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Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer

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Abstract

Based on the analysis of the chemical structure of polycarboxylate-type superplasticizers with polyoxyethylene (PEO) side chains, the dispersing properties for cement particles were investigated. Analyzed characteristics were the PEO side chain length, the degree of backbone polymerization, the composition of functional groups such as carboxylic and sulfonic groups, and the purity of polymers. Their relative effectiveness as dispersants was evaluated in cement paste by measuring paste flow, plastic viscosity, and shear yield stress at different water/cement ratios (w/c). Although the effects of chemical structure on the paste fluidity were not significant at high w/c, they became significant at w/c below 25%. Polymers with longer PEO side chains, lower degrees of backbone polymerization, and higher contents of sulfonic groups showed higher dispersing power. Higher concentrations of ionic functional groups in the aqueous phase delayed the setting of cement paste.

Keywords: Chemical structure; Superplasticizer; Polycarboxylate; Dispersion

1. Introduction

Polycarboxylate-type superplasticizers (SPs) have become more popular recently [1]. A characteristic of this type of SP is that its chemical structure has the potential to be modified because it is composed of several components and it is a polymer.

There have been many studies on the working mechanisms of SPs [2–10]. However, they are studies from the standpoint of cement chemistry. In these studies, the chemical structures of SPs were not analyzed in detail. This may be because these SPs were polymers with wide molecular weight distribution and it was not easy to characterize their chemical structures. It is also not easy to modify only one component of the polymer of polycarboxylate-type SPs while keeping the rest of the structure the same.

Some researchers have discussed the significance of the chemical structure of polycarboxylate-type SPs [11–14]. In these cases, the discussion was based on an assumption that the SPs had been successfully synthesized according to an appropriately designed chemical structure, but no detailed analysis was performed.

In this study, based on the analysis of the chemical structure of polycarboxylate-type SPs containing polyoxyethylene (PEO) graft chains (PEO side chains), as well as sulfonic and carboxylic acid groups, the effects of chemical structure on the fluidity and setting of cement paste at different water cement ratios (w/c) were investigated.

2. Experiments

2.1. Materials

The SPs used were based on polymethacrylates. Our aim was to control two parameters: the length of the side chains and the degree of polymerization of the main chain (backbone chain). The SPs were synthesized by polymerizing various ethylenic monomers of industry-grade purity. The mean degrees of polymerization in the PEO side chains were 9, 23, and 40. The degree of backbone polymerization was also varied in the case of the PEO side chain of 23 groups (23 EO). The synthesis was carried out following the method of Kinoshita et al. [15]. The cement used was a commercial normal Portland cement classified by JIS R 5210. The characteristics of the cement are shown in Table 1.

2.2. Chemical structure of SP

A generalized chemical structure for the SPs is shown in Fig. 1. The backbone chain was a polymer of methacrylic acid partially esterified with methoxy-terminated PEO

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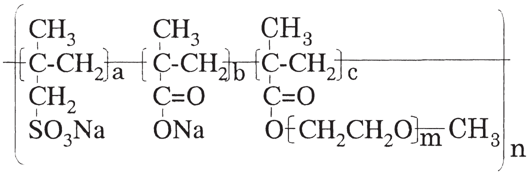
Table 1
Characteristics of cement

mass %										Blaine specific surface area (cm^2/g)
Ignition loss	Insoluble	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	
2.0	0.2	20.9	4.5	2.9	64.9	1.2	2.0	0.3	0.5	3200

chains. Methallyl sulfonic acid was also copolymerized into the backbone chain. It is believed that the adsorption of this kind of polymer on cement occurs via the carboxylic acid group [4]. The essential structure for the dispersion of cement particles is believed to be the PEO side chain [11,13].



$$\left[\left(\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle SO_3Na}{\displaystyle CH_2}}{C}}\text{-}CH_2 \right)_a \left(\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle ONa}{\displaystyle C{=}O}}{C}}\text{-}CH_2 \right)_b \left(\overset{\displaystyle CH_3}{\underset{\underset{\displaystyle O\left(CH_2CH_2O\right)_m CH_3}{\displaystyle C{=}O}}{C}}\text{-}CH_2 \right)_c \right]_n$$

Fig. 1. Generalized chemical structure for the range of synthesized superplasticizers.

2.3. Evaluation

2.3.1. Chemical structure of SPs

The molecular weight was evaluated by size exclusion chromatography (SEC) using a column of Shodex OHpak SB806M (Shodex, Tokyo, Japan). Polyethylene glycols were used as the calibration standards. Mean molecular weight of dispersant polymer was calculated from the SEC data, taking into account the unreacted macromonomers of PEO.

The amount of carboxylic acid group of unreacted monomer in polymer solution, C_u, was measured by ion chromatography. The total amount of carboxylic acid group, C_t, was known from the proportion of the starting material. By subtracting C_u from C_t, the amount of carboxylic acid group included in the polymer was calculated. The amount of sulfonic acid group of unreacted monomer in polymer solution, S_u, was measured by ion chromatography. By subtracting S_u from S_t (the total amount of sulfonic group known by the proportion of starting materials), the amount of sulfonic acid group included in the polymer was calculated. The length of PEO side chains was evaluated by the NMR spectroscopy for ^1H. The amount of PEO side chains was calculated from the proportion of starting materials and unreacted macromonomers by SEC.

Based on these measurements the mass ratio of each component, such as carboxylic acid group, sulfonic acid group, and PEO side chain, became clear. The data were converted to molar ratios. From the data of molar ratios and the average molecular weight of polymer, the mean numbers of each component were calculated for a polymer with the average molecular weight. Then the degree of backbone polymerization chain was calculated.

