Study on New Viscosity Agent for Combination Use Type of Self-Compacting Concrete

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Abstract
The authors succeeded to make a liquefied viscosity agent Welan gum with AE superplasticizer. When the Welan gum is added into a given concentration of AE superplasticizer and agitated well, Welan gum particles swell in the AE superplasticizer, resulting in stable suspension without much viscosity increase.

1. Introduction
With regard to the variation of the fluidity of concrete that is caused by errors in the measurement of unit water addition and so on, it is said that the combination use type of self-compacting concrete (SCC) has smaller variation than powder type of SCC, and that is the advantage of the combination use type.

On the other hand, the combination use type requires additional labor for casting of the viscosity agent. Therefore a liquid type of superplasticizer that includes the viscosity agent has been developed (Ebara et al 1998). The viscosity agent applied in this type of superplasticizer is a so-called ion-increasing viscosity chemical admixture, and it was reported that the performance to control fluidity variation of this polymer was less than that of Welan gum in combination type of SCC (Sakata et al 1999).

Therefore we attempted to make a liquefied Welan gum with AE superplasticizer and evaluated its performance.

2. Liquefaction of viscosity agent Welan gum with AE superplasticizer

2.1 General description
The authors tried to make a liquefaction of Welan gum with polycarboxylic type of AE superplasticizer. Generally speaking, when normal viscosity agents such as methyl hydroxypropyl cellulose or hydroxyethyl cellulose are dissolved in AE superplasticizer, the viscosity of the such system becomes too high and impossible to measure.

But when Welan gum is added to a given concentration of AE superplasticizer, the particles of Welan gum swell and become suspended in the AE superplasticizer. Taking advantage of this property, we attempted to achieve liquefaction. The following items were evaluated.

2.2 Determination of concentration of AE superplasticizer for swelling

(1) Used materials
Welan gum was used as the viscosity agent. The chemical structure of Welan gum is shown in Fig. 6. A polycarboxylic type of superplasticizer of which active solid was 40 wt% was used as the AE superplasticizer.

(2) Test method
Several concentrations of liquid type of AE superplasticizer were produced by dilution with ion-exchanged water. 0.5 wt% of Welan gum powder was added for each concentration of diluted AE superplasticizer, and the blend was agitated with a propeller mixer for 15 minutes to disperse the Welan gum particles uniformly. After that, the viscosity of each suspension was measured with a Brookfield medium viscosity type of viscometer.

The temperature of each sample was adjusted to 25±1°C. The viscosity was measured under 60 rpm of the rotational ratio of the spindle.

On the assumption that 10 liters of non-diluted superplasticizer are added to 1 m³ of concrete, this 0.5 mass % of Welan gum means the addition of 50 grams of Welan gum powder to 1 m³ of concrete.

The test factor was the variation of the concentration of the superplasticizer. Nine levels were defined, 0%, 10%, 50%, 70%, 85%, 90%, 99% and 100%. 0% means just ion-exchanged water, and 100% means just superplasticizer (SP conc.) without dilution.

(3) Test results and considerations
The relationship between the concentration of AE superplasticizer (SP conc.) and the viscosity of each sus-
pension is shown in Fig. 1. As shown in Fig. 1, the viscosity is high (1100 mPa•s) in the case of only ionic exchanged water, and it becomes even higher in the case of 10% of SP conc.

Generally speaking, water-soluble polymers including Welangum have good molecular expansion in ion-exchanged water without the existence of electrolytes, and they show their original viscosity, because it is said that the degree of molecular expansion depends on the strength of the hydrogen bonding of the hydroxyl groups between the water-soluble polymer and water molecular, and ions of electrolytes interrupt this bonding in part. But the addition of a very small amount of electrolytes such as superplasticizer to the solvent causes a slight tangle between the molecules, resulting in a little higher viscosity than when there are no electrolytes.

When SP conc. was diluted 50% to 99%, the viscosity became lower in accordance with the increase of SP conc., but still precipitation of Welangum was not observed.

In the case of 100% SP conc., the viscosity decreased to 50 mPa•s and precipitation was observed at the bottom of the container.

These results indicate that Welangum cannot swell enough and this causes separation or precipitation at high concentrations of electrolytes.

Under the intermediate concentration of dilution, which is between the concentration of viscosity increase and the concentration at which the separation or precipitation is caused, Welangum has intermediate expansion of molecular condition, which means that the molecules does not expand thoroughly but do not become insolubilized. The molecules are in a swollen condition, under which they disperse uniformly and the density of the particles becomes very similar to that of a solvent. Therefore, the system is considered to be stable for a certain period.

