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Slump loss control of cement paste by adding polycarboxylic type slump-releasing dispersant

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Abstract

A polycarboxylic type slump-releasing dispersant, which is a copolymer of maleic anhydride and acrylic acid (MA-co-AA) with an average molecular weight of 800, was used to compensate the slump loss of cement paste by naphthalene sulfonated formaldehyde condensate (NSF). The different ratios of MA-co-AA to NSF were added to the target $CaCO_3$ particles or cement paste to evaluate adsorptive properties, dispersive stability, zeta potential, slump loss, and rheological behavior with time elapsed. The mixing of MA-co-AA with NSF resulted in the increase of adsorption amount of dispersant per unit weight of $CaCO_3$ particle, but there were no differences in the zeta potential. The result for 20 wt% of MA-co-AA showed an excellent control effect of slump loss of cement paste and increasing apparent viscosity. The optimum dosage of NSF containing 20 wt% of MA-co-AA (NM-2) for the control of slump loss was between 1.0 and 1.5 wt% by cement weight for paste with water-to-cement ratio of 0.35. The optimum dosage of NM-2 depended on the water-to-cement conditions to obtain the effective slump loss control of cement paste. From the results of this research, the slump loss of cement paste could be controlled effectively by the addition of 1.0 to 1.5 wt% of the copolymer containing 20 wt% of MA-co-AA mixed with NSF. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Rheology; Admixture; Cement paste; High-range water reducers

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It has been generally known that a rapid stiffening termed "slump loss" of fresh concrete is significant, when chemical admixtures such as dispersant and superplasticizer are used in conjuction with Portland cement in concrete. This phenomenon may result in a significant fluidity loss of cement paste. Slump loss can cause broader scale problems involving workability as well [1,2]. The principal causes of this slump loss can be largely divided into two parts of chemical and physical coagulation. Chemical coagulation is produced by the reaction between chemical admixture and cement component as hydration occur. Physical coagulation is caused by the collision of cement particles.

Slump loss of cement paste also could result from the drop of dispersive capacity caused by the vanishing of dispersant with time elapsed. Yamaguchi et al. [2] indicated that slump loss could be produced from forming a three-dimensional network structure resulting from physical coagulation of cement particles. If the number of cement particles, n_0/cm^3, after concrete is mixed exceeds the interactive potential (V_{max}) between particles, the number of cement particle decreases like two-molecular reaction and becomes n/cm^3 after time t elapsed. This phenomenon is described in Eqs. (1) and (2):

$$1/n - 1/n_0 = 2\kappa k_{at}\exp(-V_{max}/\kappa T) \tag{1}$$

where T is the absolute temperature (K), κ is the Boltzmann constant, and k_{at} is a constant. In this case, the number of cement particles is reduced to half of n_0/cm^3, and the half-reducing time $t_{1/2}$ is calculated as follows when $n = n_0/2$.

$$t_{1/2} = 2\pi(a^2/3)\kappa k_{at}(1 + \rho_c W/C)\exp(V_{max}/\kappa T) \tag{2}$$

where W/C is the water-to-cement ratio, ρ_c is the average density, and a is the radius of particle. Until now, many methods have been suggested for the slump loss control of cement and concrete [3–5]. One method is to control fluidity of the cement and water system with time, in which both superplasticizer and a fluidity retention compound were used to compensate for slump loss. The fluidity of cement paste is due to the $Ca(OH)_2$ produced during hydration of cement hydrolyzing the functional group ($-COO^-$) of acid anhydride in polycarboxylic acid polymer (so-called slump-releasing effect). Another method is to retain the stable dispersion of cement paste by preventing the coagulation of ce-

