

Basic Research of Improving the Mortar Flow by Thermal Stimulation to Superplasticizer

Mizuki Takigawa¹, Fraidoon Rahmanzai², Rio Kita² and Shigeyuki Date²

¹Graduate School of Eng., Tokai University, Hiratsuka, Kanagawa Japan

²Tokai University, Hiratsuka, Kanagawa Japan

Abstract. Polycarboxylic acid-based superplasticizers are being used for various fields of concrete work, however little has reported on changing basic performance by thermal fluctuation. In this study, heating superplasticizers itself is hereinafter as referred to as “thermal stimulation”, the effect of thermal stimulation and heat retention of superplasticizer on the fresh mortar, moreover the influence of molecular structural changed of superplasticizer by thermal stimulation were investigated. As the result, it was confirmed that improving fluidity of the mortar flow on this condition the highly heat temperature and heat over a long time by thermal stimulation of superplasticizer. In addition, it turned out that this phenomenon was caused molecular structural changed by thermal stimulation, and the result was revealed that the effect of thermal stimulation varies according to the type of polymer.

1 Introduction

The superplasticizer can be fulfilled various requirements such as quality, durability, slump life, and adequate construction performance, it is being widely used for the construction work. The performance of superplasticizer is affected by ingredients, dosage, type of cement, ambient temperature, mix proportions and so on [1-2]. In addition, the superplasticizer such as high-range water reducer and high-range AE water reducers can be used not only to reduce mixing water but also to improve construction performance and strength of concrete while maintaining slump value [2-3].

In general, it is widely known that the fluidity of mortar and concrete with superplasticizer can be fluctuated with affected by ambient temperature [4-6]. However, little is known about the fluidity of mortar and concrete were improved by direct thermal stimulation to superplasticizer. Other researchers [7-10] have reported that the fresh property of concrete using polycarboxylic acid or polycarboxylic acid ether type superplasticizer can be influenced by the chemical structure of base polymer as main ingredient, in particular, the type, length, arrangement and presence of functional groups on the backbone or sidechain [11-12]. Furthermore, it has reported that the dispersion efficiency of cement increases in step with the number and length of hydrophobic grafts, and polymer molecular of hydrophobic grafts will be adsorbed onto the surface of cement particles. The hydrophobic graft of the polymer adsorbed on the cement particles can inhibit the approach

of other cement particles due to its steric hindrance effect and it has been reported that the fluidity of cement paste will be improved by preventing aggregation [13-14]. These studies indicated the thermal stimulation effect in superplasticizer exert influence to increase the length of hydrophobic graft about coil-like configuration, as in consequence, potential for causing steric hindrance was considered. In this study, to elucidate the mechanism of improvement of fluidity by thermal stimulation to polycarboxylic ether type superplasticizer, change of flowability of mortar before and after heating was confirmed, and three-dimensional structural analysis of polymer was also conducted.

2 Experimental procedures

2.1 Outline of thermal stimulation

Atrophying or entangling polymers are extended and disintegrated by heating, and as a result, the adsorption area to cement can be improved, so a higher dispersion effect will be expected. This is the hypothesis of the principle of thermal stimulation. Generally, the length of the side chain is considered to be shorter for the slump keeping polymer than for the dispersion polymer. For this reason, it is considered that the slump keeping polymer is more effective for disintegrating effect of intertwined polymer by thermal stimulation. Therefore, it is inferred that the superplasticizer containing a large amount of slump keeping polymer has a higher fluidity improving effect.

2.2 Material used

Material used are shown in Table 1. In this study used of cement is Ordinally Portland Cement (Density; 3.16g/cm³), and fine aggregate is river sand from Yamakita Kanagawa prefecture (Density; 2.69g/cm³). 2 kinds of superplasticizer as high range water reducing agent mainly used for precast concrete (hereinafter referred to as “PCa type”) and high range water reducing agent AE type mainly used for ready mixed concrete (hereinafter referred to as “RMC type”) were used for this study. All types superplasticizers contain polycarboxylic acid ether-based polymer.

