

Scientific paper

Effect of Chemical Structure on Steric Stabilization of Polycarboxylate-based Superplasticizer

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Abstract

The effects of chemical structures of graft copolymer on cement-dispersing performance were investigated to elucidate the fluidizing mechanism of polycarboxylate-based superplasticizer containing graft copolymer with polyethylene oxide graft chains. A graft copolymer with longer graft chains showed better dispersing stability with a small amount of adsorption. The adsorption study indicated that the graft chains elongated as the adsorption density increased. The thickness of the graft chain in the copolymer that adsorbs on a cement particle also depends on the average distance between two graft copolymers and the graft chain spacing within the copolymers, depending on the geometric features of the copolymer. The modified steric stabilization model incorporating the extension of graft chains due to adsorption and the geometric restriction of the copolymer gives a useful explanation of the relationship between adsorption and the flow of paste containing different graft copolymers.

1. Introduction

Polycarboxylate-based superplasticizer primarily composed of comb-like copolymers with a graft chain of polyethylene oxide (PEO) provides excellent dispersibility of cement particles and significantly enhances the fluidity and fluidity-retaining performance of concrete even at a low water-binder ratio. This makes these superplasticizers essential for producing high-performance concretes such as high-strength concrete and self-compacting concrete.

The dispersibility of cement particles is generally considered to result from electrical and steric repulsion among the particles. However, many researchers have reported that the absolute value of the zeta potential of cement particles adsorbing a polycarboxylate-based superplasticizer is smaller than that of a conventional naphthalene-based superplasticizer (Yoshioka 1997). This indicates that the excellent cement-dispersing capability of graft copolymers is primarily derived from their steric repulsion rather than electrostatic repulsion.

According to the conventional theory of steric stabilization, the steric force is expected to increase as the length and density of the graft chains in copolymers increase (Yoshioka 1997). However, Ohta *et al.* pointed out that the cement-dispersing effect could not be explained simply by changes in steric repulsion due to the graft chain length, but that it strongly depends on chemical structure such as the geometrical balance between the main chain and graft chains (Ohta 1997). However, the effect of chemical structure on the dispersing effect of graft copolymers has not yet been un-

derstood quantitatively.

In this study, the effect of the graft chain length of a graft polymer on the fluidity of paste and the conformation of adsorbed graft copolymers on the cement particle surfaces were investigated in order to elucidate the effect of the chemical structure of these dispersants on their dispersing ability. The interparticle potential between cement particles covered with adsorbed copolymer layers was then determined, taking into account the interactions between adjacent graft chains. From these results, the author proposed a modified steric stability theory incorporating the effect of chemical structure on the conformation of an adsorbed graft chain copolymer.

2. Experiment

2.1 Materials and samples

Normal portland cement was used as a typical cement available on the market. The characteristics of the cement are given in **Table 1**. Three types of maleic anhydride graft copolymers were used as the superplasticizer. In order to focus on the graft chain length, graft copolymers were synthesized with polyethylene oxide additions of 7, 34, and 90 mol. Their molecular structure and chemical properties are shown in **Fig. 1** and **Table 2**, respectively. The molar ratio of allyl ether to maleic anhydride in the copolymer is 1.0. The molar ratio of allyl ether to maleic anhydride is the same for all copolymers in this study. The molecular weights listed in **Table 2** were determined using gel permeation chromatography, and molecular weight calibration was performed using polyethylene glycol.

Cement pastes were prepared by mixing cement with distilled water containing superplasticizer to obtain a water-cement (W/C) ratio of 0.40. The mixing time was 3 minutes. The temperature of the paste after mixing was controlled to be within $20 \pm 2^\circ\text{C}$. The dispersant dosage

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Table 1 Physical properties and chemical composition of normal portland cement.

Density (g/cm ³)	Chemical composition (mass %)								Blaine fineness (cm ² /g)
	Ig.loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O _{eq}	
3.16	1.86	20.83	4.75	2.70	63.15	2.43	2.03	0.60	3340

Table 2 Chemical properties of maleic anhydride graft copolymer with polyethylene oxide.