From this test, it is considered that a suitable range of the concentration of dilution of SP conc. is between 90% to 99%, and the viscosity is approx. 150 mPa•s, under which conditions Welangum molecules are under a swollen condition.

This 150 mPa•s is the viscosity at which liquid can be measured with ease.

2.3 Confirmation of long term stability
(1) Used material and test method
The used materials were the same as those described in 2.2. Test method. The viscosity of the suspension composed of Welangum and AE superplasticizer with three levels, which were 90%, 95% and 99% of SP conc., was measured. The viscosity measurements were done just after the preparation, as well as 2 weeks, 1 month, 3 months and 6 months after the preparation of the suspension. Visual observation to check the existence of precipitation was also done in each case.

(2) Test results and consideration
The relationship between the elapsed time and the viscosity is shown in Fig. 2.

As shown in Fig. 2, the viscosity decreased after the lapse of 2 weeks and precipitation was also observed in the case of 99% of SP conc.. However in the case of 90% of SP conc. and 95% of SP conc., the viscosity had been between 130 to 150 mPa•s from the preparation until 6 months later, and no precipitation was observed. Therefore, it is considered that the suspension at which the concentration of SP conc. is 90% to 95% is stable for at least 6 months.

2.4 Confirmation of fluidity of SCC
(1) Used materials and formulations of concrete
The used materials and formulations of concrete are shown in Table 1 and Table 2. As shown in Table 2, the addition rates on the materials except on chemical admixture are the same in every formulation. Four cases were evaluated, consisting of no addition of viscosity agent, addition of the superplasticizer containing ion-increasing viscosity chemical admixture, addition of liquefied Welangum in superplasticizer, and separate addition of Welangum and superplasticizer.

(2) Test method
As the way to assess the stability of the fluidity, the error of the measurement on the percentage of surface moisture
on sand was assumed. Three types of concrete where the unit quantity of water was varied $-7$, $+7$, and $+7$ kg/m$^3$ in relation to the basic formulation were evaluated. These variations correspond to the $\pm 1\%$ of the percentage of surface moisture in sand. Slump flow of the concrete was adjusted to approx. 650 mm. Mixing of the concrete was done using a 100-liter pan-type mixer at 60 rpm. The mixing method consisted in mixing the mortar for 90 second first, adding gravel, mixing for 90 second, letting the mix stand for 5 minutes, and finally mixing the mix mixed again.

The volume of each mix was 50 liters. Immediately following the final mixing, slump flow tests, V-funnel tests, air content tests and box compacting property tests were carried out. The box that was used was the standard box recommended by rank 2 of JSCE (JSCE 1998).

### 3) Test results and considerations

The test results of the slump flow tests are shown in Fig. 3. In response to the variation of $\pm 7$ kg/m$^3$ of unit quantity of water, there was a variation of 150 mm in the case of no addition of viscosity agent, 85 mm in the case of ion-increasing viscosity chemical admixture added superplasticizer, 20 mm in the case of liquefied Welangum in superplasticizer, and 27 mm in the case of separate addition of Welangum and superplasticizer. From these results, it is considered that admixture which is made by the liquefaction of Welangum with superplasticizer has enough capability to stabilize the fluidity.

The test results of V funnel tests are shown in Fig. 4. In every case, there was a tendency for the flow time to be reduced in accordance with the increase in the amount of water. In the case of Welangum addition regardless of liquefaction or separate addition, the variation was smaller than that in the case of ion-increasing viscosity chemical admixture added superplasticizer. On air content in the variation of water quantity, it was 7.5% to 2.4% in no addition case, 6.3% to 4.5% in the case of ion-increasing viscosity chemical admixture added superplasticizer, 5.3% to 4.0% in liquefied Welangum case and 5.7% to 4.4% in separate addition case.

The test results of the box compacting property test are shown in Fig. 5. In the case of no addition, the height of compacting was lower than 300 mm, which was recognized as the height indicating sufficient compacting performance. In the cases of ion-increasing viscosity chemical admixture added superplasticizer, liquefied Welangum, and separate addition, sufficient compacting performance was shown in the variation of unit water quantity.

Based on the above results, it is considered that when liquefied Welangum is applied in SCC, sufficient performance can be obtained.
3. Performance of newly developed viscosity agent

3.1 Diutan gum

Though Welan Gum provided an easier SCC production, it became relatively viscous at low temperatures resulting in a demand for a precise control over the SCC production. Thus a polymer with a viscosity more insensitive to temperature was researched in the similar biogum group to Welan Gum.