2.3.2. Fluidity tests

Cement pastes were mixed at 20°C and at w/c in the range 23 to 40%, using a Hobart mixer. First, SP and water were weighed into a bowl. Then 1 kg of cement was added and mixed for 1 min at low speed and a further 3 min at high speed. The amount of SP added is expressed as a percentage of dry solid with respect to the mass of cement.

The fluidity of cement paste was evaluated by a flow test and by using a rheometer. Flow was measured at 20°C by pullout spread of cement paste from a pipe of 50-mm inner diameter and 51-mm height, in accordance with JASS 15 M103. The spread was the average of two perpendicularly crossing diameters. From the spread (F), relative flow area ratio (Γ) was calculated by Eq. (1) [16].

Table 2
Chemical structure of synthesized polycarboxylate-type superplasticizers

	PEO chain length (mole[a])	Molecular weight (10^4) Weight average	Number average	Estimated "true" polymer content mass%	Groups/average molecule COO^-	SO_3^-	PEOchains	Degree of polymerization of the backbone chain groups[b]
SP1	9	2.18	0.58	91.7	72	7	23	109
SP2	23	3.64	1.06	83.3	73	7	23	111
SP3	49	9.86	1.77	71.6	133	11	43	203
SP2L	23	8.64	1.31	87.2	207	31	66	313
SP2S	23	2.19	0.92	75.0	43	5	14	66

All values were calculated on the assumption that molecular weights of all polymers took their weight average values.

[a] Mean number of ethyleneoxide groups.

[b] Mean number of ethylenic monomers per molecule.

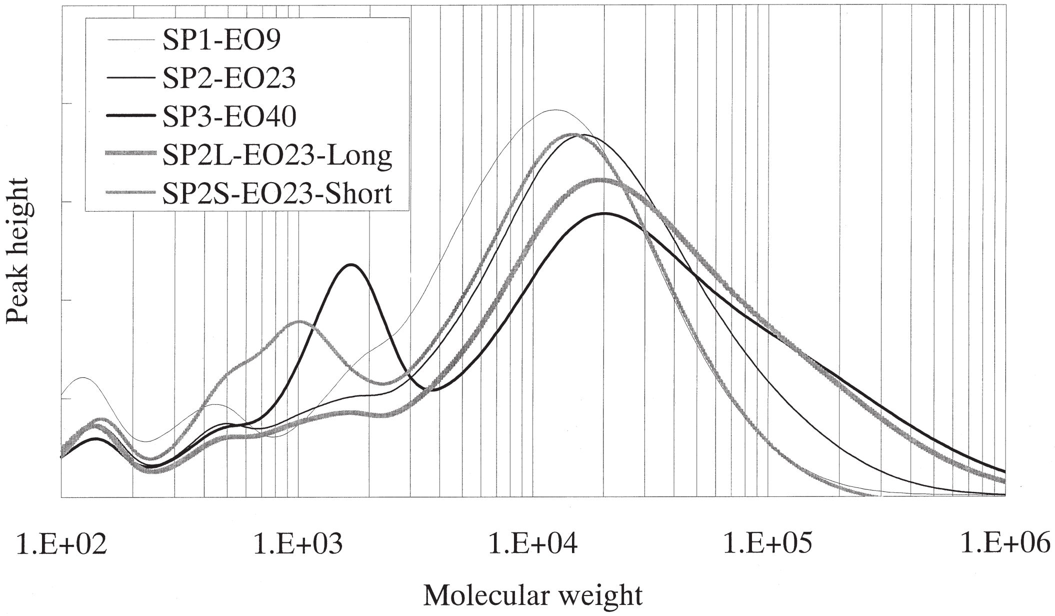


Fig. 2. Molecular weight distribution of superplasticizers.

$$\Gamma = F^2/50^2 - 1 \quad (1)$$

Rheoparameters (i.e., plastic viscosity and shear yield stress) were evaluated at 20°C by using an oscillation-type rheometer, CJV2000 made by A & D Corp., Tokyo, Japan. Setting of cement paste was evaluated at 20°C by using an automated setting tester (Maruto Testing Machine, Co., Tokyo, Japan). Γ usually shows an inverse relationship with shear yield stress. In low Γ range, the method of spread measurement is insensitive. However, it is possible to quantify the rheological behavior by shear yield stress.

2.3.3. Adsorption of SP on cement particles

The amount of SP adsorbed was evaluated by means of a total organic carbon analyzer, TOC-5000 (Shimadzu, Kyoto, Japan). The aqueous phase of cement paste was separated by centrifuging at 13,500 rpm for 1 min by using a centrifuge MC-150 (TOMY, Tokyo, Japan). The reduction in the total organic carbon analyzer measurement, compared to that of the mixing water with SP before contact with the cement and that in the aqueous phase of cement paste with SP just after mixing, was assumed to give the amount of SP adsorbed on cement particles. The pastes used for this eval-