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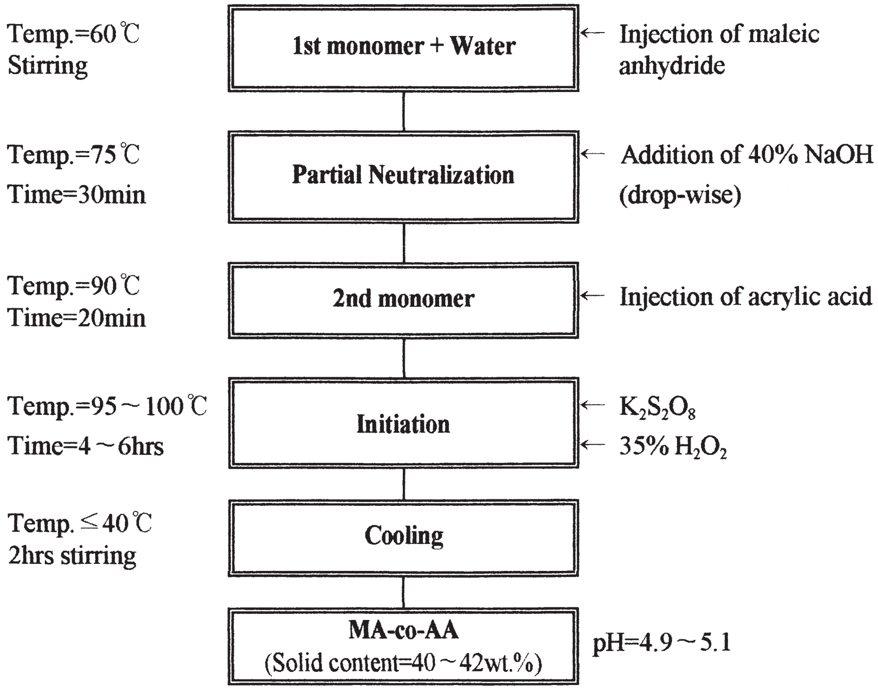


Fig. 1. Flow diagram for the synthesis of MA-co-AA.

ment particles due to specific adsorption and steric effects of polycarboxylic acid polymer adsorbed in cement particle. Naphthalene sulfonated formaldehyde (NSF) has been widely used as a superplasticizer for cement and concrete, but the application is limited due to its large slump loss with time elapsed [6].

In this study, polycarboxylic type slump-releasing dispersant (MA-co-AA) from maleic anhydride (MA) and acrylic acid (AA) as a monomer was synthesized to retain the fluidity of cement paste and then mixed with NSF. To evaluate the effects of this dispersant, measurements of properties such as fluidity and zeta potential, slump loss, and rheological behavior were made as a function of the amount of dispersant added and time elapsed.

1. Experiment

1.1. Experimental materials

1.1.1. Synthesis of MA-co-AA

Copolymerization of MA and AA proceeded by free radical reaction, using an initiator such as $K_2S_2O_8$ and H_2O_2. The final solid content of MA-co-AA was in the range from 40 to 42 wt%. The synthetic process is shown in Fig. 1.

1.1.2. Physical properties of the dispersants

NSF and MA-co-AA were used as a superplasticizer and a slump-releasing dispersant, respectively. The physical properties of NSF and MA-co-AA are presented in Table 1. Notations of dispersants according to mixing ratio of MA-co-AA to NSF are listed in Table 2.

1.2. Experimental methods

1.2.1. Adsorption property

Adsorption rate was estimated by determining adsorption ratio of dispersant on $CaCO_3$ particles with the contact time at a constant amount of dispersant added (C × 1.0 wt%) in $CaCO_3$-H_2O system ($W/CaCO_3 = 2.0$). Contact times were increased as 2, 5, 10, 20, 30, and 60 min. The adsorption amount was measured by determining the adsorption ratio of dispersant with the amount of dispersant added (C × 0.5 to 2.0 wt%). In this test, the adsorption rate and amount of dispersant were measured using ultraviolet spectrophotometry and determined by Eq. (3):

$$\text{Adsorption conc. } (C_A) = \text{Initial conc. } (C_I) - \text{Residual conc. } (C_R). \tag{3}$$

