

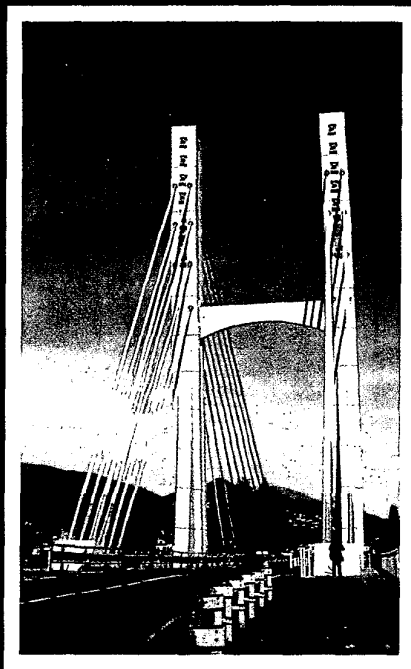
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**EIGHTH CANMET/ACI
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SUPERPLASTICIZERS AND
OTHER CHEMICAL ADMIXTURES
IN CONCRETE

LES SUPERPLASTISANTS AUTRES
ADJUVANTS CHIMIQUES
DANS LE BÉTON

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LE BÉTON**



SP-239

Editor:
V. M. MALHOTRA
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Superplasticizers and Other Chemical Admixtures in Concrete

**Proceedings
Eighth International Conference
Sorrento, Italy, 2006**

V. M. Malhotra

**Superplasticizers and
Other Chemical Admixtures
in Concrete**

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8th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete

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PREFACE

In May 1978, the Canada Centre for Mineral and Energy Technology (CANMET), in association with the American Concrete Institute (ACI), sponsored a 3-day conference in Ottawa, Ontario, Canada on the use of superplasticizers in concrete. Selected papers from the symposium were published as ACI SP-62.

In 1981, CANMET, again in association with the American Concrete Institute, sponsored a second 3-day international conference in Ottawa on the use of superplasticizers in concrete. The proceedings of the conference were published as ACI SP-68.

The purpose of the third international conference in 1989 was to review the progress made since the meetings in 1978 and 1981, and to bring together representatives of the chemical admixtures, cement, and concrete industries to exchange information and to delineate new areas of needed research. The scope of this conference was expanded to include chemical admixtures other than superplasticizers. The proceedings of the conference were published as ACI SP-119.

In October 1994, CANMET, in association with the American Concrete Institute and several other organizations, sponsored the fourth conference in Montreal, Quebec, Canada. The objective of this conference was to bring attention to the new developments in chemical admixtures since the last conference in 1989. The proceedings of the conference were published as ACI SP-148.

In October 1997, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with the American Concrete Institute and several cement and concrete organizations in Italy, sponsored the fifth conference in Rome, Italy. This conference was aimed at transferring technology in the fast-moving field of chemical admixtures. The proceedings of the conference were published as ACI SP-173.

In October 2000, the Committee for the Organization of CANMET/ACI International Conferences (ACI Council), in association with several

organizations in Canada and France, sponsored the sixth conference in Nice, France. More than 50 papers from more than 20 countries were received and reviewed by the ACI review panel, and 37 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-195.

In October 2003, the Committee for the Organization of CANMET/ACI International Conference (ACI Council), in association with several organizations in Canada and Germany, sponsored the seventh conference in Berlin, Germany. The conference attracted more than 275 delegates, and the proceedings of the conference, consisting of 39 papers, were published as ACI SP-217.

In October 2006, the Committee for the Organization of CANMET/ACI International Conference (ACI Council) sponsored the eighth conference in Sorrento, Italy. More than 60 papers from more than 25 countries were received and peer reviewed by the CANMET/ACI review panel in Budapest, and 36 were accepted for publication in the proceedings of the conference. The proceedings were published as ACI SP-239. The cooperation of the authors in accepting the reviewers' suggestions is greatly appreciated.

During the conference, a special dinner was held in honor of Michele Valente to recognize his outstanding and sustained contributions in the area of chemical admixtures, and his continued support of the CANMET/ACI symposia and conferences.

Thanks are extended to the members of the review panel for their contributions toward the publication of this volume. The help and assistance of A. Bilodeau, Chair of the PowerPoint presentations review panel, is gratefully acknowledged. Thanks are also extended to Pavan Gupta for coordinating the technical program and for the supervision of the PowerPoint presentations. The assistance of Gordon Brearley and Maria Venturino, both of CANMET, and Pierrette Veillette of the Handy Chemicals Ltd., Candiac, Canada, in the processing of the manuscripts and other associated duties is acknowledged. Acknowledgement is also made

to Rebecca Hartford and Lindsay Kennedy, both of ACI, for their assistance in getting the proceedings ready in time for the conference.