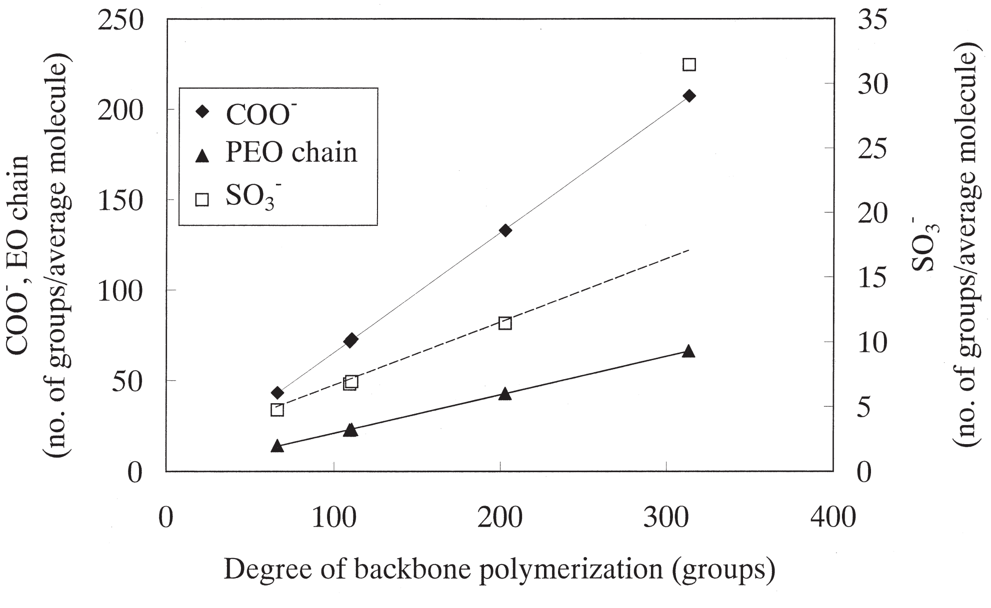


Fig. 3. Functional group composition of synthesized superplasticizers.

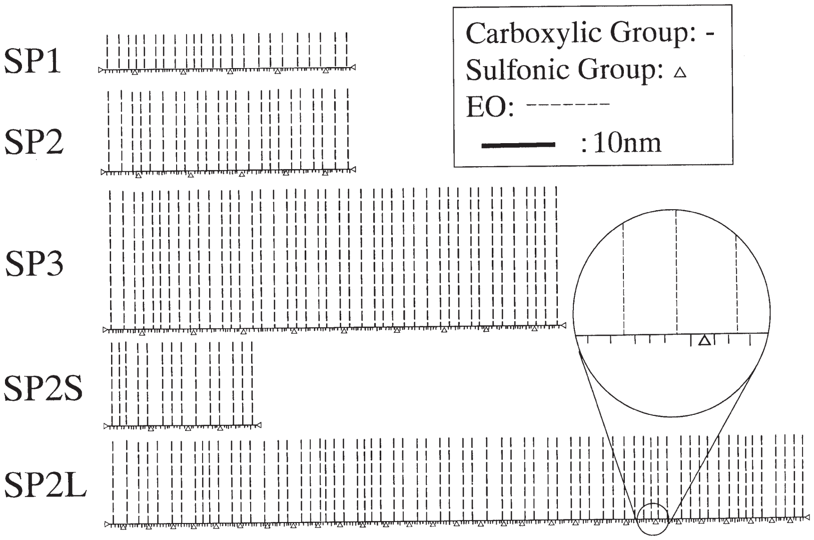


Fig. 4. Schematic diagram of synthesized superplasticizers.

uation were made with 0.2 mass% of total SP and 0.30 w/c. The adsorption ratio was calculated from the measured data. Because the effective polymer content was different for each SP, the effective polymer content of the SP was taken into account for the calculation of the adsorption ratio.

3. Results

3.1. Evaluation of chemical structure of SP

3.1.1. Molecular weight

The SP analyses are summarized in Table 2, and molecular weight distributions are shown in Fig. 2. Each SP gave more than one peak, but the highest molecular weight peaks were in the range of 10,000 to 20,000. Unreacted components like macromonomers of PEO corresponding to the PEO side chain length also can be observed at the low molecular weight end at 500 for 9 EO, at 1,100 for 23 EO, and at 1,900 for 40 EO, corresponding to the molecular weights of macromonomers. Based on the observation that a significant amount of longer PEO side chains (40 EO) remained as monomers, it seems to have been difficult to polymerize the monomers containing the longer PEO side chains. Based on these data, the effective "true" polymer contents were calculated by subtracting the estimated percentages of unreacted monomers. The stated amounts of SPs added to cement pastes are corrected values using these effective polymer content percentages.

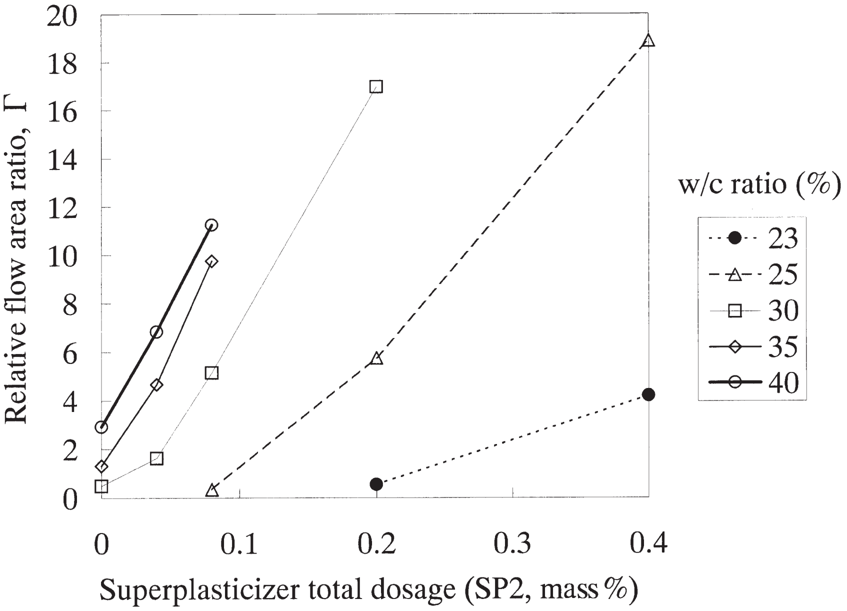


Fig. 5. Superplasticizer total dosage vs. Γ.