Diutan gum, same as Welan gum, is produced by the method of aerobic fermentation using corn syrup as the material and Alcaligenes bacterium built in. The only difference on the production from that on Welan gum was applied bacterial strain. More specifically, bacterium of which bacterial number is ATCC31555 is applied for Welan gum and ATCC53159 is for Diutan gum. Both chemical structures are shown in Fig. 6. Both main chains are composed of the repeating unit of four sugars, which are glucose, glucuronic acid, glucose and rhamnose. A significant structural difference of Diutan gum to Welan gum is the longer side chain. Welan gum has either one rhamnose or one mannose as its side chain, whereas Diutan gum has a two-rhamnose side chain. Unlike some other anionic polymers, Diutan gum and Welan gum are compatible with cement products. It is believed that the molecular side groups sterically shield the carboxylate group on the main chain, and prevent the reaction with calcium ions. The longer side chain of Diutan gum may offer a more effective shielding effect of the carboxylic acid function on the main chain than that achieved with the shorter side chain of Welan gum.

An additional consequence of the longer side chain is that Diutan gum has a lower charge density than Welan gum. Therefore it is assumed that Diutan is less affected by the effect of cement or superplasticizer variation than Welan gum.

Furthermore, molecular length measurements using atomic force microscopy or scanning probe microscopy methods have also shown Diutan gum to be up to 3 times longer than Welan gum, with the molecular weight of Welan gum being calculated as 0.66 to 0.97 million Daltons and Diutan gum between 2.88 and 5.18 million Daltons. These differences contribute significantly to the performance of Diutan gum compared to Welan gum.

3.2 Solution test

(1) Used materials and test methods

Diutan gum and Welan gum were used as viscosity agent, and ionic exchanged water was used as solvent. The viscosity of each concentration of solution was measured at each shear rate by DSR (Dynamic Shear Rheometer). The test factors were the concentration and temperature of the solution. The concentrations were 0.05%, 0.10%, 0.25%, 0.50%, 0.75% and 1.00%, and the temperatures were 0°C, 10°C, 20°C, 30°C and 40°C.

(2) Test results and consideration

The relationship between the shear rate and the viscosity at each concentration of the solution of Diutan gum and Welan gum are shown in Fig. 7. The relationship between the shear rate varied from 1 sec⁻¹ to 0.01 sec⁻¹ and the viscosities are shown in Fig. 8. As shown in
Fig. 8, Diutan gum has a stronger thickening effect than Welan gum under the same concentration and shear rate conditions.

Welan gum is known to have a much stronger pseudo-plastic property than other viscosity agents such as methylcellulose (Sakata et al. 1996). However Diutan gum shows higher pseudo-plasticity than Welan gum. Diutan gum also shows almost the same viscosity as Welan gum with a half addition.

The relationship between the temperature and the viscosity at shear rate 1 sec⁻¹ is shown in Fig. 9. As shown in Fig. 9, the change viscosity was almost null over the range of 0 to 40 °C.

Authors previously reported that Welan gum shows very little change in viscosity over changes in temperature compared to other viscosity agent such as methylcellulose (Sakata et al. 1996). The relationship between the temperature and the relative viscosity, which was calculated as the ratio of each viscosity to the viscosity at 20 °C as is shown in Fig. 10. We can understand that the increase in viscosity of Diutan gum at low temperature was very small compared to that of Welan gum.

4. Concluding remarks

Liquefaction of Welan gum with AE superplastizer was attempted. The rheology of the newly developed Diutan gum solution was also examined. The following conclusions can be drawn.

1. In the case of the polycarboxylic type of AE superplastizer evaluated in this study, a diluted solution with a concentration of 90% to 99% with ion-exchanged water is suitable. The addition of 0.5% of Welan gum to the solution is considered to yield ideal swelling. The viscosity of liquefied Welan gum is approx. 150 mPa.s, which is relatively low.

2. In the case of 90% to 95% of superplastizer, the swollen condition was maintained at least 6 months and no separation was observed.

3. When liquefied Welan gum is applied to SCC, the stability of fluidity is similar to that in the case of separate addition.

4. A Diutan gum solution shows the same viscosity as Welan gum with almost half the addition amount as well as a stronger pseudo-plastic property.

5. The temperature dependency of Diutan gum solution is less than that of Welan gum.

References