The Italian Advisory Committee chaired by Mario Collepari deserves special thanks for the outstanding contributions to the success of this conference.

V.M. Malhotra, P.Eng.

Editor

Chair, Eighth CANMET/ACI International Conference
on Superplasticizers and Other Chemical Admixtures in Concrete

October 2006

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Recent Developments in Superplasticizers

by M. Collepardi and M. Valente

Synopsis: Superplasticizers are considered to be the most important chemical admixtures in cement mixtures due to their influence on the hardened concrete properties (related to the water-cement ratio) as well as on those of the concrete in the fresh state (workability and workability loss).

During the last decade a new family of polymers based on polycarboxylate as the main polymer chain and polyether as side graft chains have been developed. This new family of products appear to be in general more effective in terms of higher water reduction, lower slump loss and lower retarding effect at very early ages.

More recently these performances have been enhanced in view of some specific applications: a) in precast concrete structures, the very early strength (such as at 12-16 hours) can be increased even in cold climates and in the absence of steam curing; this effect depends on the number and length of the polyether graft chain which are responsible for the dispersion effect related to the steric hindrance; b) in ready-mixed concrete mixtures, the slump maintenance behavior can be designed as a function of the transport time and placing temperatures, so that fresh superplasticized concrete mixtures can be transported from the batching plant to the job site without any slump loss even in summer times; this effect depends on the gradual liberation of special molecular groups which are responsible for the adsorption of these polymers on the surface cement grains; c) a new series of polycarboxylate polymers has been synthesized in which functional chemical groups, acting as shrinkage-reducing admixtures, again are gradually liberated by the superplasticizer polymer as a function of the pH of the aqueous phase related to the cement hydration.

Keywords: adsorption; polycarboxylate; polyether; shrinkage; slump loss; steric hindrance; superplasticizer; water-reduction; zeta potential

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Mario Collepari is author or co-author of numerous papers on concrete technology and cement chemistry. He is also the recipient of several awards for his contributions to the fundamental knowledge of superplasticizers and their use in concrete.

Michele Valente is President of General Admixtures. He is the Past President of ATECAP, the Italian Association of Ready-Mixed Concrete and he is the author of many scientific papers on concrete technology.

INTRODUCTION

Superplasticizers are unanimously considered to be the most important chemical admixtures for concrete. This is due to the numerous properties of concrete which can be improved by using superplasticizers. When superplasticizers are used without any change in the mixture composition they really act as admixture-enhancing fresh concrete workability. On the other hand, when they are used at given workability and cement content, they can act as high-range water reducers and then they can increase both early and later strength as well as improve durability and water-tightness. These admixtures can also reduce drying shrinkage and thermal stress of concretes when they are used at given workability and water-cement ratio (w/c) because of the higher aggregate/cement ratio..

Moreover, special high-performance concretes can be manufactured by combining superplasticizers with mineral additions such as silica fume (high strength concrete), fly ash (high volume fly ash concrete for mass concrete structures) or granulated ground blast-furnace slag (chloride-resistant concrete).

DEVELOPMENT OF NEW SUPERPLASTICIZERS

During the last three decades [1-2] the main ingredients of the superplasticizers were synthetic water-soluble polymers such as sulfonated melamine formaldehyde (SMF) condensate and sulfonated naphthalene formaldehyde (SNF) condensate. These admixtures are polymers based on a single repeating unit (sulfonated naphthalene or melamine molecule) which do not allow for much variation of the molecular structure. Advances in superplasticizers, containing alternative water soluble synthetic products, have been proposed in the last decade to reduce the slump-loss drawback [3-17]. More recently, these new superplasticizers - all based on the family of polycarboxylate polymers (PC) - have been deeply investigated, and numerous papers on these admixtures have been presented at the CANMET-ACI International Conferences on "Superplasticizers and Other Chemical Admixtures" [18-24]. Polycarboxylate superplasticizers are based on two or more structural groups that provide for more diversity in possible molecular structures with respect to those based on SNF or MSF [25]: for example, by changing the number of carboxylic groups per polyether unit, the adsorption of polymers on the cement surface can be significantly changed; moreover, the molecular weight of polyether molecule can be adequately adjusted to form polymers

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with different performance characteristics in terms of reduction in mixing water or retarding effect on the early cement hydration.

DISPERSION MECHANISMS OF CEMENT AGGLOMERATES

Superplasticizers cause dispersion of particles of coarse agglomerates which predominate in the cement paste of the concrete [26]. Due to the dispersion effect, there is a fluidity increase in the cement mixture (Fig.1). In the past, the dispersion effect was ascribed only to the development of the same electrostatic (negative) charge on the cement particles. The electrostatic attractive forces, existing among cement particles and causing agglomeration, would be neutralized by the adsorption of anionic polymers negatively charged, such as SNF or SMF, for the presence of SO_3^- groups on the surface of cement particles. The dispersion of cement particles (Fig.2) would be related with the electrical repulsion produced by the negatively charged groups (SO_3^-) on the other side of the main polymer chain [27].