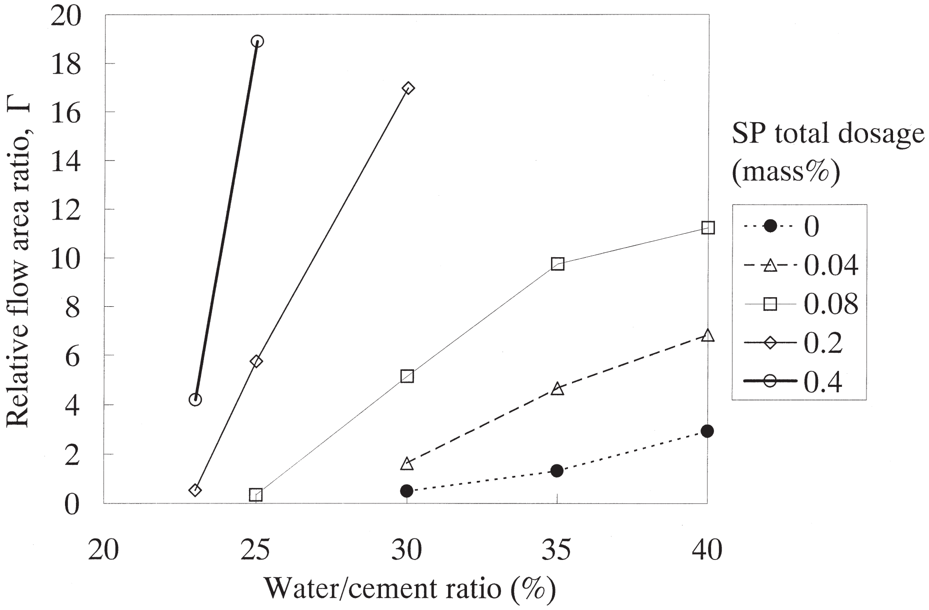


Fig. 6. w/c vs. Γ.

3.1.2. Molecular composition

The composition of each SP is summarized in Table 2 and Fig. 3. The mean number of carboxylic group, sulfonic group, and PEO side chains per molecule was proportional to the degree of backbone polymerization, except for the sulfonic group in SP2L. Therefore, the proportions of functional groups were almost the same for each SP except SP2L, which had a higher proportion of sulfonic groups.

Comparing SP2 and SP2S, the degree of backbone polymerization varied from 66 to 111 without significant change of functional group composition. Thus the effects of backbone chain length can be examined by comparing SP2 and SP2S.

The mean length of the backbone chain was the same in SP1 and SP2. That of SP3 was twice as long. This means that the effects of changes in PEO side chain length can be examined by comparing SP1 and SP2.

Schematic diagrams of these SP molecules are shown in Fig. 4, based on the results in Table 2. In Fig. 4, the following bond lengths are assumed: 0.154 nm for C-C and 0.143 nm for C-O. No attempt is made to represent the bond angles or molecular conformations.

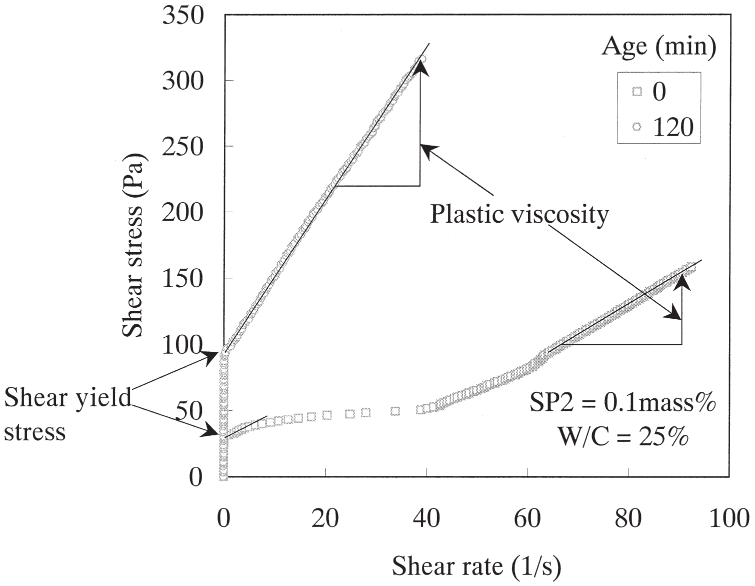


Fig. 7. Shear stress-shear rate curve by an oscillation rheometer.

