reaction conditions in the cement paste, the changes of the mini slump spread are regularly measured for 120 min after mixing the w/c 30% cement paste. The results are shown in Fig. 9.

The P(C-g-E)s that were synthesized at R.T. 50 °C and R.H. 5 h have lower dispersion abilities than do the other ones in cement paste but have same dispersion stabilities as the other ones. From this phenomena and the P(C-g-E) yield results, we can induce that the monomers that had not reacted in the P(C-g-E) synthesis have much effect on the dispersion ability but have no effect to the dispersion stability in cement paste [8,9].

The P(C-g-E)s that were synthesized at 70 and 90 °C have almost same dispersion abilities and stabilities in cement paste, but the P(C-g-E) synthesized at 70 °C has a little better dispersion stability than that of the one synthesized at 90 °C.

In addition, the P(C-g-E)s which were synthesized for 7 and 9 h have almost same dispersion abilities and stabilities in cement paste, but the P(C-g-E) synthesized for 9 h has a little better dispersion stability than that of the one synthesized for 7 h.

The P(C-g-E)s that were synthesized in APS concentrations 0.1%, 0.5% and 1.0% have almost same dispersion abilities and stabilities in cement paste, but the P(C-g-E) synthesized in APS 0.1% has a little worse dispersion stability than that of the other ones. In addition, like the result in the mini slump spread test, the effect of APS

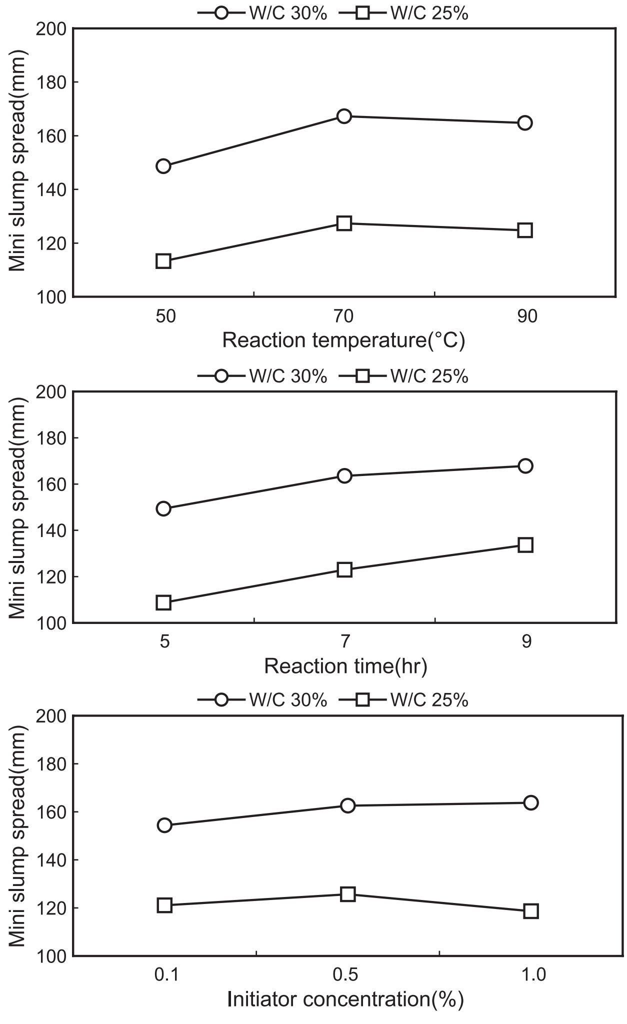


Fig. 8. Comparison of dispersion ability of cement paste added with P(C-g-E)s.