The electrostatic repulsion of cement particles was determined through zeta potential measurements. Additional available experimental results did not confirm this mechanism for the superplasticizing action of the polycarboxylate polymers. These results would indicate that the dispersion of cement particles, responsible for the fluidity increase caused by superplasticizer, is not necessarily related to the electrostatic repulsion associated with zeta potential measurements.

The dispersion mechanism performed by the PC-based superplasticizers (Fig. 3) is related more to a steric hindrance effect produced by the presence of pendant ethylene oxide (EO) side graft chains, rather than to the presence of negatively charged anionic groups (COO^-) which are responsible for the adsorption of the polymers on the surface of cement particles. In other words, the pendant graft chains of the polymer molecules adsorbed on the surface of cement would hinder by themselves from flocculating into large and irregular agglomerates of cement particles (Fig. 3).

SLUMP RETENTION

Slump loss appears to be the most serious problem at least for ready mixed concrete industries. When a concrete mixture must be transported for a long time, particularly in hot weather, it should keep as far as possible at its initial slump level to avoid the practice of redosing the concrete with water above and beyond that required in the mixture proportion. Results of investigations of retempered concrete indicate that many of the properties of the hardened concrete (strength, durability, abrasion resistance, etc.) are significantly affected, since retempered concrete does not perform as well as concrete which has not been retempered [28]. However, slump loss is un-avoidable because of the intrinsic requirement for concrete mixtures which should set and harden in a relatively short time. Therefore, a right and proper compromise would be a zero-slump-loss concrete mixture for about 1 hour. By using superplasticizers based on SNF or SMF polymers it is not easy to achieve this target, because in general slump loss is higher in superplasticized concrete with respect to the corresponding plain mix at given initial

slump (Fig. 4). The lower the w/c, the higher is the slump loss for the same initial slump level. It seems that the lower w/c in superplasticized concrete and the consequent smaller distance among cement particles (Fig. 5) cause a more significant slump loss when the same amount of water is lost through evaporation or by reaction with cement during the transportation time.

Several methods have been adopted to control the rate of slump loss. One method is to add the superplasticizer at the point of discharge but there are some practical problems associated with this approach. For instance, the concrete into the truck-mixer before the superplasticizer addition would be too stiff when a high-quality concrete, (with low w/c), should be produced. Moreover, dosing the superplasticizer at the work site is too time consuming and does not allow an accurate control of the final slump and admixture dosage.

Other methods to control slump loss include adding a higher than normal dosage of superplasticizer or using some type of retarding admixture in the formulation. However, there are some limits in this approach, because sometimes the final effect is to produce concrete with un-acceptable low early strength or, surprisingly, to aggravate more seriously slump loss. For instance, slump loss accompanied by a surprisingly quick set may sometimes occur by using retarders such as sugar, sucrose, corn syrup or calcium lignosulfonate [29]. The cement content, as well as the chemical and mineralogical composition of cement, play an important role in determining such a singular slump loss although the detailed mechanism is not clear: it seems that the content of C_3A , gypsum and alkali, as well as the form of calcium sulfate used as set regulator, can affect the rate of slump-loss.

Also redosing the superplasticizer at different intervals of time has been suggested [30] to reduce slump-loss, but this method appears to be not always easy to be adopted in practice. Moreover, the total dosage of superplasticizer, as well as the relative cost, cannot be kept under control according to a given plan.

Therefore a superplasticizer is required which by itself is capable to maintain the slump for a long period of time independently of the temperature or the type and content of cement. Colleparidi et al. [13] studied the effects of a PC-based superplasticizer on the properties of ready-mixed concrete mixtures. This admixture acts as both an immediate superplasticizer and a slump loss reducing agent, and appears to be more effective than that based on SNF. Although the PC-based superplasticizer has been used at a lower content of active polymer (0.30% versus 0.40%), it was more effective than that based on SNF for the water reducing capability (w/c = 0.43 versus 0.47) as well as for the maintenance of the initial slump level (Fig. 6).

Tanaka et al. [17] studied the effect of a CLAP-based superplasticizer (Cross Linked Acrylic Polymer) on the slump-loss of concrete mixtures. This superplasticizer is a partially cross-linked copolymer of acrylic acid and polyethylene glycol mono-alkyl ether (Fig. 7). According to Tanaka and co-workers the cross-linked polymer is hydrolyzed by the alkaline water phase of the cement paste and then converted into a PC-based polymer (Fig. 8). The negative carboxylic groups due to the alkaline hydrolysis would be adsorbed on cement surface of cement particles and then would be responsible for the dispersion of cement particles and the fluidizing action of the admixture. The low slump-loss effect of this superplasticizer should be related with increasing number of the protruding side

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chains of the acrylic polymer which would prolong the dispersion of hydrated cement particles through a steric hindrance effect.

