# Effects of Grafting Densities of Comb-Like Copolymer on the Dispersion Properties of Concentrated Cement Suspensions

Jiaping Liu[1,*], Qianping Ran[1,2], Changwen Miao[1] and Min Qiao[2]

[1]*State Key Laboratory of High Performance Civil Engineering Materials (Jiangsu Research Institute of Building Science), Nanjing, 210008, P. R. China*
[2]*Jiangsu Bote New Materials Co. Ltd., Nanjing, 210008, P. R. China*

Effects of grafting densities of comb-like copolymer on the dispersion properties of concentrated cement suspensions are investigated systemicly in this paper. For comb-like copolymers the adsorbed amount increases at the same dosages as the grafting density decreases, while the efficiency of dispersion is improved by increasing the grafting densities. Based on the theory of Flatt at level of scaling law, the molecule size and the occupied surface area of the comb-like polymers with different grafting densities are calculated. The comb-like polymers with higher grafting density has bigger molecular size. For comb-like polymer dispersant, the steric repulsion provided by the side chains is the main drive of the dispersion, so the Flory energy is employed to explore the relationship between steric repulsion and grafting density. The calculation tells us that higher grafting density results in higher Flory energy which represents stronger steric repulsion. The calculation method based on the scaling law and Flory theory is successfully used to interpret the dispersion mechanism, and it is anticipated that this method can be applied to explain the effect of other parameters of PCE comb-like polymers on the dispersion properties of cement suspensions, ceramics suspensions, slurries and so on. [doi:10.2320/matertrans.M2011344]

## 1. Introduction

Comb-like copolymers are relatively more efficient and new types of cement dispersants with a very flexible chemical structure.[1–5] It is easy to modify and adapt this molecular structure in order to maximize the targeted properties and also meet specific properties for different applications. Thus it has attracted significant attention and been extensively studied in the recent 20 years.[1–7] These comb-like copolymers are composed of a polyelectrolyte backbone and nonionic polyethylene glycol (PEG)-based "teeth" side chains grafted onto the backbone at frequent intervals. It is considered that, in comb-like copolymers the carboxylate ions in the backbone mainly act as the drive of the adsorption because of the electrostatic attraction between anionic polycarboxylate backbone and cationic surface of cement particles, meanwhile the hydrophilic PEG side chains extend into the solution and mainly provide the steric repulsion, which is the main drive for the dispersion of cement particles.[5,6] Recently, the impact of the length of side chain on the dispersion of cement was widely studied.[7–9] But the steric repulsion provided by one molecule of comb-like copolymers relies not only on the length of the side chain but also on the number of side chains in one polymer molecule. The grafting density is the ratio between the number of side chains and charged groups per one polymer molecule, and variation of grafting densities allows adjustment of different properties, such as a strong initial dispersing effect and/or high dispersion retention of fresh cement pastes.[10–12] G. Ferrari[10] reported that comb-like polymer with the higher charged groups exhibited higher adsorption, excellent dispersing effects and short dispersibility retention; whereas those polymer with lower charge density showed low adsorbed amount and low initial dispersing effects, but excellent flowability retention.

Similar results concerning this structure–property relationship have been reported by other researchers.[11,12] However, those studies usually focused on the relationship between the adsorbed amount and dispersing effect. A number of published papers have confirmed that the performance of the comb-like polymer as a dispersing agent in cement depends on not only adsorbed amount, but also the conformation of adsorbed polymers.[13,14]

This study aims to contribute to a precise understanding the impact of the grafting densities in comb-like copolymers on dispersing effect in cementitious systems from the point of adsorption and conformation. Thus, we synthesis and characterize a series of polycarboxylate comb-like copolymers (hereinafter called PCE) with different graft densities and the same length of side chain in this study as shown in Fig. 1. The effects of the graft densities on the adsorption and dispersion properties of cement paste were investigated systematically, which will help in understanding the relationship between the molecular structure and apparent properties and elucidating the dispersion mechanism of comb-like copolymers. A successful dispersant should be the combination of dispersability and adsorption. In this paper, it is focused to study which kind of comb-like structure has high efficiency of dispersion, which is a quite academic question. Finally relationship between the dispersion and the molecular structure is interpreted in method of calculation based on scaling law and Flory theory,[14,15] and this method can be applied to explain the effect of other parameters of PCE comb-like polymers on the dispersion properties of cement suspensions, ceramics suspensions, slurries and so on.