2.3 Experiment condition

The Conditions of experiment and other conditions are shown in Table 2 and Table 3 respectively. The combination of 30% of water cement ratio and the combination of 2.0 of sand cement ratio. The setting the dosage of superplasticizers are C×0.56% of PCa type and C×0.84% of RMC type. In Case1, provide a regular time of heating of superplasticizer and setting the heating temperature was 40°C, 50°C and 60°C. In Case2, provide a regular temperature of heating of superplasticizers and setting the heating time was 0.5 hour and 24 hours. In addition, in this study, superplasticizers without heating in temperature of 20°C were used as control. Mixing water’s temperatures used was unify to 20±2°C, and mixing temperature was set within 23°C regardless of whether thermal stimulation. The initial flow of all specimen was set to 110±5 mm.

2.4 Method of thermal stimulation

Each kind of superplasticizer was put in small bottles and was kept in a hot water as the same temperature. Moreover, this one was put in heat chamber, and superplasticizers ware heating to keep warm. Also, all the bottles were shielded to prevent from evaporation of water in the superplasticizer and to maintain solid content.

2.5 Method of experiment

Mixing procedure is shown in Fig.2. Fresh test of the mortar was conducted in accordance with the JIS R 5201 “Physical testing methods for cement”. Even in the case of the usual non-thermal stimulation of superplasticizers, it was kneaded by the same procedure. The atmosphere temperature during kneading and freshness test was 20 ± 3 ° C. Moreover, the effect of thermal stimulation the value of mortar flow compared with presence or absence of thermal stimulation by the index shown in Equation (1).

$$\Delta FL(\%) = \frac{Fs-Fi}{Fi} \times 100 \quad (1)$$

Fs; Mortar Flow after thermal stimulation (mm)
 Fi; Mortar Flow before thermal stimulation (mm)

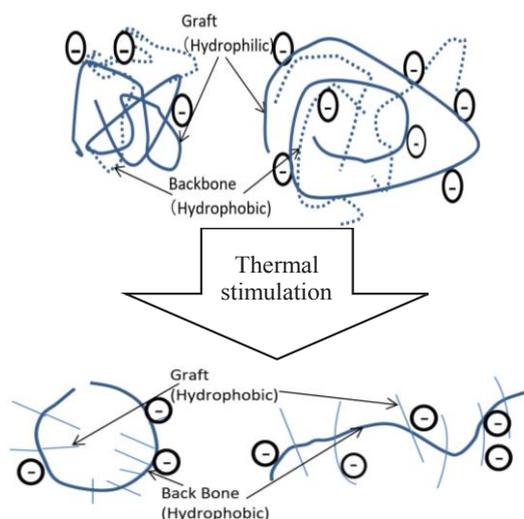


Figure 1. The image of polymer structures changing by thermal stimulation.

Table 1. Material Used.

Materials		Properties
Cement	N	Ordinally portland cement Density: 3.16 g/cm ³
Fine aggregate	S	River sand from Kanagawa Density: 2.69g/cm ³ Water absorptivity: 1.49%
Super plasticizer	PCa	High range water reducing agent
	RMC	High range water reducing agent AE Type

Table 2. Conditions of experiment.

Cond.	Type of Ad	W/C (%)	S/C	Ad/C (%)	Heat temp. (°C)	Heat time (hr)
Case1	PCa	30	2.0	0.56	40	0.5
	RMC			0.84	60	
Case2	PCa	30	2.0	0.56	60	0.5
	RMC			0.84		24

Table 3. Other conditions.