Hamada et al. [22] developed a new family of acrylic polymers based on the following changes with respect to the traditional PC-based superplasticizer:

- a new superplasticizer, called PE because of the much longer side chains of ethylene oxide (EO): 130 moles of EO instead of 10-25 moles as in traditional PC-based superplasticizer (Fig. 9); this change, combined with a lower number of carboxylic groups (COO^-), produces a lower adsorption speed and reduces the typical retarding effect related to the early adsorption;
- a modified PE-based superplasticizer where a great number of carboxylic groups are replaced by a slump-loss controlling agent (SLCA) to achieve a still higher slump retention with minimal setting retardation: indeed, due to the relatively low number of carboxylic groups in SLCA (Fig. 10) the initial adsorption and the dispersing effect are negligible as well as the setting retardation; however, subsequently due to the hydrolytic effect related with the OH^- presence in the aqueous phase of the cement paste, the number of carboxylic units increases (Fig. 11) and the slump can still increase by prolonging the mixing time due to the increasing adsorption of the polymer on the surface of the cement particles.

The behavior of fresh concrete in the presence of PC and SLCA-based superplasticizers is schematically shown in Fig. 12.

Figure 13 schematically shows the heat of cement hydration and Figure 14 shows the concrete hardening in the absence and in the presence of PC or PE acrylic superplasticizers.

Sugiyama et al. [32] synthesized a new series of superplasticizers in which functional groups called EPBE acting as shrinkage reducing agent (SRA), capable of reducing surface tension, were attached to the structure of various polycarboxylate polymers (Fig. 15). Figure 16 shows the drying shrinkage behavior of concretes with PC-based superplasticizer or modified EPBE-PC-based admixture: the drying shrinkage of the latter is lower than that of the former.

Nakanishi et al. [24] invented another multi-function and multi-purpose admixture incorporating a shrinkage reducing group (based on diethylene glycol monobutyl ether) acting as SRA on the PC chain acting as a water reducing agent.

CONCLUSIONS

Superplasticizers are able to enhance the placing characteristics of concrete mixtures by increasing the workability level at a given w/c. Therefore they allow to make easy placement of concrete mixtures even with low w/c as required by strength or durability reasons.

The main drawback of superplasticized concrete mixtures with sulphonated polymer-based admixtures is the slump-loss. This can reduce the advantage of using these superplasticizers particularly in hot weather, with long transportation times and reactive cements.

A new family of superplasticizers based on acrylic polymers is available with improved placing characteristics: a) flowing concretes can be produced at lower w/c with

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respect to concrete mixtures containing sulphonated superplasticizers; b) the slump-loss is much more reduced with respect to concrete mixes with sulphonated superplasticizers; c) multi-purpose superplasticizers with shrinkage reducing properties have been invented by incorporating special functional groups on the PC chain.

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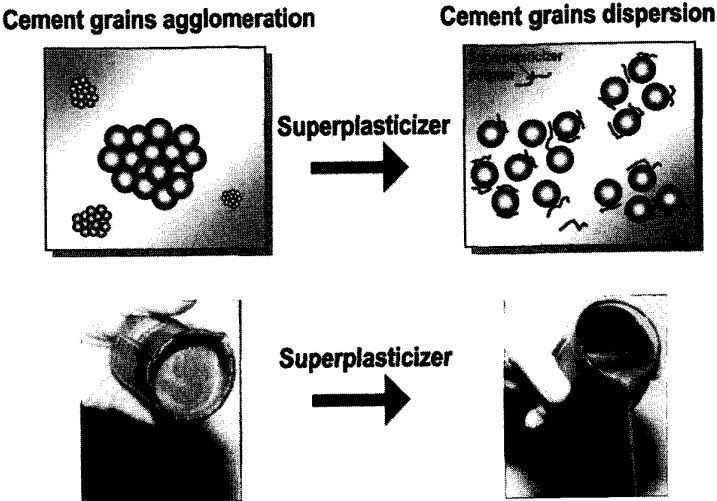


Fig. 1 – Relationship between cement grains dispersion and fluidifying effect on the cement.

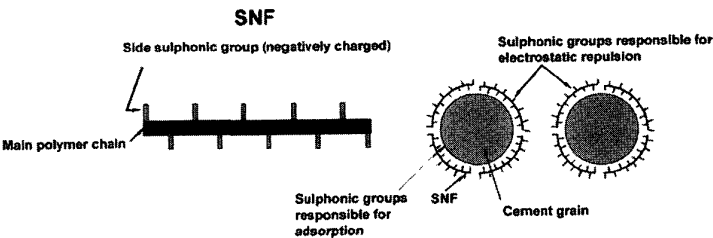


Fig. 2 — Schematic picture of sulfonated polymer (SNF) and its electrostatic repulsion effect on the dispersion of cement particles.