## 2. Experimental

### 2.1 Cement

An ordinary Portland cement (42.5, Lafarge Cement Co., China) which meets the requirements of GB8076 standard

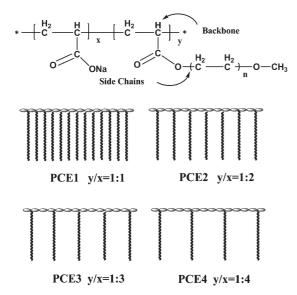*Corresponding author, E-mail: liujiaping@cnjsjk.cn

Fig. 1   Illustration of the chemical structure of comb-like copolymers with different graft densities.

Table 1   Phase composition and physical properties of the cement.

| Phase composition/% | | | | Percent volume diameters/μm | | | | BET surface area/m²·g⁻¹ |
|---|---|---|---|---|---|---|---|---|
| $C_3S$ | $C_2S$ | $C_3A$ | $C_4AF$ | $d_{10}$ | $d_{50}$ | $d_{90}$ | VMD | |
| 52.17 | 21.16 | 7.49 | 8.21 | 3.74 | 19.82 | 52.05 | 25.04 | 0.8424 |

Here, $C_3S$, $C_2S$, $C_3A$ and $C_4AF$ represent dicalcium silicate, tricalcium aluminate, tricalcium silicate and tetracalcium aluminate ferrite, respectively. $d_{10}$, $d_{50}$ and $d_{90}$ represent the particle size bellow which the volume percent is 10, 50 and 90% respectively. VMD was the average mean particle size.

was used in this study. The cement composition was determined by X-ray fluorescence and Bogue analysis. The particle size analysis using a Helos-Sucell Laser particle size analyzer (SYMPATEC Instruments, German) showed the average mean particle size is about 25 μm. The BET surface area is $0.8424\,m^2 \cdot g^{-1}$. The characteristics and compositions of the sample are given in Table 1.

## 2.2   Comb-like copolymer dispersants

The comb-like polymers dispersant (hereinafter called PCE) composed of sodium polyacrylate backbone and uncharged polyethylene glycol (PEG) teeth as shown in Fig. 1 were prepared in our laboratory. Details of the preparation procedure and characterization methods were described elsewhere.[4,7] In this study, a series of comb-like copolymers with different graft densities and the same length of side chain have been chosen and tested. The grafting density of the copolymer can be set by simply choosing the appropriate mixing molar ratio between sodium acrylate (SAA) and methoxy poly(ethylene oxide)-acrylate (MPEGAA). The grating density $\tau_g$ can therefore be calculated by the eq. (1). The number average molecular weight of methoxypolyethyleneglycol (MPEG) side chains and the composition of PCE have been estimated classically by ¹H-NMR spectroscopy. The molecular weight of PCE was determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS) equipped

Table 2   Molecular characteristics of comb copolymer dispersant.

| | Molar composition/% | | $M_n$[*1] | $M_w$[*2] | $DPw$[*3] | $\tau_g$[*4] | $m$[*5] |
|---|---|---|---|---|---|---|---|
| | SAA | MPEGAA | | | | | |
| PCE1 | 55 | 45 | 23160 | 33180 | 57 | 0.45 | 26 |
| PCE2 | 67 | 33 | 23600 | 33490 | 72 | 0.33 | 24 |
| PCE3 | 76 | 24 | 21510 | 32680 | 90 | 0.24 | 22 |
| PCE4 | 82 | 18 | 21730 | 30980 | 105 | 0.18 | 19 |

[*1]$M_n$ = number average molecular weight, [*2]$M_w$ = weight average molecular weight, [*3]$DPw$ is the degree of polymerization calculated according to $M_w$, [*4]$\tau_g$ is the grafting density calculated by eq. (1). [*5]$m$ is average number of side chain in one comb-like polymer molecular.

with TSK-GELSW (TOSOH) columns. The used PCE architectures and their molecular characteristics are listed in Table 2. All PCE were used as sodium salts. The degree of polymerization ($DPw$) is calculated based on the average molecular weight obtained for each copolymer.

$$\tau_g = \frac{y}{x+y} \tag{1}$$

Where $x$ and $y$ are the molar fraction of SAA and MPEGAA per comb-like copolymer, respectively.