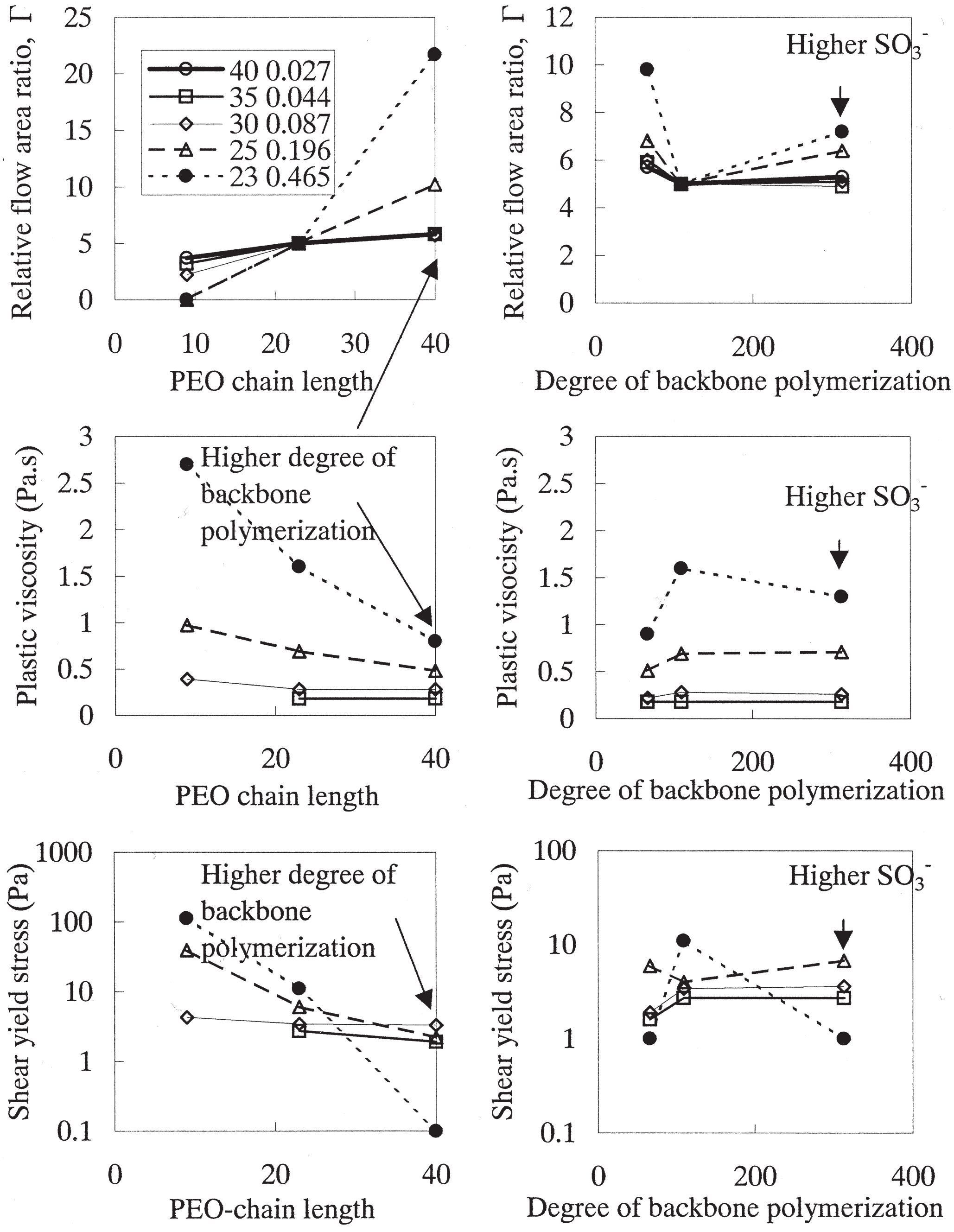


Fig. 8. Effects of chemical structure of superplasticizer on the paste rheology.

3.2. w/c and SP dosage

The effects of total SP2 dosage on the fluidity of cement pastes with various w/c are shown in Fig. 5. The effects of w/c on the fluidity of cement paste with various total SP2 dosages are shown in Fig. 6. In a region of higher w/c, the effects of w/c on the fluidity were not very significant, as shown in Fig. 6. It became more significant at lower w/c. On the other hand, the fluidity was more sensitive to SP2 dosage in higher w/c than in lower w/c, as shown in Fig. 5.

At lower w/c, a slight fluctuation of water content in concrete can cause large variations of the fluidity. At higher w/c, a small fluctuation of water content can be negligible but a small fluctuation of the amount of SP can cause significant variations in fluidity. This is why the fluidity of superplasticized concrete is difficult to control in actual jobs; it can be affected by small fluctuations in the surface water of sand.

3.3. Effects of chemical structure of SPs on paste fluidity

The effects of PEO side chain length and the degree of backbone polymerization on the fluidity of cement paste were investigated. Fluidity tests were carried out for cement

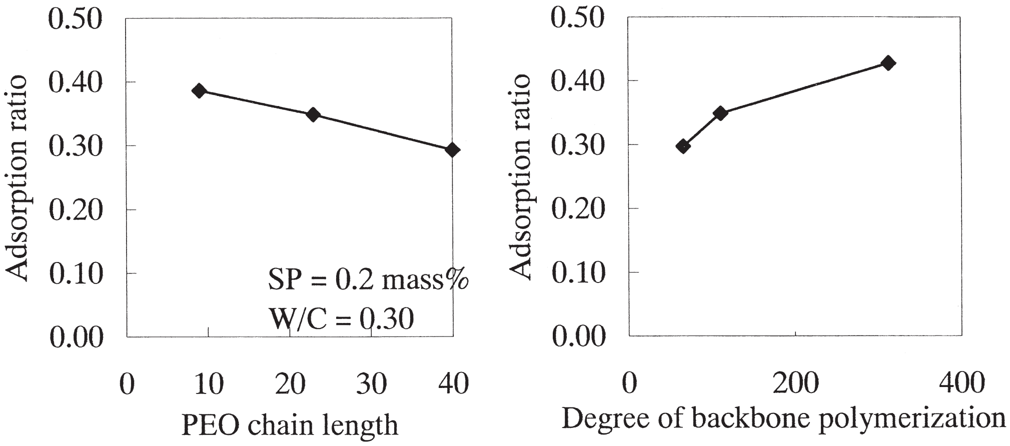


Fig. 9. Effects of chemical structure of superplasticizer on the adsorption behavior.