1.2.2. Zeta potential

Zeta potentials (ζ) on the surface of cement particles in suspension solution ($W/CaCO_3 = 15.0$) were measured by Zeta Potential Analyzer (Micrometrics Inc., Germany). Zeta potentials were determined using Eqs. (4), (5), and (6):

Table 1
Physical properties of dispersants

Dispersants	Specific gravity	pH	Viscosity (cP)	Solid content (%)	Appearance
NSF	1.204	9.1	180	40.00	Dark brown liquid
MA-co-AA	1.246	4.8	67	41.67	Transparent liquid

Table 2
Notations of dispersants with mixing ratio of NSF and MA-co-AA

	Mixing ratio (wt%)	
Names of dispersant	NSF	MA-co-AA
NM-1	90	10
NM-2	80	20
NM-3	70	30
NM-4	60	40

$$\varphi = \frac{W_p/\rho_p}{W_p/\rho_p + W_l/\rho_l} \tag{4}$$

where φ is the weight fraction ratio:

$$V\varepsilon = \frac{\Delta W \cdot \lambda_{kd}}{t \cdot I \cdot \varphi \cdot (1-\varphi) \cdot (\rho_p - \rho_l)} \tag{5}$$

where Vε is electrophoretic mobility, λ_{KCl} is 0.01N KCl solution-specific resistance, and ΔW is W_2 (sample weight in cell after test) − W_1 (sample weight in cell before test):

$$\zeta = \frac{4\pi \cdot V_\varepsilon \cdot (1-\varphi) \cdot \eta}{D} \tag{6}$$

where ζ is the zeta potential (± mV), η is the viscosity of solution, and D is the density of the solution.

1.2.3. Fluidity of cement paste (minislump)

A minislump measurement devised by Perenchio et al. [7], which measured the pat area of the cement paste formed by a miniature cone (height of 57 mm, top diameter of 19 mm, and bottom diameter of 38 mm), was used. After mixing at 250 rpm, cement paste (W/C = 0.35) with dispersant, the mixture was transferred into a miniature cone with coated lucite and then the cone was raised vertically after 1 min elapsed. Measured pat area (cm^2) was denoted as minislump. The mixing was followed by the 2:3:2 mixing method. The slump was monitored over time to determine slump loss, and measurements were made every 30 min up to 120 min. Before each test, the cement paste was covered to prevent moisture loss between measurements.

1.2.4. Rheological property

Apparent viscosities of cement paste were measured with the increase of shear stress after mixing by using a coaxial cylinder type viscometer (Rheolab UM, MC 20 [Physica Inc., USA], and Z3 DIN [bob radius 12.5 mm, cup radius 13.56 mm, maximum shear stress 1441 Pa]). On the basis of this test, slump loss was evaluated indirectly as well as rheological behavior of cement paste with time elapsed of 5, 30, 60, 90, and 120 min.

2. Results

2.1. Adsorption property

The adsorption rates of various dispersants with increasing of contact time on the surface of $CaCO_3$ particles are shown in Fig. 2. NSF shows a rapid adsorption rate within 5 min and approachs equilibrium after 20 min. Adsorption rates of dispersants containing MA-co-AA are lower than those of NSF and slowly decrease as the content of MA-co-AA increases. But the adsorption rates of NM-1 and NM-2 are quite similar to those of NSF. In the cases of MA-co-AA alone, the adsorption rate increases linearly with increasing contact time. As adsorption rates of dispersants are nearly constant values, we chose 20 min to estimate an equilibrium adsorption of dispersant.