Temperature of control	20°C
Temperature of mixing water (W + Ad)	20±2°C
Mixing temperature	≤23°C
Initial flow value	110±5(mm)

In addition, Dynamic Light Scattering (hereinafter referred to as “DLS”) which is one of the researching methods of Light Scattering analysis was used for structural analyses of the polymer [15]-[19]. Fig.3 are

shown in the schematic of DLS's machine used. DLS is the method that can measure the density of molecule relate molecule's Brownian motion into samples and the can get the data of the diffusion coefficient, particle size distribution, and molecular structure. In this study, the geometrical size of polymer evaluated to change that between relaxation time and scattered light intensity. 2 kinds of superplasticizers were prepared giving thermal stimulations (heating on 60°C-24hr) and no-heat that diluted at 150-fold with ultrapure water. This analysis diluted purpose of superplasticizers because reproducing mix properties and dilute the concentration of color. Therefore, after diluting temperature was 20°C±2°C as the same mixing water's temperature as to this was analyzed. Immediate after diluting time was 0 hour, filtered by 0.45µm, and ongoing was measured for 3 solid hours after calibrating. Moreover, the measured angle that exposed samples to a laser was θ. In this experiment, θ=90°, and measured temperature was 25°C. Equation (2) and (3) were used to make a graph.

Self-correlation function

$$g^{(2)}(t) = \frac{\langle I(0) \cdot I(t) \rangle}{\langle I(0) \rangle^2} = 1 + |g^{(1)}(t)|^2 \quad (2)$$

Correlation function of relaxation time

$$g^{(1)}(t) = \int e^{-\frac{t}{\tau}} G(\tau) d\tau \quad (3)$$

τ; Relaxation time (ms)

I; Scattered light intensity

G; Distribution function of the relaxation time

g⁽¹⁾(t); Normalized correlation function of scattering light optical electric-field

g⁽²⁾(t); Normalized correlation function of scattered light intensity.

3 Results and discussion

3.1 Relation between thermal temperatures and thermal times and changing rate of flow

Fig.4 and Fig.5 were shown in the relation between the thermal temperature of superplasticizers and thermal times and changing rate of mortar flow. It was evident from Fig.4 and Fig.5 that in both of PCa type and RMC type improved the fluidity of mortar as the thermal temperature of superplasticizers raised and took the long time to heat of superplasticizers. Moreover, the also improving the fluidity of mortar were confirmed from Fig.5, it was also found that the effect of thermal stimulation was higher as the initial flow value was smaller. In addition, from Fig.4 and Fig.5 was confirmed that compared PCa type with RMC type, RMC type of fluidity of mortar was more improved than PCa type. This result can be considered that it relates to the difference in principal component of superplasticizers. In general, almost superplasticizer's principal component of RMC type blended dispersion polymers with slump keeping polymers, on the other hand, almost

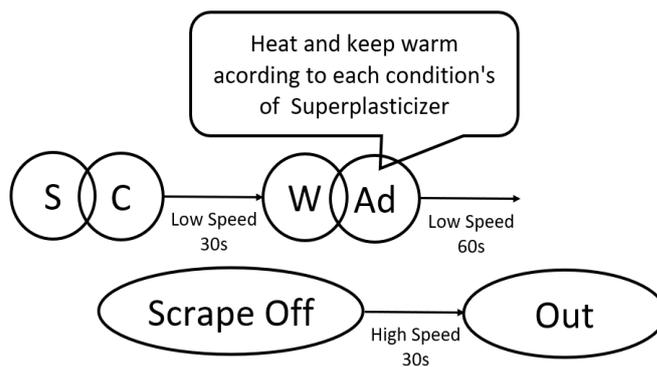


Figure 2. Mixing procedure.

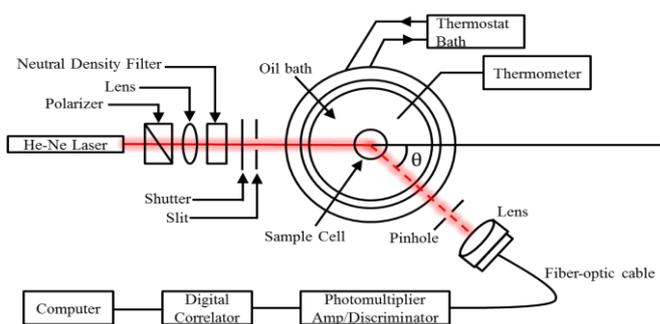


Figure 3. The schematic of DLS's machine used.

superplasticizer's principal component of PCa type is made by dispersion polymers than slump keeping polymer. The results of this study, the effect of thermal stimulation suggest highly activation effect more slump keeping polymer than dispersion polymer. However, further studies are needed to unravel the mechanism of this phenomenon, it should use various types of superplasticizers, and use different conditions of the experiment.