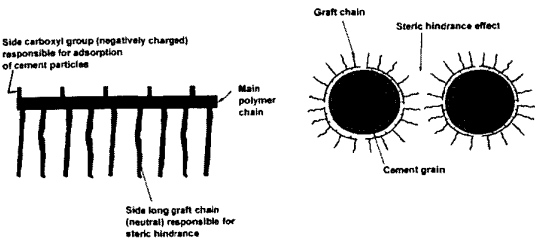


Fig. 3 — Schematic picture of the polycarboxylate (PC) superplasticizer and its steric hindrance effect on the dispersion of cement particles.

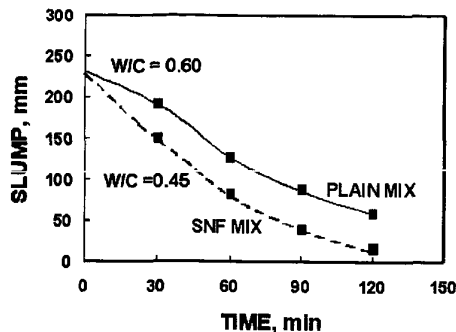


Fig. 4 – Slump loss at 20 °C for plain and superplasticized mixes at the same initial slump. Superplasticizer: 0.4% as dry SNF polymer by weight of cement.

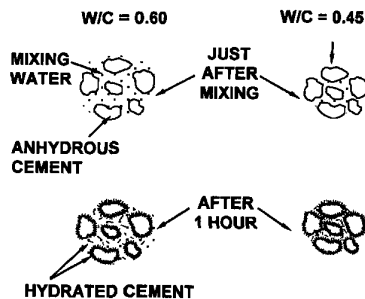


Fig. 5 – Schematic picture of cement paste in a plain ($w/c = 0.60$) and superplasticized concrete ($w/c = 0.45$).

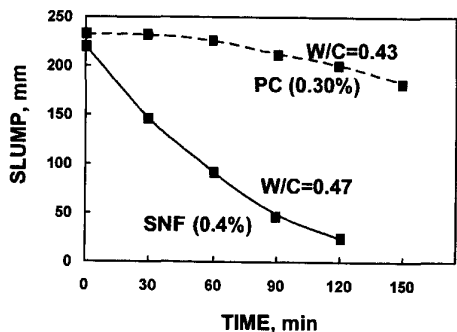


Fig. 6 – Slump loss of superplasticized concretes at 20 °C with PC or SNF polymer based admixtures [13]. Percentages on the curves refer to dry polymer.

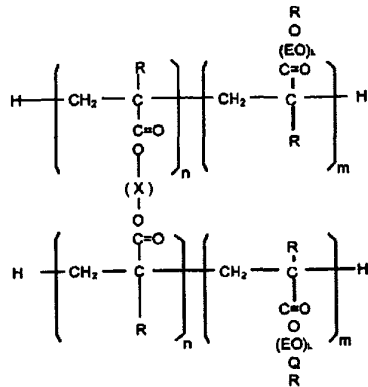


Fig. 7 – Chemical Structure of CLAP (cross-linked acrylic polymers). X is the cross linking group.

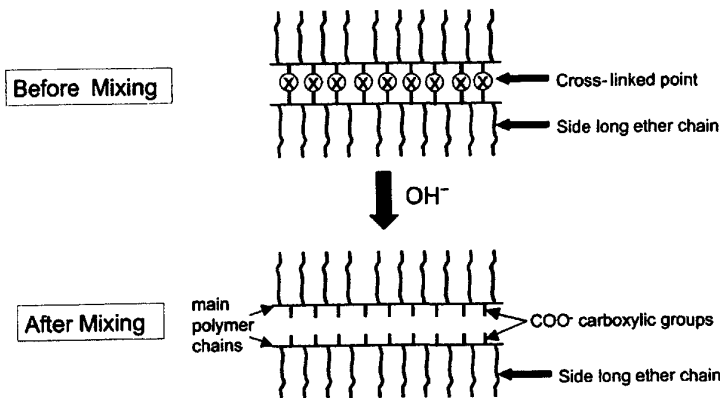


Fig. 8 – CLAP-based superplasticizer hydrolyzed by the alkaline water of cement paste: the number of COO^- progressively increases with time and this is responsible for the low slump loss.