Fig. 3 shows the adsorption amounts of various dispersants on the surface of $CaCO_3$ particles when the amount of dispersant added increases from 0.5 to 2.0 wt%. The adsorption of NSF increases nearly linearly, but its value is relatively low compared to dispersant containing MA-co-AA. Adsorption of MA-co-AA alone increases sharply initially but becomes slow above 1.0 wt%. From an overall viewpoint, MA-co-AA has a larger adsorption amount than NSF

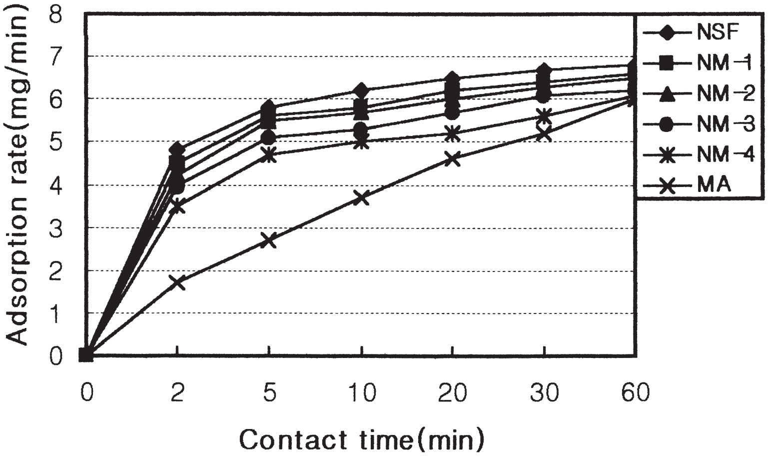


Fig. 2. Adsorption rate changes of various dispersants with increase of contact time in $CaCO_3$ suspension solution ($W/CaCO_3 = 2.0$; amount of each dispersant added = C × 1.0 wt%).

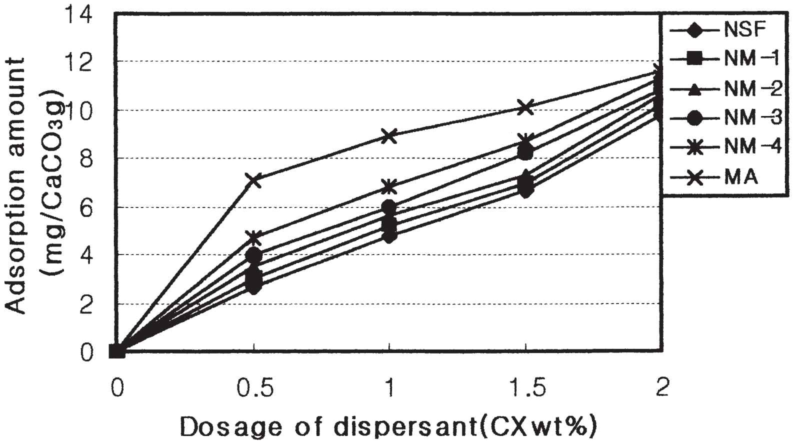


Fig. 3. Adsorption amount changes of various dispersants with the increase of dispersant in $CaCO_3$ suspension solution ($W/CaCO_3 = 2.0$; contact time = 20 min).

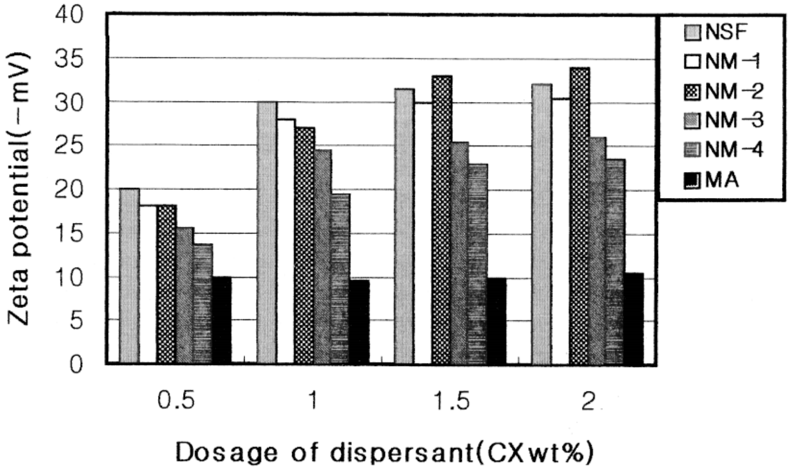


Fig. 4. Zeta potential changes for various dispersants with amount of dispersant in $CaCO_3$ suspension solution ($W/CaCO_3 = 15.0$; amount of each dispersant added = C × 0.5 to 2.0 wt%).