Type of graft copolymer	Polyethylene Oxide chain (EO mol)	Weight-average molecular weight of a copolymer	Weight-average molecular weight of a graft chain	Average number of graft chains in a graft copolymer
n = 7	7	28100	353	58.7
n = 34	34	21200	1542	12.7
n = 90	90	44800	4010	10.8

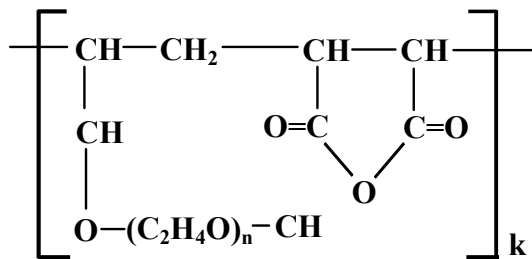


Fig. 1 Chemical structure of graft copolymer.

was expressed as the solid percentage by mass of cement.

2.2 Experimental procedure

(1) Fluidity evaluation of cement paste

The fluidity of cement paste was evaluated by the flow value measured in accordance with JASS 15 M-103. A cylindrical cone (50 mm in diameter, 51 mm in height) was filled with the cement, and then the cone was pulled up in order to measure the spread diameter after the flow stopped. Flow tests were conducted with different dosages of superplasticizer.

(2) Measurement of adsorption

The liquid phase of the cement paste was separated by a centrifuge immediately after 3 minutes of mixing and filtrated through a membrane filter (0.5 μm). The amount of organic carbon in the liquid phase was then determined with a total organic carbon analyzer (TOC). The adsorbed amount of graft copolymer was determined based on the difference in the amounts of total organic carbon before and after adsorption. The amount of total organic carbon measured by TOC includes the organic carbon deduced cement and polymer filtrate. Hence the total organic carbon for paste without superplasticizer was measured before measuring adsorption. Next, the amount of TOC deduced superplasticizer was calculated by subtracting the organic carbon deduced cement and polymer filtrate from the measured total carbon for the paste after adsorption.

In general, superplasticizer is not adsorbed evenly on the cement surface, but is strongly adsorbed on specific hydrates such as ettringite, which is the hydration product of C₃A and C₄AF. However, the C₃A and C₄AF phases are not separated from the C₃S and C₂S phases. Further, the graft chain in the copolymer that adsorbs on the C₃A and C₄AF phases could stretch horizontally along the surface of cement particles, apparently covering the surrounding C₃S and C₂S phases. Thus, when the density of adsorbed graft chain is large, it is apparent that the copolymer adsorbs evenly on the cement. The adsorption of graft copolymer molecule per unit area of cement then can be calculated from the adsorption per unit area and the molecular weight of graft copolymers using the following equation:

$$A = \frac{B}{Na \cdot M_w} \quad (1)$$

where A = number of adsorbed copolymer molecules per unit area of cement, M_w = weight-average molecular weight of the graft copolymer, Na = Avogadro's number and B = adsorption per unit area of cement of graft copolymer.

When discussing the adsorption of graft copolymers, it is more appropriate to deal with specific surface areas measured by the BET method whereby the microstructure on the cement particle surfaces can be evaluated at the same size as the polymers. Ohta *et al.* (Ohta 2000) compared the Blaine specific surface and the BET specific surface area of various powders and found a strong correlation between them. This is shown in Eq. (2). In this study as well, the adsorption per unit surface area was calculated by determining the BET specific surface area of cement from the Blaine specific surface area using Eq. (2).

$$S_{\text{BET}} = 2.213 \cdot S_{\text{Blaine}} + 426.8 \quad (2)$$

where S_{BET} = BET specific surface area and S_{Blaine} = Blaine specific surface area.

3. Results and discussions

3.1 Fluidity of paste with graft copolymer

Figure 2 shows the relationship between the dosage of polymer and the paste flow. The flow increases as the dosage increases, regardless of the type of copolymer. The flows of pastes containing graft copolymer with degrees of PEO polymerization (n) of 7 and 34 show similar flows, whereas the flow of paste in which the degree of PEO polymerization is 90 is smaller than those of the other pastes by 30 to 50 mm, with the same dosage.

3.2 Adsorption characteristics

Figure 3 shows the adsorption isotherms of graft copolymer onto cement. The graft copolymers with a degree of graft chain PEO polymerization $n = 7$ show a type H isotherm curve as classified by Giles (Giles 1974), whereas those with $n = 34$ and 90 show type L isotherms. Type H represents a high affinity between the adsorbed molecules and the adsorbent. On the other hand, type L refers to a Langmuir-type isotherm, in which the interactions between the adsorbed molecules and between such molecules and the adsorbent are not as strong as those of type H. It is therefore evident that a graft copolymer with a PEO graft chain of $n = 7$ is adsorbed on cement particles with a very high affinity, whereas no such strong interaction is generated between a graft copolymer with a PEO graft chain with $n = 34$ and 90 and cement.