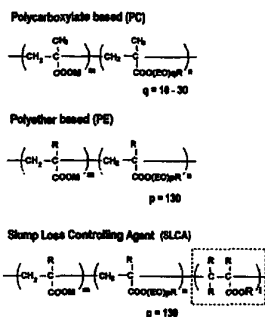


Fig. 9 – The chemical structure of polycarboxylate type (PC), polyether type (PE), and slump-loss-controlling agent superplasticizer (SLCA); q and p are the number of moles of EO in PC and PE or SLCA polymers [22].

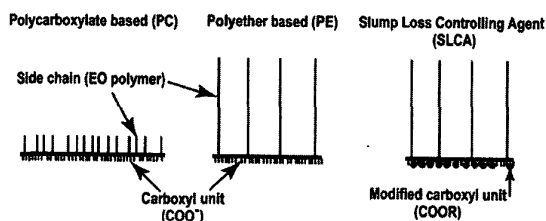


Fig. 10 – The schematic molecular structure of polycarboxylate type (PC), polyether type (PE) and slump-loss-controlling agent superplasticizer (SLCA) (adapted from Reference 22).

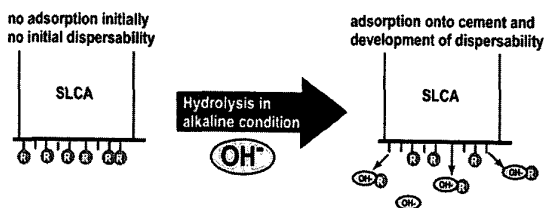


Fig. 11 – The mechanism and the hydrolysis reaction of SLCA in alkaline condition of cement paste (adapted from Reference 22).

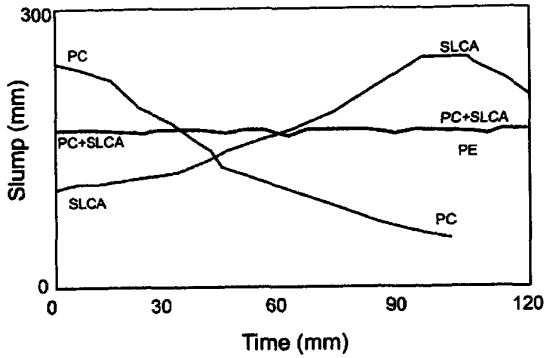


Fig. 12 – Schematic trend in the slump loss behavior with different acrylic superplasticizers (PC, PE, SLCA, PE+SLCA) in concrete mixtures with CEM II A/L 32.5R (340 kg/m^3), $w/c = 0.45$.

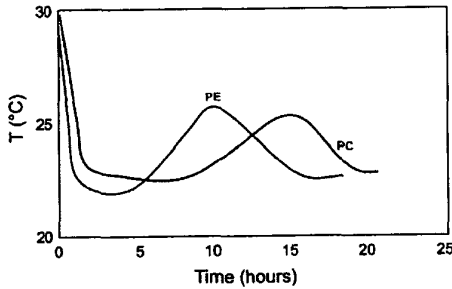


Fig. 13 – Heat development in portland cement pastes with PE or PC polymers.

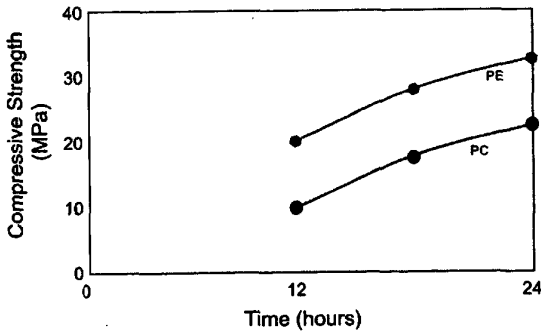


Fig. 14 – Compressive strength development of concrete with PE or PC.

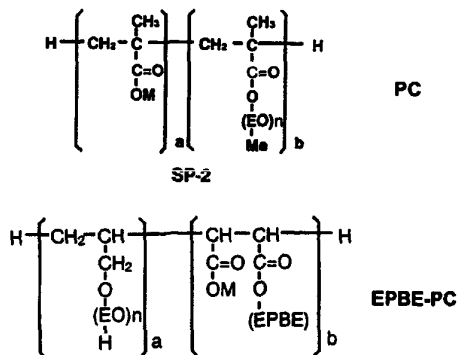


Fig. 15 – Chemical structures of PC and EPBE-PC [32].

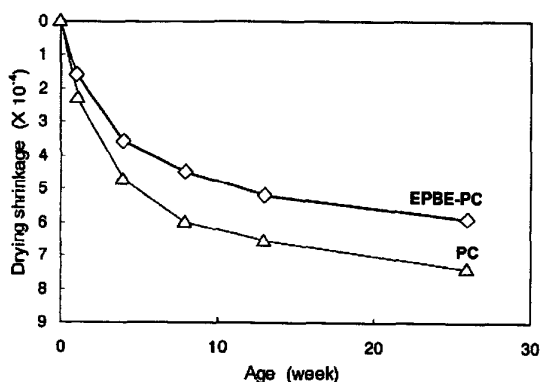


Fig. 16 – Shrinkage of concretes with PC-based superplasticizer or modified PC-based superplasticizer by EPBE groups [32].