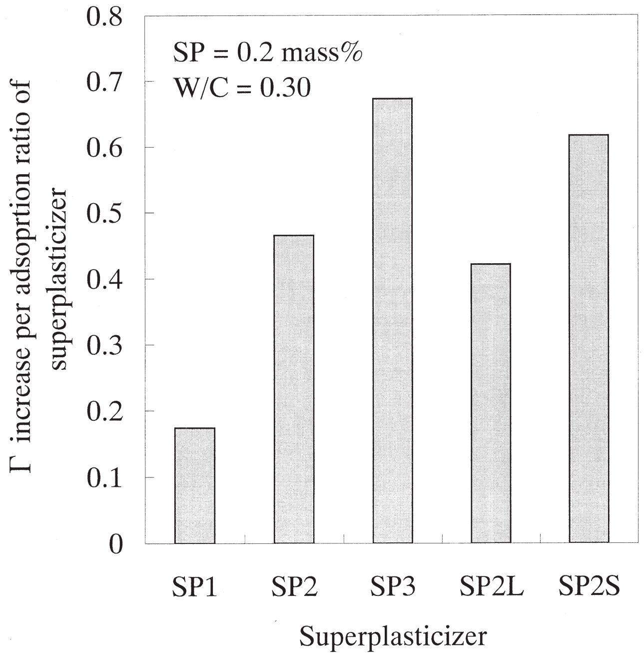


Fig. 10. Relative dispersing power per absorbed superplasticizer.

pastes containing various total dosages SPs. However, SP does not contain only dispersant components but also unreacted monomers. Therefore, it is necessary to correct the SP dosage to an “effective polymer dosage.” The total SP dosages were corrected to effective polymer dosages by taking into account the true polymer contents as shown in Table 2. The effective polymer dosages of SPs at each w/c were calculated to show five of Γ for SP2.

Plastic viscosity and shear yield stress were evaluated from the relationship between shear stress and shear rate, such as in Fig. 7 for SP2. In some cases in the measurement, cement paste showed a behavior of Bingham fluid as in the case of 120 min in Fig. 7. However, in some cases, the relationship between shear rate and shear stress was not so simple—for example, the case of 0 min in Fig. 7. It was not clear why the paste showed complicated behavior in the case of 0 min in Fig. 7. However, it is useful to compare the rheological behavior variations by the different chemical structures of SPs. In this paper, the shear yield stress and plastic viscosity were defined from the measurement results as follows.

Shear yield stress was defined as the intercept point on the Y-axis. The intercept point was decided by extrapolating

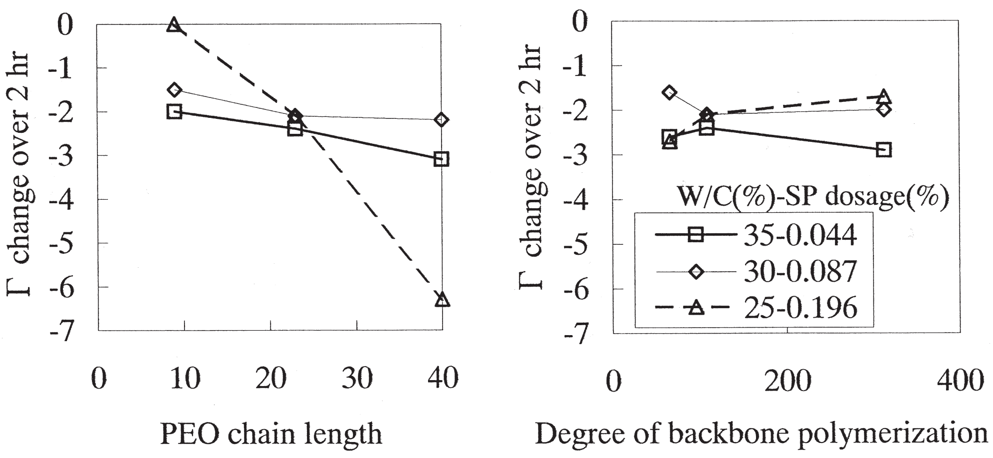


Fig. 11. Time change of G during 2 h.

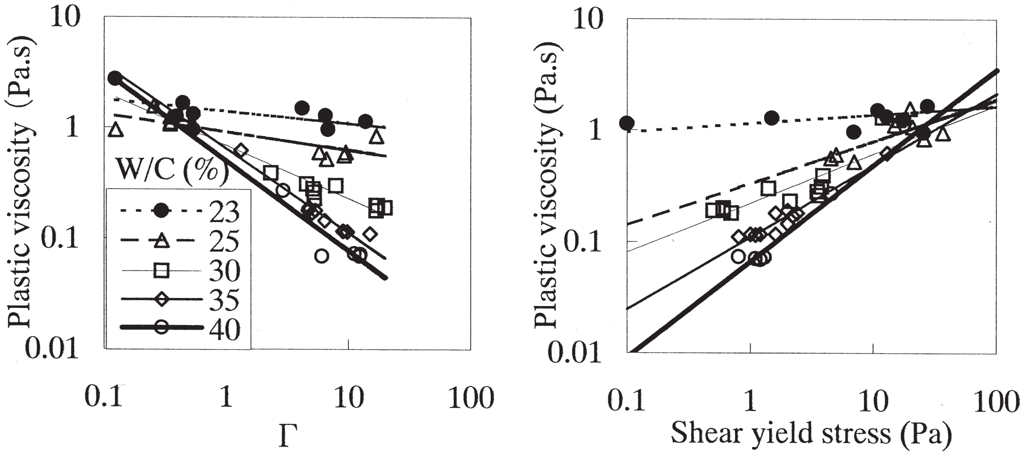


Fig. 12. Relationship between plastic viscosity and G or shear yield stress of cement paste with various types and dosages of superplasticizers.

the linear part nearest the Y-axis as shown in Fig. 7. Plastic viscosity was defined as the slope of the linear part of the relationship around 50 to 100 1/s of shear rate. In the case of higher plastic viscosity, it was calculated at lower shear rate on the assumption of the same relationship, around 50 to 100 1/s of shear rate, because of the mechanical limit of the rheometer used.