3.3 Relationship between adsorption properties and fluidity

Figure 4 shows the relationship between the amount of adsorbed copolymer and the paste flow. The paste flow increases as the adsorbed amount of copolymer increases. However, the correlation between the amount of adsorbed copolymer and the paste flow was seen to depend on the type of graft copolymer. This implies that the dispersing effect of graft copolymers on cement particles varies depending on the length of the graft chains.

The number of graft chains attached to the main chain differs according to the type of graft copolymer, and accordingly, the amount of adsorbed copolymer does not correspond one-to-one with the adsorption density of a graft chain on the surface of a cement particle. The number of adsorbed graft chains of copolymer per unit area of cement was calculated based on the number A of adsorbed copolymer molecules per unit surface area of cement given by Eq. (1), and the average number of graft chains in a graft copolymers is given in Table 2. Hereafter, this is referred to as the density of adsorbed graft chain. The relationships between the density of the adsorbed graft chain and flow value of paste are shown in Fig. 5. It is clear that the degree of graft chain PEO polymerization strongly influences the fluidity of the paste. Graft copolymers with graft chains of $n = 7$, for instance, require a graft chain density of approximately $1.3/\text{nm}^2$ to achieve a flow of 250 mm, whereas those with a graft

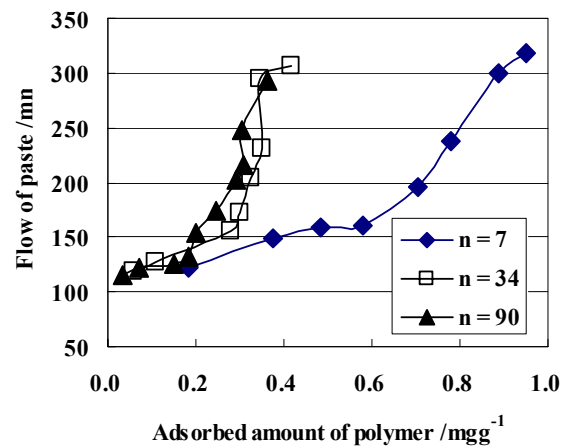


Fig. 2 Changes in paste flow with dosage of graft copolymer.

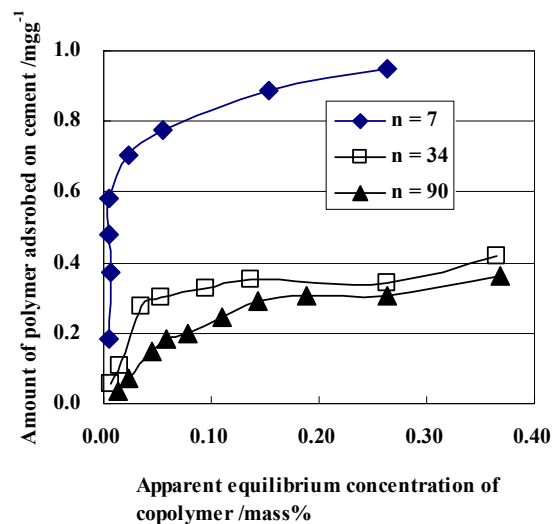


Fig. 3 Adsorption isotherms of graft copolymers.

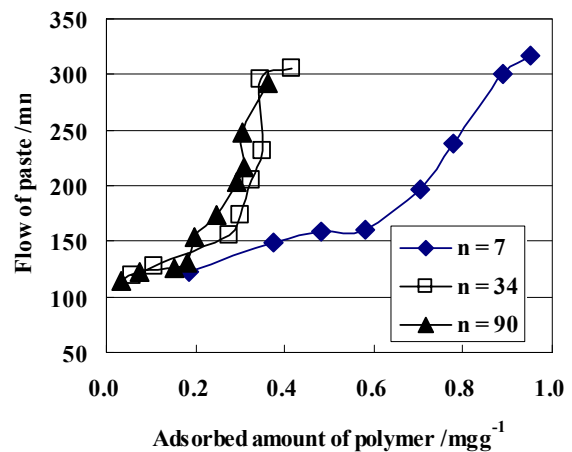


Fig. 4 Relation between amount of adsorption of graft copolymer and paste flow.

chain of $n = 34$ and 90 require graft chain densities of only 0.2 and $0.09/\text{nm}^2$, respectively, to achieve the same flow.