Use of Chemical Admixtures to Modify the Rheological Behavior of Cementitious Systems Containing Manufactured Aggregates

**by A. Jeknavorian, K. Hazrati, A. Bentur, H. Koyata,
D. McGuire, and P. Sandberg**

Synopsis: Aggregate shape, texture, and grading have been known to have a significant effect on the rheological performance of fresh concrete. Moreover, while the optimization of aggregate selection can provide both technical and economical benefits, the availability of materials and construction operations can often dictate the use and proportioning of certain aggregate sources, such as manufactured sands, which can adversely impact the rheology of cementitious mixtures. The use of certain chemical admixtures has been found to often minimize the need to increase cement and water contents in order to overcome the loss of workability that can accompany aggregate sources which feature flat, elongated, angular, and rough particles. *In this study, a wide range of natural and manufactured sands, characterized for gradation, mineralogy, shape, texture, and cleanliness, are evaluated for their effect on mortar rheology, with and without a viscosifying-type chemical admixture. While associations between aggregate characteristics and their impact of mortar rheology may not be readily evident, the ability of this class of admixture can be shown to mitigate the rheological effect of certain sands, and in some cases allow for optimizing the mixture to lower paste contents.*

Keywords: aggregates; petrographic analysis of aggregates; rheology; viscosity-modifying agent; yield stress

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INTRODUCTION

Diminishing local availability of naturally occurring sands for use as fine aggregates in the production of concrete, coupled with regulatory pressures to utilize by-products from quarry operations, has brought about a growing dependency on manufactured sands [1,2]. Moreover, an economic advantage is often possible when replacing fine aggregates with manufactured sands. The production of manufactured sands results from by crushing rock deposits to produce a fine aggregate, which is generally more angular and has a rougher surface texture than naturally weathered sand particles. Furthermore, rock dust (microfines), a by-product of the crushing operation consisting of particles less than 75 μm , can amount to as much as 20 – 30% of the manufactured sand. While some countries such as India, Spain, and Australia permit from 15-25% microfines in the fine aggregate, concrete fine aggregate gradation limits such as found in the ASTM C 33 Standard Specification for Concrete Aggregates [3] permit up to 7% finer than 75 μm for some applications assuming the absence of clay or shale. To comply with various particle grading standards, the rock dust is removed by washing with water creating a waste slurry whose accumulation imposes considerable detrimental impact on the aggregate industry.

When manufactured sands are substituted for naturally sourced fine aggregate, even with the fine than 75 μm fraction controlled, the workability of concrete mixtures are generally reduced, and in some cases, the concrete mixture can be more prone to segregation. Furthermore, the increased friction that results causes higher pumping pressures, increase the effort associated with concrete placement and finishing operations [4]. These performance attributes associated with manufactured sands result from a combination of the angular particle shape and rough surface texture [5], both contributing to increased void space in the aggregate packing. Both factors contribute to increased surface area, which will require increased water content to maintain consistent workability.

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To overcome the adverse effects manufactured sands can contribute to concrete mixtures, one option is to increase the paste volume in the form of either higher cement or cement along with a supplementary cementitious material (SCM). Chemical admixtures, especially polycarboxylate-based high range water reducing agents, have been found to be useful to minimize the need for both increased water and paste contents that could be required with manufactured sands [6].

This study is concerned with evaluating the interaction of both natural and manufacturing sands with a bio-polymer type viscosity-modifying agent (VMA), a class of admixture finding increased use with angular-shaped fine aggregates. From various particle shape and mineralogical analyses made on sands from five sources, along with yield and viscosity measurements on mortar mixtures, prepared with and without VMA, predictions are attempted to associate the key particle attributes responsible for changes in mortar rheology and the effectiveness of the VMA to maintain mortar workability without altering mixture components.

TEST PROGRAM

Seven (7) manufactured and eight (8) natural sands, identified in Table 1, were tested for gradation (ASTM C 136 [7]), particle shape and texture (ASTM C 295 petrographic analysis [8]), % finer than 75 μm , and Uncompacted Void Content (ASTM C1252 [9]). Mortar mixtures were prepared using the mixture proportions reported in Table 1 with each manufactured and natural sand. Yield and viscosity measurements were performed on the mortar mixtures using a prototype Contec coaxial cylinder rheometer shown in Figure 1. The outer cylinder rotates at a programmable velocity while the inner cylinder is stationary and registers the applied torque from the mortar. By assuming the mortar to flow like a Bingham fluid, the yield value and plastic viscosity are calculated from the slope (viscosity) and yield value (intercept) in a torque-velocity diagram. In this study, focus was mainly on the yield value as it has been shown to correlate inversely with slump.