Γ, plastic viscosity, and shear yield stress are shown in Fig. 8 with relationship to the chemical structures, PEO side chain length, and the degree of backbone polymerization. Longer PEO side chains generally gave higher fluidity (i.e., higher Γ), lower plastic viscosities, and lower shear yield stresses. The effect of PEO side chain length was more significant at lower w/c. The effect of chemical structure on the plastic viscosity correlated inversely with its effect on Γ. Longer PEO side chains gave lower plastic viscosities. On the contrary, although Γ was adjusted to be constant at various w/c for SP2 with 23 EO chain length, the plastic viscosity of pastes made with SP2 varied depending on the w/c. The plastic viscosity was higher at lower w/c.

The changes in shear yield stress showed good inverse correlation with Γ. The logarithm of the shear yield stress linearly decreased with the increase of PEO side chain length. The effect was more significant at lower w/c. Shear yield stresses with SP2 were in a narrow range.

As for the degree of backbone polymerization, there was no clear relationship with Γ. It may be because SP2L with 313 of backbone polymerization had a higher sulfonic group content than the other polymers. Comparing the data of SP2 and SP2S, a lower degree of backbone polymerization gave higher fluidity. The effect was more significant at lower w/c, like the case of PEO side chain length. If the ten-

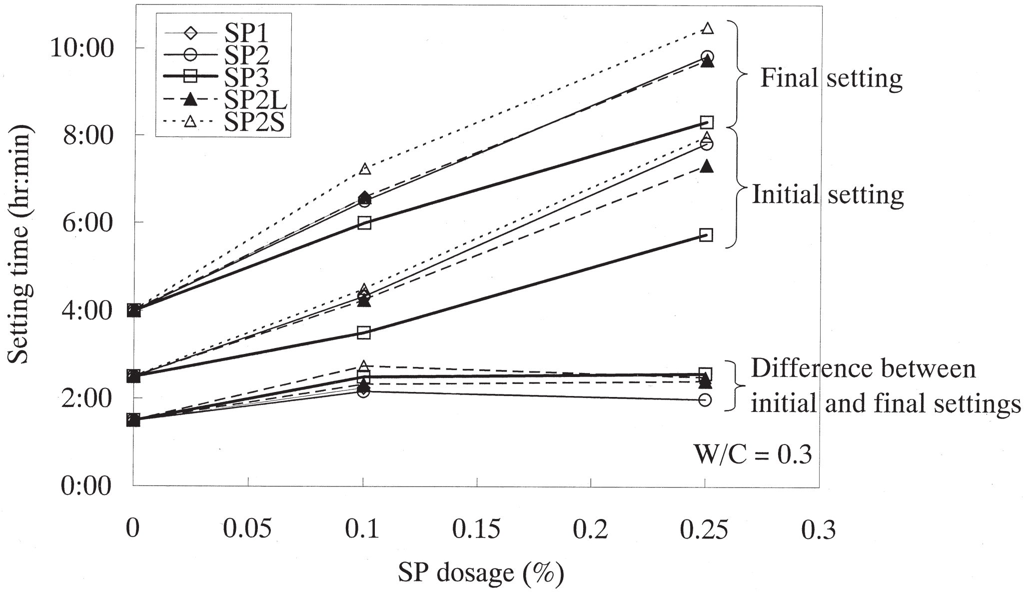


Fig. 13. Effects of superplasticizer addition on setting of cement paste.

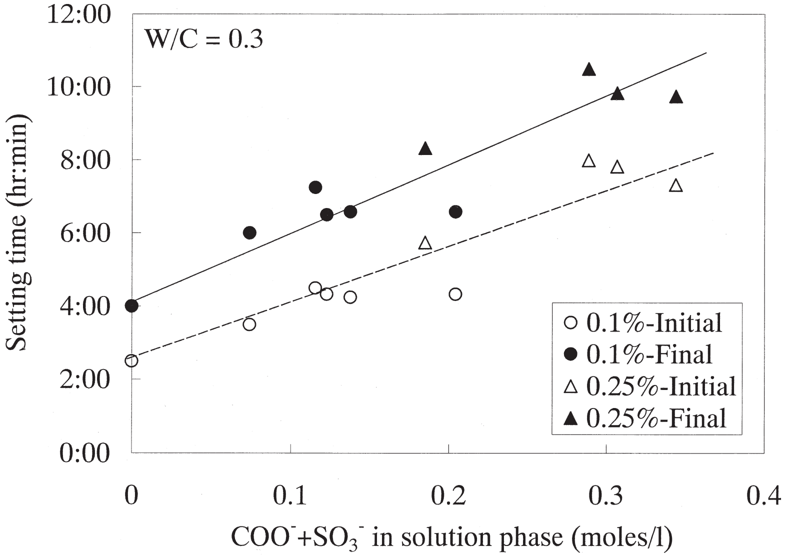


Fig. 14. Relationship setting and contents of functional group in solution phase.

dency had been the same for SP2L, it would have been thought that the sulfonic group enhanced the dispersing power.

3.4. Adsorption behavior of SP and the dispersing power per adsorption amount on cement

SP is thought to work only after the adsorption on cement particles. Therefore, it is useful to compare their adsorption behaviors. Adsorption data are shown in Fig. 9 for a total SP dosage of 0.2 mass% and w/c of 0.30. SPs with shorter PEO side chains and higher degrees of backbone polymerization showed a higher adsorption ratio.