3.4 Comparison with interparticle potential based on the conventional steric stabilization theory

The dispersing effect of a polycarboxylate-based superplasticizer composed of a graft copolymer is derived from the steric force of the graft chains. All graft copolymers include some monomers, but cement dispersion by the superplasticizer due to steric force is derived only from polymers. According to Evance and Napper (Evance 1973), the steric interaction potential, V_s , and Van der Waals attraction potential, V_a , between two spherical particles with adsorbed polymer layers are given by the following equations.

$$V_s = \frac{(2\pi)^{5/2}}{27} \langle r^2 \rangle^{3/2} v^2 (\alpha^2 - 1) \alpha \phi kT \quad (3)$$

$$V_a = -\frac{A}{6} \left\{ \frac{2}{S^2 - 4} + \frac{2}{S^2} + \ln \left(\frac{S^2 - 4}{S^2} \right) \right\} \quad (4)$$

where $\langle r^2 \rangle^{1/2}$ = average distance between polymer chain ends in the solution, α = expansion factor of graft chains, v = number of adsorbed graft chains per unit area, ϕ = function of the segment density distribution of adsorbed graft chains and H , H = distance between particle surfaces, k = Boltzmann constant, T = absolute temperature, A = Hamaker constant, $S = (H/a) + 2$, a = radius of the particle.

The coagulation and dispersion of cement particles are determined by the total interparticle potential energy, V_t , which is the sum of V_s and V_a . Further, the dispersion stability of particles due to steric force is governed by the minimum value of the total potential energy curve, V_{min} . It is said that dispersion is stabilized with a V_{min} of no greater negative than $-5kT$.

Figure 6 shows a curve of V_t between a cement particle with adsorbed copolymer layers, where the particle

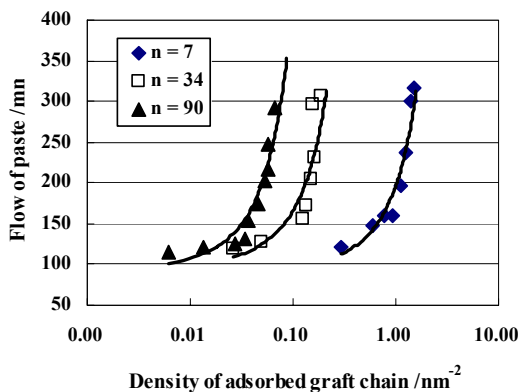


Fig. 5 Relation between density of adsorbed graft chain and paste flow.

radius is $1 \mu\text{m}$ and the number of adsorbed graft chains per unit area is $0.15/\text{nm}^2$. The other parameters necessary for calculation are selected from the literature as follows: the Hamaker constant, A , is $1.7 \times 10^{-21}\text{J}$, based on the results of Hattori *et al.* (Hattori 1980), the segment density profile of the adsorbed polymers, ϕ , is the values determined by Napper (Napper 1970), and the expansion coefficient of graft chains, α , is 1.05 (Nawa 1997). According to conventional steric stabilization theory, it was expected that the cement particles would disperse more due to longer graft chains when the graft chain adsorptions were the same as those shown in Fig. 6. This agrees with the results shown in Fig. 5; the flow value of paste with a higher degree of graft chain PEO polymerization was significantly higher, leading to a more stabilized dispersion of cement particles when the amounts of graft chain adsorption densities were the same.

Figure 7 shows the interparticle potential curves of graft copolymers using measured graft chain adsorption at a paste flow of 200 mm as shown in Fig. 5. The absolute value of V_{min} is not the same, but becomes larger with the polymerization of graft chains. Furthermore, it was simultaneously found that the V_{min} value for the graft

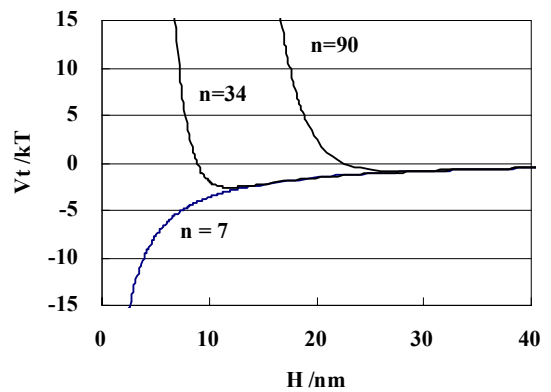


Fig. 6 Interparticle potential curves.