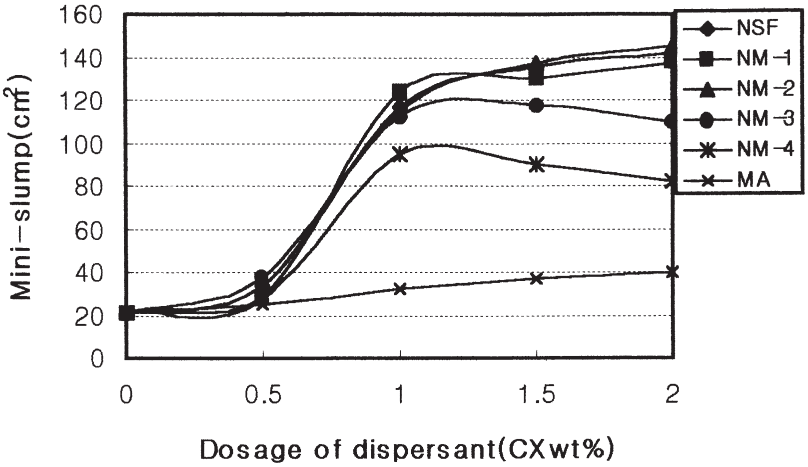


Fig. 5. Fluidity changes of cement paste with amount of dispersant added (W/C = 0.35; amount of each dispersant added = C × 0.5 to 2.0 wt%).

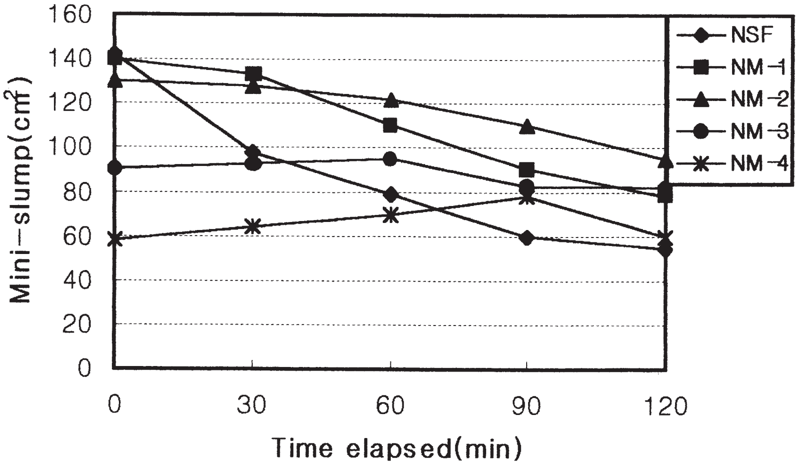


Fig. 6. Slump loss of cement paste with time elapsed at constant amount of various dispersants added (W/C = 0.35; amount of each dispersant added = C × 1.0 wt%).