## 2.3   Adsorption measurements

The amount of PCE comb-like copolymers adsorbed was determined by means of a total organic carbon analyzer, Multi N/C3100 (analytikjene AG, Germany). 20 g of solution containing various amount of PCE and 10 g of cement were mixed by a magnetic stirrer for 5 min at 20°C. The sample solution was separated by suction filter. The aqueous phase was separated by centrifuging at 13,000 rpm for 5 min by using a centrifuge. The supernatant was immediately decanted and dilute with deionized water for TOC. Several aliquots of each sample were measured. The difference in the concentration before and after contact with the cement is assumed to be adsorbed polymer. The adsorbed number of side chain per unit area of cement ($N_d$) then can be calculated from the adsorption amount and the molecular weight and composition of comb-like dispersants according to the following eq. (2):

$$N_d = \frac{A_s \cdot 10^{-3}}{S_w \times M_w} \cdot N_A \cdot m \tag{2}$$

Where $S_w$ is the cement BET surface area (m²·g⁻¹); $M_w$ is the molecular weight of the comb-like dispersant (g·mol⁻¹); $A_s$ is the adsorbed amount of dispersant adsorbed onto the cement surface (mg·g⁻¹); $N_A$ is Avogadro's number and $m$ is average number of side chain in one comb-like polymer molecular.

## 2.4   Dispersion behavior

Cement pastes were mixed at 20°C and at water to cement ratio (w/c) = 0.23, using a Hobart mixer. First, PCE and water were weighed into a bowl. Then 300 g of cement was added and mixed for 1 min at low speed and a further 2 min at high speed. The amount of PCE added is expressed as a percentage of dry solid with respect to the mass of cement. The cement paste was used to measure fluidity and
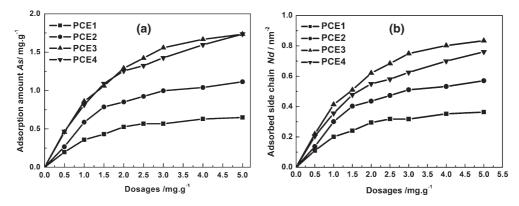
Fig. 2  Adsorption amounts of PCE comb-like copolymers on cement surface (a) and the adsorbed number of side chain per unit area of cement (b) as a function of the amount of PCE introduced.

rheological behavior at the same time. The fluidity of cement paste was evaluated by a flow test. The paste flow was measured at 20°C by pullout spread of cement paste from a cone (upper inner diameter is 36-mm, lower inner diameter is 60-mm and 60-mm height), in accordance with GB8076-2008.

## 3.    Results and Discussion

### 3.1    Adsorption behavior

The adsorption behavior of PCE comb polymers and the adsorbed number of side chain for varying graft densities onto the surface of cement as a function of the amount introduced are shown in Fig. 2. In all PCE comb polymers [Fig. 2(a)], their initial adsorbed amount increases rapidly as the dosages added increases from 0.5–2.0 mg·g$^{-1}$. Within this period, the surfaces of cement particles are more active and also contain more empty sites. Therefore, the adsorption can carry on continuously. At the higher dosages (>2.0 mg·g$^{-1}$), the adsorption amount increases more slowly, and approaches gradually a constant characteristic plateau. It can be seen that for PCE comb-like copolymers the adsorbed amount increases at the same dosages as the grafting density is decreased, which is ascribed that the densely grafting side chains provide strong hindrance to the adsorption. However, a slight difference can be seen for PCE4, probably due to the fact that the high content of carboxylate results in the coil conformation of polymer in high salt concentration and thus decreases its adsorption.[16] The same rules can be found in the situation of adsorbed number of side chains as function of the dosage as shown in Fig. 2(b). But it can be clearly seen that PCE3 and PCE4 have much more difference in the adsorbed number of side chains than in the adsorbed amount because of the relatively low grafting density of PCE4.