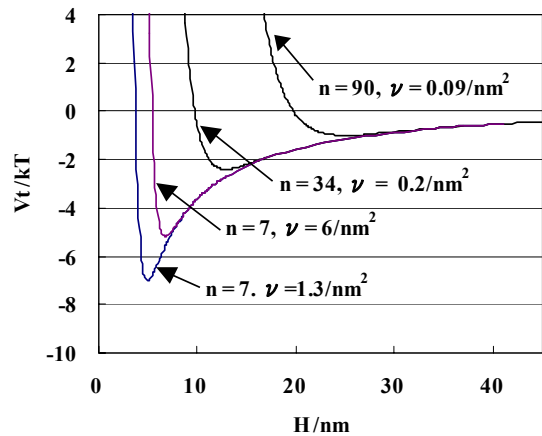


Fig. 7 Interparticle potential curves using the measured graft chain adsorption.

copolymers with a graft chain of $n = 7$ cannot be increased to the levels of those of copolymers with $n = 34$ and 90, even if the graft chain density is increased to as high as $6/\text{nm}^2$. Accordingly, it is judged that the conventional theory of steric stabilization is not capable of qualitatively estimating the dispersing ability of a superplasticizer composed of a graft copolymer, and is inadequate to quantitatively predict dispersing ability for the material design of superplasticizers.

3.5 Considerations on the conformation of graft chains in the adsorption layer

(1) Size of graft copolymer molecules

The geometrical sizes of monomers composing the main and graft chains of the graft copolymers were calculated from the chemical structures shown in **Fig. 1** and the measurement data of molecular weights given in **Table 2**. The C-C bond of the main chain was assumed to be 0.1256 nm as adopted by Ohta *et al.* (Ohta 2000). In regard to monomers composing graft chains, the atomic distances were determined using the length of covalent bonds (C-C bond distance: 0.154 nm, C-O bond distance: 0.143 nm). **Table 3** gives the geometrical size of each graft copolymer.

(2) Extension of graft chains

P. M. de Gennes pointed out that the conformation of graft chains attached to a particle surface on one end changes from random coils to combs as the adsorbed graft chains increased (de Gennes, 1980). He demonstrated that the adsorption thickness of polymers (graft chains) adhering to particle surfaces, L , was the same as random coils (**Fig. 8 a**) while the intervals between graft chains were relatively larger than the size of random coils, but when the adsorption increased and with this, the coverage increased, graft chains extended farther than random coils because they came closer to one another (**Fig. 8 b**). It should be kept in mind that de Gennes's idea could be applied to a polymer attached directly to the surface of particles. However, this idea cannot be applied directly to the graft copolymers dealt with in this study because the graft chains in a copolymer are not attached to the surface of cement and the distance between graft chains depends on not only the adsorbed amount of copolymer, but also the geometric restriction of the copolymer. Therefore the author modified de Gennes's concept to make it applicable to graft copolymers.

For the graft copolymer used in this study, the intervals of graft chains in graft copolymers are shorter than their radius of rotation. It follows that a graft chain adjacent to others in the same molecule ought to exist out of the radii of rotation of other chains. This means that, as graft chains become longer, they are restrained into certain shapes, enabling them to avoid contact with other chains. The bond angle, internal rotation angle, and excluded volume effect of main chains are smaller than those of graft chains because the length of the main chain is smaller than that of the graft chains except for the co-

polymer with a graft chain of $n = 7$. Accordingly, the author assumed that main chains were linearly adsorbed onto cement particles as shown in **Fig. 9**.

Since graft chains bond with the main chain, the distance between graft chains on the main chain, s , becomes shorter than that of random coils as the graft chain length increases. It then follows that the graft chains of the graft copolymers are expected to extend, according to de Gennes' idea, regardless of the adsorption density. However, graft chains can extend in 2-dimension as they are not restrained in directions other than the direction of the main chain axis. On the other hand, the radius of molten polymers extending two-dimensionally is regarded as being similar to the radius of random coils (de Gennes 1979). Accordingly, it is assumed in this study that coils of graft chains with a length greater than the average distance between the graft chains on the main chain, extend two-dimensionally to reach the same size

Table 3 Geometric size of graft copolymer in the stretching conformation.