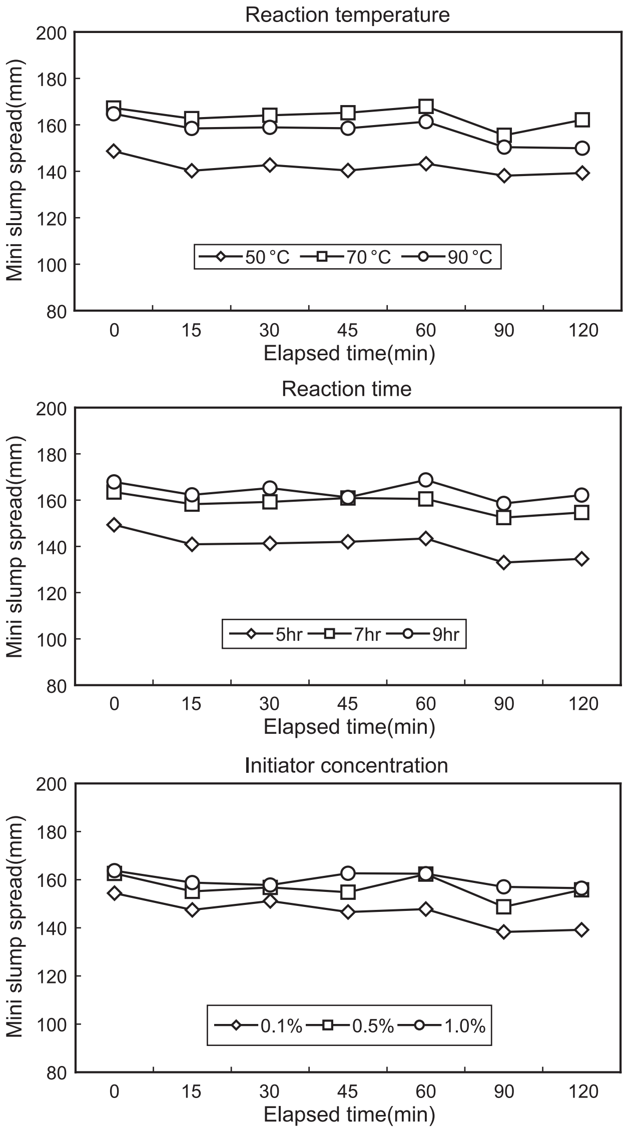


Fig. 9. The dispersion stability of cement paste added with P(C-g-E) at w/c=30%.

concentration on the dispersion stability of P(C-g-E) in w/c 30% cement paste is negligible.

3.3.2. Dispersion stabilities of P(C-g-E)s in w/c 25% cement paste

To more clearly verify the dispersion stability of P(C-g-E) in cement paste, the changes of the mini slump spread were tested in the severe condition of cement paste, which was made with w/c 25%. The testing results are shown in Fig. 10.

In the case of w/c 30% cement paste, the changes of the mini slump spread for 120 min after mixing of water were not so much. But in w/c 25% cement paste, the changes of the mini slump spread for the elapsed time were very large.

The P(C-g-E)s that were synthesized at R.T. 50 °C and for R.H. 5 h have a little lower dispersion abilities in cement paste than do the other ones that were synthesized in different conditions. But the dispersion stabilities at w/c 25% cement paste were very bad. That is, the mini slump spread losses of cement paste added with those were very large. From these results, we can see that the monomers that had not reacted in the P(C-g-E) synthesis have a little affect to the dispersion ability but have much affect to the dispersion stability at the low-w/c cement paste.

The P(C-g-E)s that were synthesized at 70 and 90 °C have almost same dispersion abilities at the low-w/c cement paste, but the P(C-g-E) synthesized at 70 °C has a better dispersion stability than do the polymer synthesized at 90 °C. From these results and the Mw analysis result of the polymer, we can guess that the heavier molecules in P(C-g-E) have more effect to increase the dispersion stability than do the lighter ones at the low-w/c cement paste.

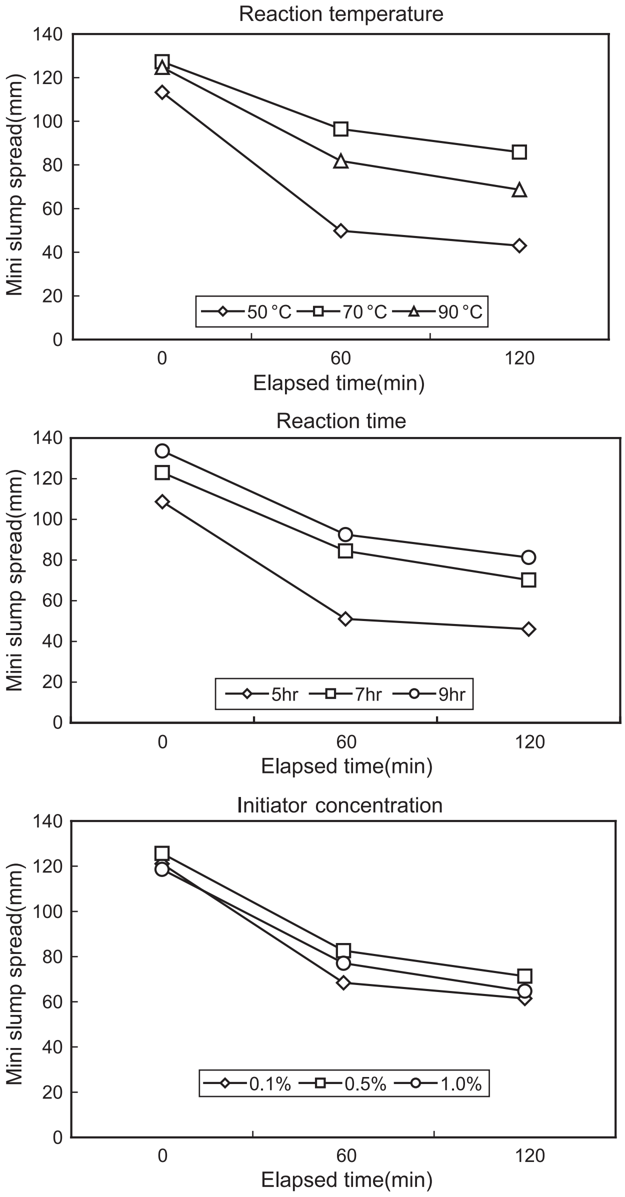


Fig. 10. The dispersion stability of cement paste added with P(C-g-E) at w/c=25%.