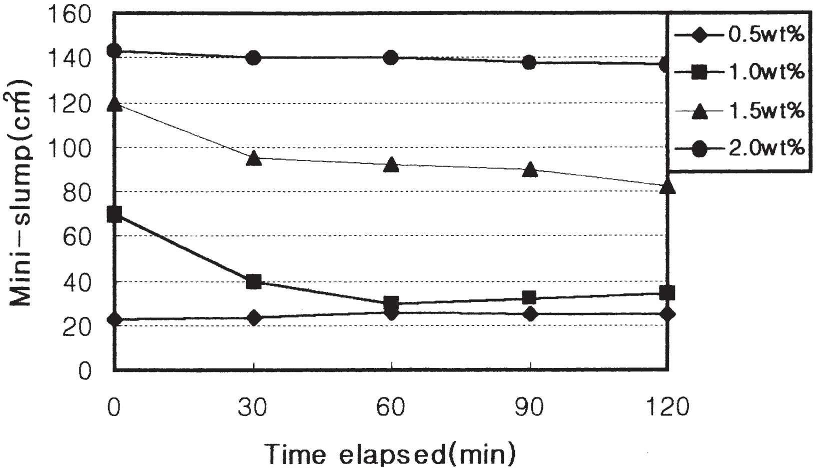


Fig. 7. Slump loss of cement paste with the amount of NM-2 added as a function of time elapsed (W/C = 0.35).

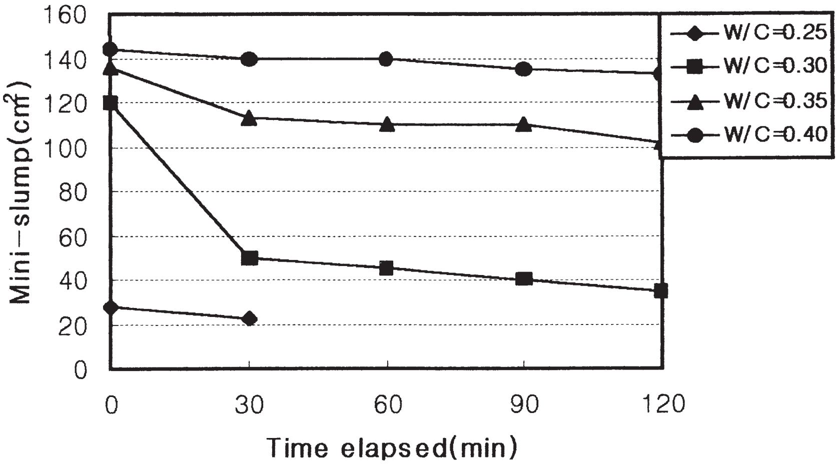
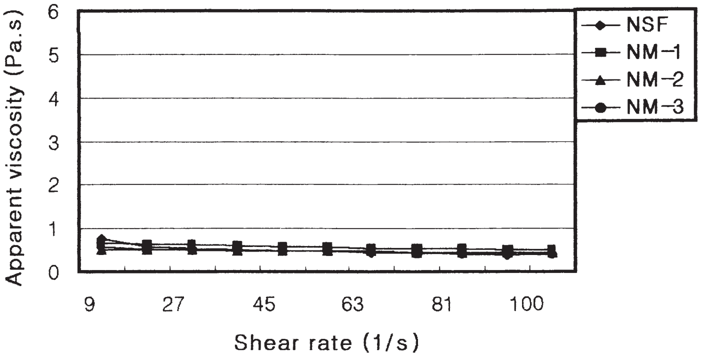


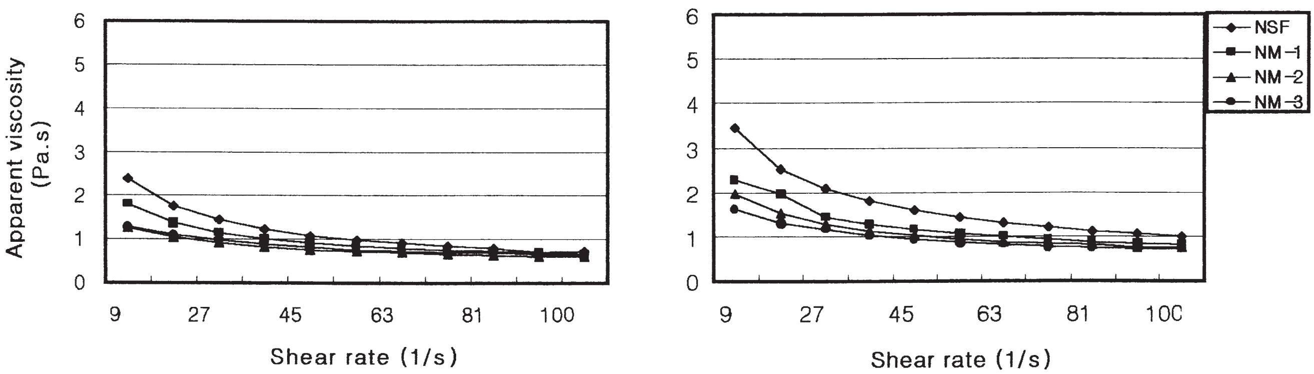
Fig. 8. Slump loss of cement paste as a function of W/C at constant dosage of NM-2 (1.0 wt%).