Type of graft copolymer	Length of main chain (nm)	Length of graft chain (nm)
$n = 7$	29.48	3.52
$n = 34$	6.38	15.4
$n = 90$	5.44	40.4

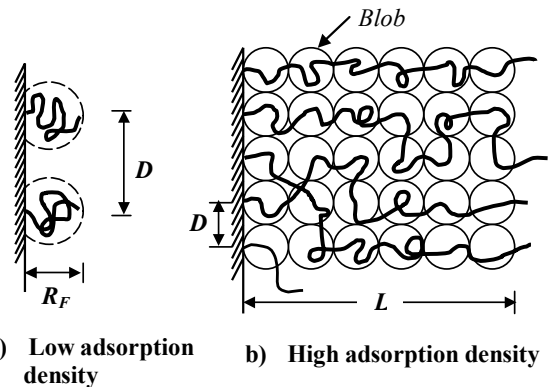


Fig. 8 Conformation of polymer grafted to the surface of particles.

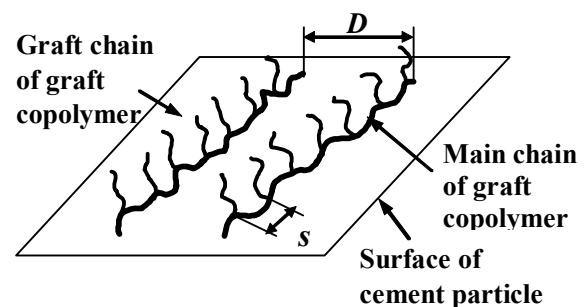


Fig. 9 Conformation of graft copolymer adsorbed on the surface of cement particle.

as random coils. The radius of random coils in a good solvent is referred to as the Flory radius, R_F .

$$L=R_F=bn^{3/5} \tag{5}$$

where b = effective segment length of PEO graft chain. When the adsorption further increases, reducing the graft chain spacing of the copolymers to a threshold value, graft chains are mainly stretched along the normal to the surface of the cement particle, as shown in **Fig. 8 b**). The projected area of two-dimensionally spreading graft chains on the cement particle surface now becomes R_F^2 , and the blobs of graft chains immediately before further extension are close-packed.

Note that D is the distance between the graft copolymers and s is the distance between the graft chains. The above-mentioned assumptions require that the threshold adsorption before the adsorbed graft chains extent, i.e., the critical adsorption density, $\sigma (= b^2/(Ds))$ satisfies the following equation:

$$\sigma < b^2/R_F^2 = n^{-6/5} \tag{6}$$

As the degree of PEO polymerization increases, increasing the graft chain length, the coils become larger and the graft chains come closer to one another, becoming apt to extend. Extended graft chains can be substituted by straight blobs with a size D perpendicular to the adsorption wall (de Gennes, 1980). The thickness of the graft chains, L , can be derived from the fact that the volume per graft chain is LD^2 and contains n monomers. Thus,

$$\Phi b^{-3}=N/(LD^2)=N/(Lb^2\sigma^{-1})$$

$$L= nb\sigma^{1/3} \tag{7}$$

Equation (7) shows that the adsorption thickness, L , is proportional to the degree of PEO polymerization, n , and is longer than the random coils. **Table 4** gives the thickness of adsorption layers determined by Eq. (7) using experimental data on saturated adsorption density of graft copolymers, σ , and the Flory radius of graft chains. According to this table, the thickness of adsorption, L , is longer than that of the random coils. The degree of extension depends on the degree of graft chain polymerization. The adsorption thickness, L (nm), is given by