3.2 Time-dependent change of scattered light intensity

Fig.6 and Fig.7 were shown in the time-dependent change of scattered light intensity both of PCa type and RMC type regardless of thermal stimulations. The scattering intensity is one of the indexes geometrically molecular size. When thermal stimulation was given spice to superplasticizers, it was diffusion and extension of superplasticizer's polymer and it is confirmed that the molecular increased in size compared to before thermal stimulation about 1.7 times for PCa type and about 3.3 times for RMC type for 3 hours.

3.3 Changing the molecular size

Fig.8 and Fig.9 were shown in changing the molecular size both of PCa type and RMC type regardless of thermal stimulations. The big molecular size was haven margin of errors, however, both superplasticizers were

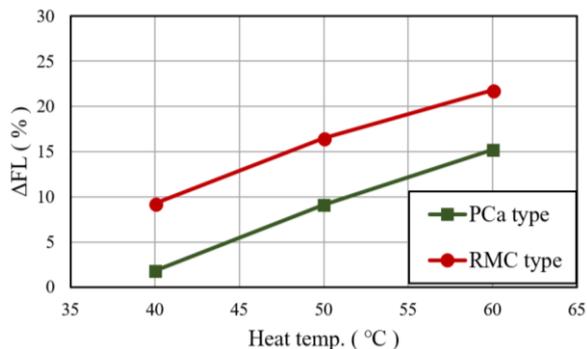


Figure 4. Relation between heating temperature and changing rate of flow.

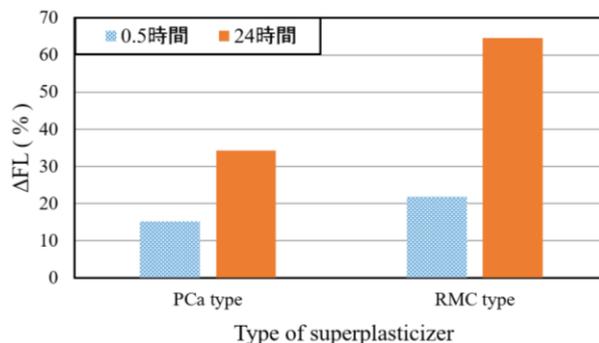


Figure 5. Relation between heating time and changing rate of flow.

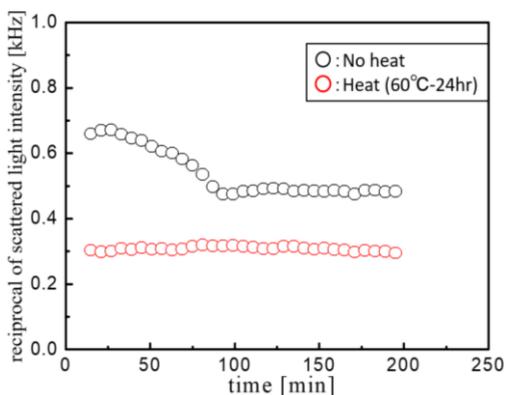


Figure 6. Time-dependent change of scattered light intensity (PCa type).

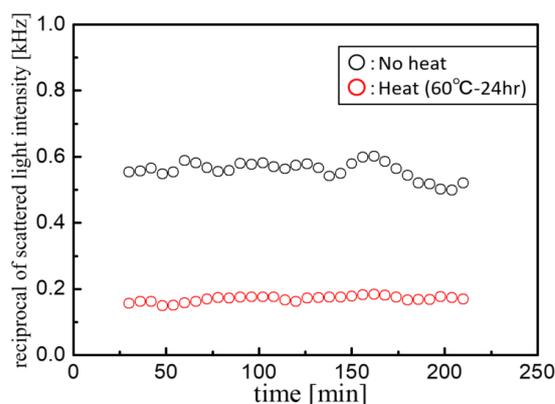


Figure 7. Time-dependent change of scattered light intensity (RMC type).