and NM series dispersant at constant contact time. This result can be explained in that sulfonic anion in NSF has more hydrophilic power than the carboxylic anion in MA-co-AA [3]. However, NSF has a weak chelating power and a pattern of nonadsorption molecule due to strong polarity and condensate of low-molecular-weight oligomer [5,8].

On the other hand, it is likely that the adsorption of MA-co-AA per unit surface area of $CaCO_3$ particles increased due to the strong tendency to form a chelate of the carboxylic anion with Ca^{2+} and its specific adsorption of tail-loop type [6]. Due to this adsorption phenomenon, NSF consequently presents a more rapid adsorption rate, whereas MA-

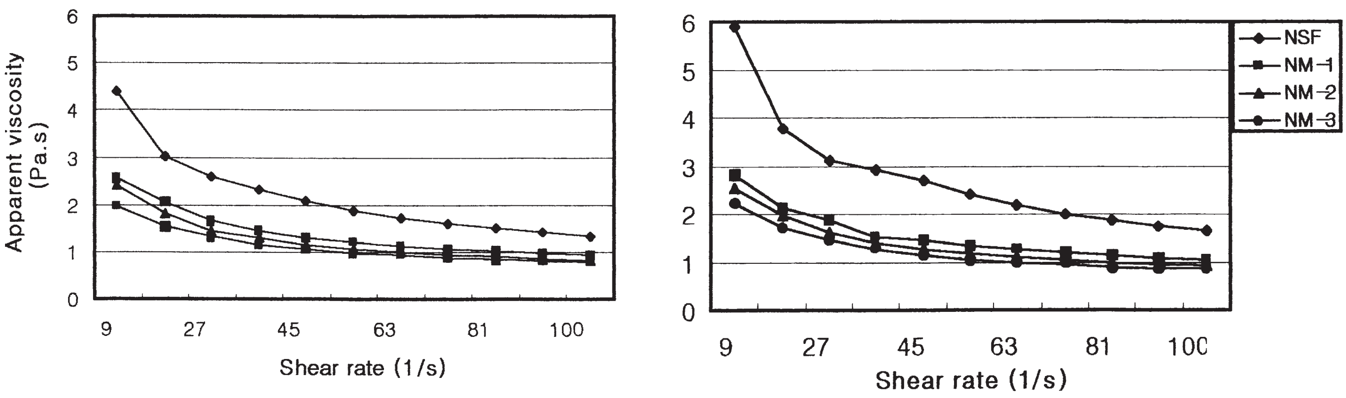


(a) Time elapsed = 5mins



(b) Time elapsed = 30mins

(c) Time elapsed = 60mins



(d) Time elapsed = 90mins

(e) Time elapsed = 120mins

Fig. 9. Apparent viscosity changes of cement paste with increasing of shear rate as a function of elapsed time (a) 5 min, (b) 30 min, (c) 60 min, (d) 90 min, and (e) 120 min. W/C = 0.35; amount of each dispersant added, 1.0 wt%.

co-AA presents a larger adsorption amount per unit surface area of particle.