$$L= 0.44n^{0.79} (n=7) \tag{8}$$

$$L= 0.44n^{0.67} (n=34, 90) \tag{9}$$

(3) Verification of graft chain extension model using past study data

Sakai *et al.* (Sakai 1997, Waseda 1997) measured the thickness of the adsorption layers of graft copolymers similarly to the present study using alumina as the adsorbent. On the other hand, the measurement value of the thickness of the adsorbed copolymer includes the thickness of the main chains adsorbed on the cement surface. In this study, the thickness of the main chains is 0.83 nm, based on the results of Ohta *et al.* (Ohta 2000). **Figure 10** shows the estimated value of thickness of graft chains obtained by subtracting 0.83 nm, the thickness of the adsorbed main chains, from experimental data provided by Sakai *et al.* It is obvious that the extension of the graft chain depends on the degree of PEO polymerization of the graft chains. For graft copolymers with graft chains of $n = 7$, which show a high affinity with cement, the thickness of the graft chains is approximately proportional to n , whereas the thickness of a graft chain of copolymers with a relatively low affinity with graft chains of $n = 34$ and 90, is proportional to $n^{0.77}$. In other words, for graft copolymers with shorter graft chains of $n = 11$ or less, the graft chain is extended as the adsorbed amount of copolymer increases. On the other hand, this infers that, in the case of graft copolymers with graft chains of $n = 34$ or more, the conformation of an adsorbed graft chain resembles that of random coils, as the density of adsorbed graft chains remains low.

Meanwhile, the values of the exponents in Eq. (7) differ from those estimated from experimental data. This

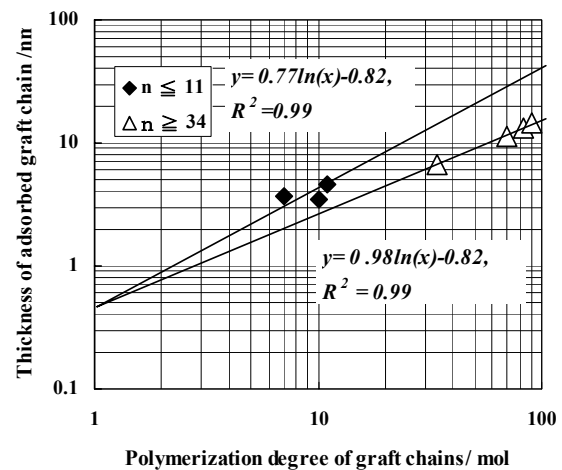


Fig. 10 Relation between polymerization degree of graft chain and the thickness of adsorbed graft chains.

Table 4 Estimated thickness of adsorbed graft chain at saturated adsorption state.

Type of graft copolymer	Density of adsorbed graft chain (nm ⁻²)	Flory radius of a graft chain R_F (nm)	Estimated thickness of adsorbed graft chain L (nm)
n = 7	0.29	1.41	2.05
n = 34	0.03	3.65	4.70
n = 90	0.01	6.55	8.81

can be attributed to the fact that the powder employed by Sakai *et al.* is Al_2O_3 , which has a higher affinity with graft copolymers than cement particles, resulting in greater adsorption and longer extension.

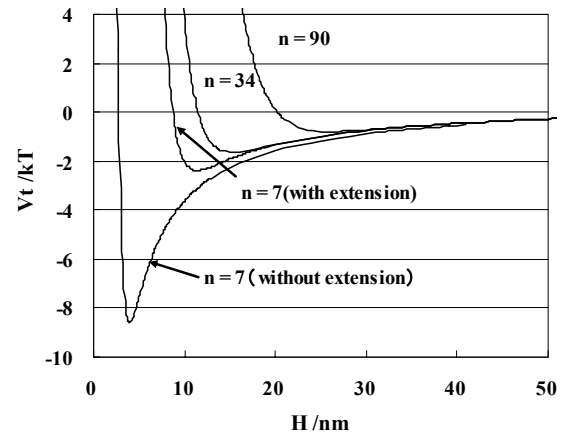
3.6 Steric stabilization mechanism incorporating extension of graft chains

In the discussion above, the author dealt with the conventional theory of steric stabilization due to graft chains of adsorbed copolymers and showed how changes in the conformation of adsorbed graft chains might be related to the changes in adsorbed amounts of copolymer. In the following, the author discusses the effect of chemical structure of copolymer on steric stabilization, as well as the following working assumptions based on the results of this study.