The order of effectiveness as a dispersant was different from that of adsorption. The effectiveness of an SP after adsorption can be examined by comparing the Γ increment per adsorption ratio as shown in Fig. 10. Based on the data in Fig. 10, SP3 had the most dispersing power, although its adsorption ratio was relatively low. As for the degree of backbone polymerization, although the SPs with a lower degree of backbone polymerization showed a relatively low adsorption ratio, they showed higher dispersing power per adsorption amount.

3.5. Effects of chemical structure of SP on the fluidity change with time

Γ changes over 2 h are shown in Fig. 11. Low w/c content pastes were especially sensitive, and increases in the PEO side chain length gave large decreases in Γ. The degree of backbone polymerization had a much smaller effect.

3.6. Correlation between rheological parameters

The relationships between plastic viscosity and Γ or shear yield stress at each w/c are shown in Fig. 12. There were linear relationships between the logarithm of plastic viscosity and the logarithm of Γ or the logarithm of the shear yield stress at each w/c. In these relationships, the type and dosage of SPs were varied. SPs reduced the plastic viscosity and shear yield stress and increased Γ. At higher

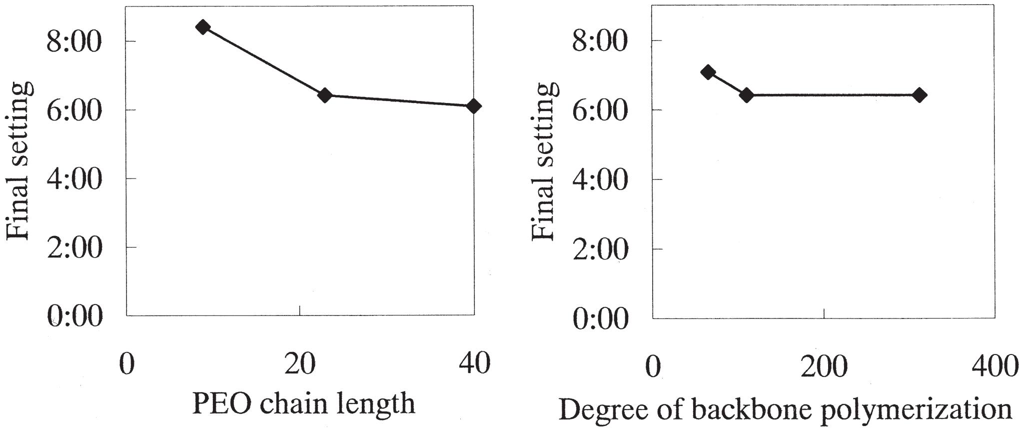


Fig. 15. Effects of chemical structure of superplasticizer on setting. SP dosages were adjusted to show five of G at w/c = 0.3.

Table 3
Summary of the effect of chemical structure on the properties of superplasticizer

	Higher fluidity	Less fluidity loss	Shorter setting
PEO chain	Longer	Shorter	Longer
Degree of polymerization of the backbone chain	Lower	–	Higher
Sulfonic group content	Higher	–	–

w/c, the addition of SP affected the plastic viscosity, Γ, and shear yield stress. At lower w/c, the addition of SP affected only Γ or shear yield stress, and did not affect the plastic viscosity as much.

3.7. Effects of chemical structure of SPs on setting

The effects of the SPs on the setting of cement paste are shown in Fig. 13. Initial setting and final setting were delayed linearly with respect to the dosages of SPs. The difference between initial setting time and final setting time apparently increased slightly on addition of 0.1 mass% of SP, but did not change with further addition of SP.

SP seems to affect the start of setting; it is thought to correlate to the hydration of alite [17]. After the beginning of alite hydration, the hydration is not affected by SP [8]. The delay of setting is thought to relate to the concentration of acidic groups in the aqueous phase. Based on the data shown in Table 2 and adsorption ratios shown in Fig. 9, the concentrations of carboxylic and sulfonic groups in the aqueous phase were calculated for the cement paste with w/c = 0.30. The dosages of SP were 0.1 and 0.25 mass%. The results are shown in Fig. 14. Both initial setting and final setting were delayed by the increase of the sum of the concentrations of the sulfonic and carboxylic groups in the aqueous phase.

SP is added to concrete to achieve a certain fluidity. Therefore, it is necessary to compare the retardation of SP while not changing the fluidity. A fluidity test and a setting time evaluation were carried out for several fixed total dosages of SP. To estimate the setting time at constant fluidity, the amount of each SP that showed the same Γ of five in the case of 0.30 w/c was calculated based on the relationship between total SP dosage and Γ, as in Fig. 5, for each SP. Then, the setting time of paste with this calculated amount of SP was estimated from the relationship in Fig. 13. The results are shown in Fig. 15. Longer PEO side chains gave significantly shorter setting times, but higher degrees of backbone polymerization gave only slightly shorter setting time.

4. Conclusions

The effects of the chemical structure of polycarboxylate-type SP on the paste fluidity and the time dependence were examined using specially synthesized polycarboxylate comb-polymers. The obtained results are summarized as follows and in Table 3.

1. Longer PEO side chains gave more fluidity at the same dosage, a larger fluidity decrease with time, and a shorter setting time.
2. A shorter mean backbone chain length gave more fluidity at the same dosage, and a slightly longer setting time. It did not affect the loss of fluidity with time very much.
3. A higher sulfonic group content in the polymers gave higher fluidity at the same dosage.
4. The setting time of cement paste depended roughly on the ionic functional group concentration in the aqueous phase of the cement paste.
5. SPs always reduced the shear yield stress significantly. They also reduced the plastic viscosity significantly at higher w/c, but much less at lower w/c.

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