### 3.2    Dispersion behavior

The effect of PCE comb-like copolymers with different grafting densities on the fluidity of cement paste is shown in Fig. 3. It can be seen that for PCE comb-like copolymers the dispersability increases at the same dosage as the grafting density is decreased [Fig. 3(a)]. For the retention of fluidity at the same dosage of 2 mg/g, Fig. 3(b) tells that the PCE polymer with higher grafting density has better retention of

the fluidity. At the same dosage PCE polymers with dense grafting side chains has low adsorbed amount, which means that the amount of residual polymers in the solution is abundant. As the hydration of cement going on, new surface is generated gradually and need more and more residual polymers to adsorb. So high grafting density results in high amount of residual polymers and then the residual polymer results in the good retention of the fluidity. Although the relationship between dispersion and dosage of the PCE polymers with different grafting densities gives us delighted results, the adsorbed part of the polymers is the dispersant actually working. So the relationship between dispersion and adsorbed amount is given in Fig. 3(c). Here, something interesting appears. It is clearly seen that the PCE polymers with higher grafting density has better efficiency of dispersion, that is, the same fluidity can be achieved at lower adsorbed amount of dispersant with higher grafting density. When transforming the adsorbed amount into adsorbed density of polymer molecule [Fig. 3(d)] and adsorbed density of side chains [Fig. 3(e)], the similar results can be got. There is a rule that the PCE polymer with high grafting density has high efficiency of dispersion but is difficult to be adsorbed. Using PCE1 as an example, although it is bad in dispersion in appearance which is due to the low activity of adsorption, PCE1 has extremely high efficiency of dispersion. Sometimes, researchers are easily deceived to consider that PCE1 is not competent for dispersion of cement, but PCE1 gives us important hints to explore the mechanism of dispersion and seek excellent dispersant.

### 3.3    Molecular size

In order to know which kind of molecular structure has high efficiency of dispersion, we should know the conformation and the molecular size of the adsorbed polymer. Gay and Raphael[15] reported a method to work out the conformation and molecular size of the comb-like polymers inside nanoscale pores based on the Flory free energy approach at level of scaling laws. Then Flatt[14] developed this method to resolve the conformation of adsorbed comb-like polymer dispersants. Based on the theory of Gay and Raphael,[15] comb-like polymers can be divided into many segments as shown in Fig. 4(a). Here each side chain has $P$ monomers and each segment has $N$ backbone monomers. In this paper, the PCE comb-like polymers can be considered in
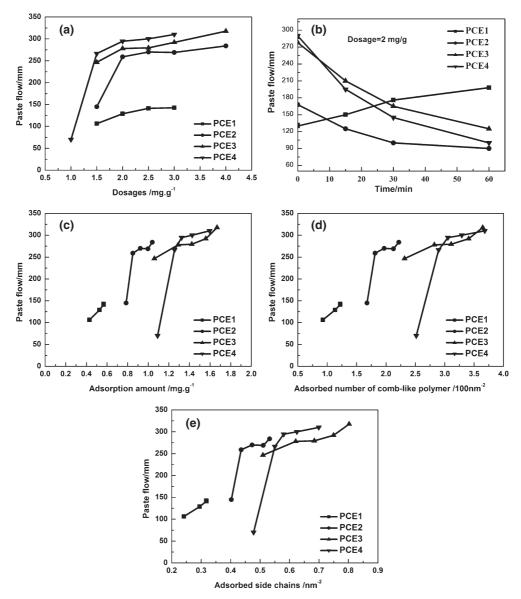
Fig. 3  Dispersion behavior of PCE with different grafting densities (a) dispersion vs. dosages, (b) dispersion vs. time, (c) dispersion vs. adsorbed amount, (d) dispersion vs. adsorbed number of comb-like polymers, and (e) dispersion vs. adsorbed side chains.
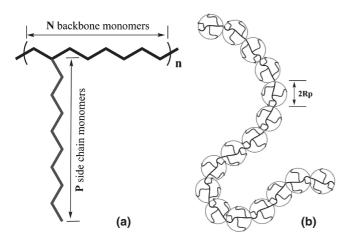