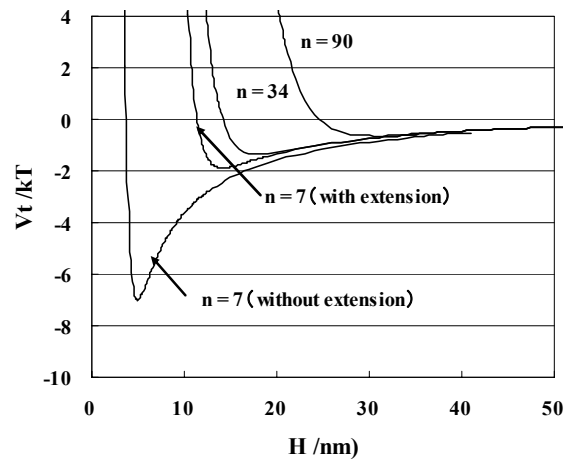
- (1) The steric dispersing ability of graft copolymers primarily results from the increment of mixing free energy of graft chains (Napper 1973). Such a steric repulsive potential is evaluated by Eq. (3).
- (2) The thickness of adsorbed graft chains depends on the adsorption density of copolymer and can be calculated using Eqs. (5) and (7).
- (3) The adsorption thickness of main chains, L' , also affects the steric dispersing effect. This effect can be evaluated as an apparent increment of thickness of graft chain equivalent to the adsorption thickness of the main chains.

The adsorptions required for the flow values between 150 and 250 mm were determined by the relationship between the graft chain adsorption density and the flow value shown in Fig. 5. The thickness of the graft chains of adsorbed graft copolymers was then estimated from Eq. (5) or (7) using the estimated adsorptions, and then the total interaction energy between two cement particles could be calculated using Eqs. (3) and (4). The results are shown in Fig. 11.

It is evident that the differences in the values of V_{\min} in the interparticle potential curves are significantly reduced by the use of the extension model, compared with the value of V_{\min} not taking into account extension. Based on this extension model of graft chains, it can be deduced that when the intervals between graft chains within a graft copolymer are excessively wider than the radius of the random coil, the graft chains do not extend, thereby preventing the cement-dispersing ability of the copolymer. Conversely, when the graft chain intervals are excessively narrow and the volumetric ratio of graft chains is greater than the main chains, the adsorption of the copolymer on cement particles decreases. In other words, the adsorption density of the graft chains decreases, thereby reducing the cement-dispersing capability of the copolymer similarly to those with graft chains of $n = 34$ and 90 shown in Fig. 4. Accordingly, it seems that there is an optimum balance between the lengths of graft chains and main chains. This provides a good explanation of the results given by Ohta *et al.* (Ohta 1997) that a graft chain length exists that improves the fluidity of



(a) Paste flow is 150 mm



(b) Paste flow is 250 mm

Fig.11 Interparticle potential curves incorporating the extension of graft chains due to adsorption.

cement paste most significantly, while a longer graft chain length conversely reduces the fluidity.

Therefore, it can be concluded that taking into account the extension of graft chains due to the interactions between adjacent graft chains, the cement particle dispersing mechanism of polycarboxylate-based superplasticizers composed of graft copolymers with polyethylene oxide graft chains basically results from the steric repulsion of the graft chain adsorption layer, and the intensity of the repulsion is strongly affected by the adsorption thickness of the graft chain determined by the adsorption density, σ , and the graft chain spacing, s , within the copolymer.

4. Conclusions

In this study, the effect of chemical structure on the cement-dispersing ability of polycarboxylate-based superplasticizers, composed of graft copolymer with different chemical structures, was investigated from the viewpoint

of the effect of chemical structure on steric repulsion due to graft chains and on the conformation of adsorbed graft chains. The results are summarized as follows.

- (1) The cement-dispersing ability of a polycarboxylate-based superplasticizer composed of a graft copolymer with PEO graft chains can be explained by the steric repulsion effect of graft chains adsorbed on cement particle surfaces.
- (2) The thickness of a graft chain in a copolymer adsorbed on a cement particle depends on the average distance between two graft copolymers and the graft chain spacing within the copolymers. When the adsorption area expressed by the product of these two parameters is greater than the area occupied by a random coil, the conformation of graft chains looks like random coils. On the other hand, when the adsorption area is smaller, then the graft chains extend into the solution, resulting in an increase in the thickness of the adsorbed graft chains layer.
- (3) The steric stabilization model incorporating the extension of graft chains due to adsorption provides a good explanation of the relationship between the adsorption and the flow of paste containing different graft copolymers. It also well explains the fact that there is an optimum graft chain length for high fluidity. Accordingly, it is judged that the effect of the chemical structure of superplasticizers on the fluidity of concrete can be quantitatively explained by the use of the graft chain extension model proposed in this study.

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