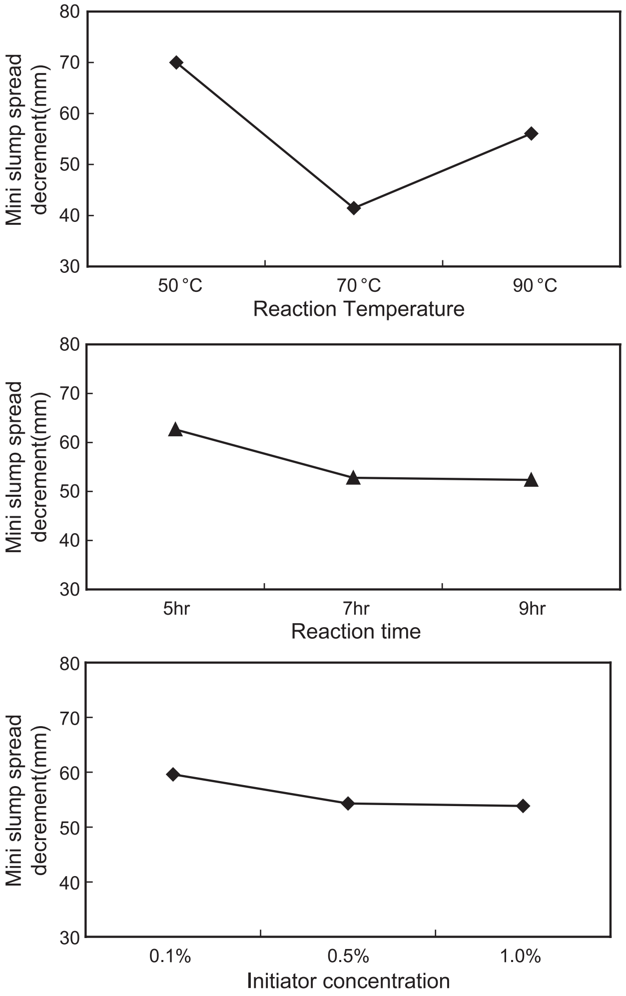


Fig. 11. Mini slump spread decrements of w/c 25% cement paste by changing the reaction conditions of P(C-g-E).

In addition, the P(C-g-E)s that were synthesized for 7 and 9 h have almost same dispersion abilities and stabilities at the low-w/c cement paste. The P(C-g-E)s that were synthesized in APS concentrations 0.1%, 0.5% and 1.0% have almost the same dispersion abilities and stabilities at w/c 25% cement paste.

Like the results of dispersion stabilities at w/c 30% cement paste, the effect of APS concentration to the dispersion stability of P(C-g-E) at w/c 25% cement paste is also negligible.

To clarify the dispersion stability of P(C-g-E) at the low-w/c cement paste, the mini slump spread decrements of cement paste added with P(C-g-E) from the mixed time to the 120 min elapsed time are shown in Fig. 11. From these results, we can see that the decrement of the mini slump spread for 120 min is strongly affected by the reaction conditions in the P(C-g-E) synthesis. The P(C-g-E) that is synthesized at 70 °C has the least decrement of the mini slump spread in the cement paste for 120 min. From this result, we can suggest that the decrements of the mini slump spread at the low-w/c cement paste has a deep relationship with the heavier molecules in P(C-g-E), as mentioned at above [12].

When the reaction time and the APS concentration in P(C-g-E) synthesis are increased, the decrements of the mini slump spread in cement paste added with the polymers are decreased even though the degree of those are very low.

4. Conclusion

To find the relationship between the P(C-g-E) synthetic conditions and the dispersibility in cement paste, the P(C-g-E)s that have superior dispersion ability and stability in cement concrete were synthesized by changing the reaction temperature, the reaction time and the initiator concentration. The molecular weights and the yields of P(C-g-E)s were analyzed by GPC. In addition, the dispersion ability and the dispersion stability of P(C-g-E) in cement paste were tested by the mini slump spread testing method. From this research, we can get some conclusions as follows.

(1) The dispersion ability and the dispersion stability of P(C-g-E) in cement paste are strongly affected by the reaction temperature and reaction time, but weakly affected by the APS dosage in the polymer synthesis.
(2) The dispersion ability and the dispersion stability of P(C-g-E) in cement paste are more affected by the heavier molecules than by the lighter ones in the polymer. Hence, the dispersibilities of P(C-g-E) are increased by the increasing of Mw/Mn in that polymer.
(3) The optimum reaction condition in this P(C-g-E) synthesis as a cement superplasticizer is reaction temperature 70 °C, reaction time 9 h and initiator (APS) concentration 0.5%.

Acknowledgements

This work was partly supported by the RRC/NMR program of KOSEF in Kongju National University.

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