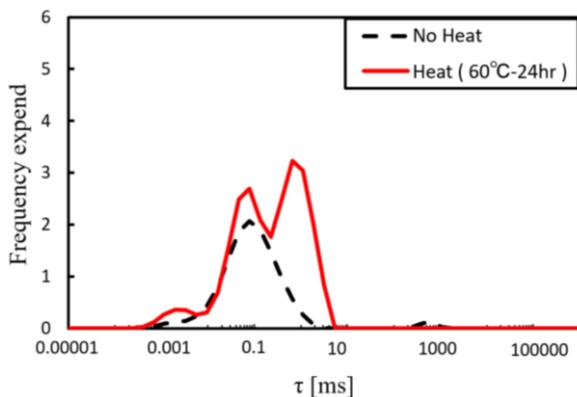


Figure 8. Changing the molecular size(PCa type).

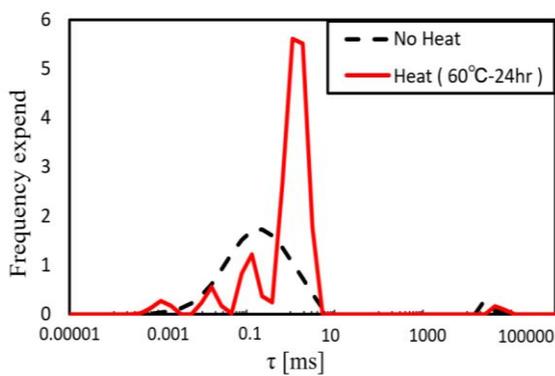


Figure 9. Changing the molecular size(RMC type).

the appearance of increased in size compared to before thermal stimulation because of it was diffusion and extension of superplasticizer's polymer. In particular, RMC type of superplasticizer was molecular size vary widely before and after thermal stimulation. It was confirmed from results of the time-dependent change of scattered light intensity that the appearance of molecular increased in size was given by thermal stimulation.

These phenomena that could be from Fig.6 to Fig.9 are assumed to improve dispersion effect because by undergo an increase in adsorbing surface area with cement of superplasticizer was given thermal stimulation

Table 4. Repeatability of the experiment.

Type of Ad	PCa		RMC	
Thermal stimulation	○	×	○	×
Num. of date	19	20	18	24
Standard deviation (mm)	3.1	4.3	3.1	3.6
Variation coefficient	3.1	2.9	2.9	1.9

and polymer was got diffusion and extension effect. Moreover, this effect was found that was haven great effected on RMC type rather than PCa type. It is assumed that improvement of dispersant was increased because of slump keeping polymer that is one of the superplasticizer's principal component was got the big effect of thermal stimulation.

And Table 4 shown repeatability of the experiment. As a result of repeated experiments to confirm the reproducibility in this experiment, it is considered that the reproducibility of this experiment could be acceptable since the variation coefficient is within 5% regardless of the presence of thermal stimulation.

As explained above, it was found that when thermal stimulation's effect of superplasticizers increased heating temperatures and heating times, it improved fluidity of mortar. In addition, it was found that this phenomenon is linked to change the polymer structure in superplasticizer by thermal stimulation.

4 Conclusion

Effect on the improvement of the fluidity of fresh mortar and heating polycarboxylic acid ether type of superplasticizers and conducted verification analysis for changing polymer structure by presence or absence of thermal stimulation was investigated and following conclusion had been obtained.

- 1) When superplasticizer was heated a long time and high temperature, improved the fluidity of fresh mortar.
- 2) Superplasticizer gave thermal stimulations, it found that the appearance of molecular increased in size.
- 3) High effect of the improved fluidity of mortar was found that was haven great effected on RMC type rather than PCa type by thermal stimulation.

In the future, it will do experiment used to be different from types of cement and other type's superplasticizers in a similar way with that consider various conditions (for example optimization effect of thermal stimulation, availability of maximization and the continuity of this effect and influence of mechanical strength) and it will conduct validate the evidence under the heating condition of superplasticizers.

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