Fig. 4  (a) Schematic representation of the comb-like polymers considered. The polymer contains $n$ segments, each segment contains one side chain which has $P$ monomers and each segment contains $N$ backbone monomers; (b) illustration of the conformation of flexible backbone worm (FBW).

conformation of flexible backbone worm (FBW) as shown in Fig. 4(b). Based on the theory of Flatt,[14] the radius of a given core ($R_p$) and the surface occupied by each molecular in dense packing model can be calculated as eqs. (3) and (4).

$$R_p = \left( 2\sqrt{2}(1 - 2\chi)\frac{a_p}{a_N} \right)^{1/5} a_p P^{7/10} N^{-1/10} \qquad (3)$$

$$S_{\text{dense packing}} = \frac{\chi}{\sqrt{2}} a_N a_p \left( 2\sqrt{2}(1 - 2\chi)\frac{a_p}{a_N} \right)^{2/5} P^{9/10} N^{3/10} n \qquad (4)$$

Here, $R_p$ is the radius of a given core, $S_{\text{dense packing}}$ is the surface occupied by each polymer molecular in dense packing model, $\chi$ is the Flory parameter which is about 0.37 at 25°C,[17] polymers have a acrylate backbone ($a_N = 0.25\,\text{nm}$) and poly(ethylene oxide) side chains ($a_P = 0.36\,\text{nm}$),[14] the number of monomers in side chains ($P$), the number of monomers in one segment ($N$) and the number of segments ($n$) are list in Table 3.

Table 3 Molecular size of comb-like copolymer dispersant.

| Dispersant | $P$ | $N$ | $DPw$ | $n$ | $R_p$/nm | $S_{dense\ packing}$[*1]/nm$^2$ | $S_{max}$[*2]/nm$^2$ | $S_{0.1\%}$[*3]/nm$^2$ | $I_f$[*4] |
|---|---|---|---|---|---|---|---|---|---|
| PCE1 | 23 | 2 | 57 | 28.5 | 3.23 | 13.3 | 936 | 46.4 | 20.2 |
| PCE2 | 23 | 3 | 72 | 24 | 3.10 | 12.6 | 727 | 46.8 | 15.5 |
| PCE3 | 23 | 4 | 90 | 22.5 | 3.02 | 12.9 | 643 | 45.7 | 14.1 |
| PCE4 | 23 | 5 | 105 | 21 | 2.95 | 12.9 | 574 | 43.3 | 13.2 |

[*1] $S_{dense\ packing}$ is the occupied surface area per one polymer molecule following the law of dense packing; [*2] $S_{max}$ is the maximal occupied surface area per one polymer molecule, which is calculated as $S_{max} = 3.14 n R_p^2$; [*3] $S_{0.1\%}$ is occupied surface area per one polymer molecule calculated from the adsorption behavior when the adsorption amount is 1 mg/g; [*4] $I_f$ is the factor to declare the degree of the dense packing at 1 mg/g of adsorption amount, which is equal to the value of $S_{max}/S_{0.1\%}$.
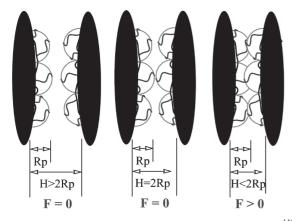


Fig. 5 Schematic illustration of the steric repulsion hypothesis.[14]



Fig. 6 The Flory energy of cement suspensions using PCE comb-like polymer with different grafting densities as dispersant.