2.2. Zeta potential

As shown in Fig. 4, the zeta potential change of the $CaCO_3$ particle surface increases with increasing amount of dispersant. The addition of MA-co-AA alone for the slump-releasing effect does not change the zeta potential. However, the zeta potential was increased from -5 to -30 mV by adding a large amount of NSF and then maintained at a constant value above 1.0 wt%. The zeta potentials of NM-1 and NM-2 verify that the powerful dispersive effect resulted from electrostatic repulsive force by strong anionic charges on the surface of $CaCO_3$ particles. However, the zeta potential values were markedly decreased for dispersants containing more than 20 wt% of MA-co-AA, such as NM-3 and NM-4. From these results, it was preferable for the mixing ratio of MA-co-AA to NSF to be limited up to 20 wt%. Consequently, it can be said that the zeta potential of $CaCO_3$ particles has the highest value under the condition of NM-2 above 1.0 wt%.

2.3. Fluidity of cement paste

In Fig. 5, cement paste ($W/C = 0.35$) admixed with 1.0 wt% NSF shows a very high fluidity value (minislump = 130 to 150cm^2). NM-1 and NM-2 have similar fluidity values of cement paste to that of pure NSF. The fluidity of cement paste with added 2.0 wt% of NM-2 exceeding 140 cm^2 shows the highest value. This result can be explained by the fact that NSF and MA-co-AA have different adsorption characteristics and increase electric repulsive force between particles by means of both the sulfonic anionic group of NSF and the carboxylic anionic group of MA-co-AA [7,8]. The increase in fluidity of cement paste correlates with the zeta potential increase caused by increase of electric repulsive force between particles.

2.4. Slump loss of cement paste with time elpased

The slump loss of cement paste added various dispersants over time is shown in Fig. 6. Not all dispersants containing MA-co-AA control the slump loss; only in the case of NM-2 is the slump loss of cement paste controlled effectively. NM-2 restrains slump loss less than 20% of initial fluidity value at 120 min. In contrast, NSF has a large slump loss exceeding 50% of initial slump. It can be said that this retention capacity of MA-co-AA results from an insoluble adsorption film $[\text{-}(COO)_2{}^{-}Ca^{2+}]$ formed from its carboxylic anionic group and introduced steric hindrance effects due to specific adsorption on cement particles [9,10].

Fig. 7 shows the effect of the dosage of NM-2 at constant W/C ratio ($W/C = 0.35$) on the slump loss control of cement pastes. The slump loss can be controlled effectively when dosage of NM-2 is over 1.5 wt% at $W/C = 0.35$. In Fig. 8, increase of W/C up to 0.40 contributes to controlling slump loss of cement paste added NM-2 at constant dosage. This result indicates that an optimum condition in terms of dosage and W/C can be determined for application of NM-2 to control slump loss of cement paste.

2.5. Rheological property

Rheological behavior of cement paste as a function of time and admixture addition is shown in Fig. 9. Cement paste containing NM-2 and NM-3 after 30 min shows a stable fluidity state by controlling slump loss. It indicates that introduction of MA-co-AA to NSF at a fixed rate delays effectively the increases of shear stress and apparent viscosity of cement paste with the increasing of shear rate in comparision with pure NSF [11,12].

3. Conclusions

The adsorption rate of NSF for $CaCO_3$ particles was higher than that of any other dispersants. However, the adsorption amounts of MA-co-AA and of mixture with NSF (NM-1, NM-2, NM-3, and NM-4) were larger than that of pure NSF. Through slump change and rheological property tests, NM-1 and NM-2 containing 10 and 20 wt% of MA-co-AA, respectively, had an excellent fluidity and a fluidity retention (slump loss control) in contrast to pure NSF. The slump loss of cement paste could be remarkably controlled by these dispersants. These properties could be affected by the amount of dispersant added and W/C ratio. The optimum dosage of NSF containing 20 wt% of MA-co-AA for controlling slump loss was 1.5 wt% by weight of cement with $W/C = 0.35$. From the overall results of this research, the slump loss of cement paste could be controlled effectively by the addition of 1.0 to 1.5 wt% of MA-co-AA mixed with NSF.

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