In Table 3, it can be clearly seen that the comb-like polymers with higher grafting density has higher value of $R_p$, which causes stronger steric repulsion when two polymer-adsorbed cement particles approach. If adsorbed polymers effectively exclude each other from their own surrounding on the surface of the cement particles, $S_{max}$ can be used to represent the occupied surface area per single polymer molecule. Otherwise in the extreme case of close packing, $S_{dense\ packing}$ can be used to represent the occupied surface area per single polymer molecule. The value of $S_{max}$ and $S_{dense\ packing}$ are in great disparity. When the adsorption amount is 1 mg/g, the actual occupied surface area per single polymer molecule is represented by $S_{0.1\%}$ which can be calculated based on the adsorption amount, molecular weight and the BET surface area of cement. $S_{0.1\%}$ is definitely the value between $S_{max}$ and $S_{dense\ packing}$, so the factor ($I_f$) is employed to evaluate the degree of dense packing. $I_f$ increases as the grafting density increases, that is, the coverage rate on the surface of the cement particle increases as increasing the grafting density, which can explain why the efficiency of dispersion increases with the grafting density increasing.

### 3.4 Flory energy

For comb-like polymer dispersant, the steric repulsion provided by the side chains is the main drive of the dispersion.[5,14,15] So in this paper, the action of steric repulsion provided by the comb-like polymers with different grafting densities is systemicly investigated. Figure 5 illustrates the action of s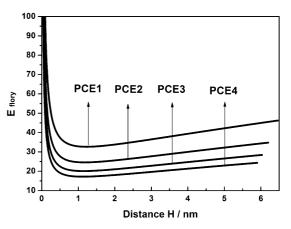teric repulsion when two polymer-adsorbed cement particles approach. When the distance $H$ is larger than or equal to $2R_p$, there is nearly no steric repulsion. When $H$ is less than $2R_p$, the steric repulsion becomes the hindrance of the further approach of the cement particles. Equation (5) can be used to calculate the Flory energy as a function of distance $H$ when two particles approach.[14]

$$E_{flory} = \frac{3}{2\sqrt{2}} \frac{R_p^2}{a_p a_n \sqrt{PN}} + \frac{3}{2\sqrt{2}} \frac{R_p^{4/3}}{a_p a_n \sqrt{PN}} H^{2/3}$$
$$+ (1 - 2\chi) \frac{4 a_p^5 P^3}{a_N^2 R_p^2 N} \frac{1}{H} \qquad (5)$$

The Flory energy of the PCE comb-like polymers with different grafting densities is given in Fig. 6 as a function of $H$. When two cement particles approach, the Flory energy increases when increasing the grafting densities. It indicates that high grafting density causes high Flory energy which represents strong steric repulsion. Strong steric repulsion is helpful for dispersion, so increasing grafting densities is helpful for increasing the efficiency of dispersion, which is consistent with the experimental results of dispersion behavior. But from the results of adsorption it is known that increasing grafting densities is bad for adsorption. A successful dispersant should be the combination of dispersability and adsorption. In this paper although PCE1 has the best ability of dispersion, its adsorption is bad. So the dispersion of PCE1 in the actual application is not satisfying. Whereas the research here supplies researchers the guidelines to optimize the molecular structure of polymer dispersant, which will promote the development of comb-like polymer dispersant for cement, ceramics and so on.

## 4. Conclusions

Based on the theory of Flatt at level of scaling law, the molecule size and the occupied surface area of the comb-like polymers with different grafting densities are calculated. The comb-like polymers with higher grafting density has bigger molecular size. The degree of dense packing ($I_f$) increases as the grafting density increases, which means that the coverage rate on the surface of the cement particle increases as increasing the grafting density. For comb-like polymer dispersant, the steric repulsion provided by the side chains is the main drive of the dispersion, so the Flory energy is employed to explore the relationship between steric repulsion and grafting density. The calculation indicates that higher grafting density results in higher Flory energy which represents stronger steric repulsion. The above conclusions tell that PCE comb-like polymer dispersant with higher grafting density has higher coverage rate on the surface of the cement particle and stronger action of steric repulsion, which induces the better efficiency of dispersion. From the experimental results of adsorption and dispersion behavior, it can be seen that the efficiency of dispersion is improved by increasing the grafting density, which is accordant with the results of calculations. So in this paper, a calculation method based on the scaling law and Flory theory is successfully used to interpret the dispersion mechanism, and it is anticipated that this method can be applied to explain the effect of other parameters of PCE comb-like polymers on the dispersion properties of cement suspensions, ceramics suspensions, slurries and so on.

## Acknowledgments

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