RESULTS

Mortar Rheology

The mortar yield stress results for all the mortar mixtures, prepared at constant w/c and a constant weight of sand, either from manufactured or natural sources, are reported in Figure 1. No consistent trend is apparent between the yield stress versus sand type indicating other factors or combination of factors must be influencing water demand changes created by the various sand properties. Mortar yield stress results, obtained with the Contec rheometer, were found to correlate well with mortar flow, and thus help to validate measurements with the rheometer (Figure 2). Attempts to further characterize the rheological impact of natural versus manufactured sands by plotting yield stress versus viscosity as shown in Figure 3 could not discern any specific trends, indicating

that certain properties of the sands can influence both yield stress and viscosity somewhat independently.

Petrographic Analysis of Fine Aggregates

All the sand samples were subjected to a petrographic analysis performed according to ASTM C 295 and C 136 Sieve Analysis. Key parameters noted during the examination were mineralogy, shape, texture, and cleanliness, and are reported in Figures 4–7 for two pairs of natural and manufactured sands, which some concrete producers are known to either blend or use interchangeably. Numerical values, ranging from 1 to 10, were assigned for shape, texture, and cleanliness, where lower the number implies high quality and suitability for concrete manufacture. As expected, the manufactured sands designated with the “HS” code have higher values versus natural sand available from a nearby location.

Correlation of Sand Properties with Yield Stress

In an attempt to identify the sand properties responsible for effecting the workability of mortar and concrete mixtures, the yield stress of mortar mixtures prepared with both natural and manufactured sands were correlated with fineness modulus, percent un-compacted voids, and a combined factor representing the sum of the values assigned for shape, texture, and cleanliness (Figures 8–10). No clear correlations were readily evident suggesting that either certain critical sand parameters have yet to be measured, or that a higher level regression-type analysis is required to uncover more complex relationships.

Probing Interaction of Sand–type using VMA Modifying Agent and Cement Paste

With the measured sand properties providing limited predictive information concerning mortar workability, changes in mortar rheology as a function of VMA addition and increased paste content were next evaluated. Starting with the control mixture described in Table 2 and prepared with each of the natural and manufactured sands identified in Table 1, the paste content was increased from 10 to 40% by mass. In addition, the control mixture with the manufactured sand was dosed with 0.003% VMA actives by weight of cement (% s/s). Yield stress was measured for the mixtures. A sample plot of the yield stress as a function of increasing cement paste is shown in Figure 11. Interestingly, the pair of selected manufactured and natural sands, exhibit a similar drop in yield stress with increasing paste content. In the case of the VMA-treated mortar containing the manufactured Mari-HS sand, a 75 Pa drop in yield stress was observed. Extrapolating the lower yield stress to the yield stress–cement paste plot, the VMA appears to have the potential of lowering the paste content by about 12% without altering the yield stress.

In Figure 12, the reduction in paste content observed with the addition of 0.003% s/s VMA to 11 mortar mixtures prepared with the various manufactured sands. Interestingly, the sands appear to have quite a diverse response to the VMA additive, exhibiting a six (6)-fold change in yield stress.

Increasing the paste content of the control mortar mixture had a similar effect on yield stress compared to the VMA (Figure 13). Once again, the mortar mixtures prepared with the various manufactured sands exhibit a different response to added paste content expressed as percent reduction in yield stress normalized for percent cement paste added.

To understand if the yield stress reductions observed by both the addition of VMA and increased paste content have a similar mechanism in reducing the increased frictional particle-to-particle forces associated with manufactured sands, the change in yield stress produced by the VMA was correlated to the ratio of percent change in yield stress to percent added paste (Figure 15). A somewhat unexpected qualitative trend suggests that sands with a low to moderate yield stress response to the VMA have a high response to increasing cement paste. This could possibly be explained by the proposed mechanisms illustrated in Figure 16, where the increased paste content enables more significant particle-to-particle separation under various degrees of shear, whereas the effect of VMA on yield stress is probably more shear history dependent.

CONCLUSIONS

Rheology measurements with a rheometer has been found to be a useful method to differentiate the effect that different natural and manufactured sands can have on the workability of mortar mixtures. Despite significant characterization of the various sands, no simple correlation has been identified to associate sand properties with effect on yield stress. A multiple regression analysis might possibly provide a predictive relationship between some set of physical parameters associated with manufactured sands and mortar and concrete workability. Moreover, changes in yield stress of a control mortar mixture batched candidate sands, and subsequently modified either by the addition of a VMA or increased paste content, could have some potential use for concrete producers as a means of predicting the need for a change in mixture proportions to assure adequate placing and pumping operations.

Acknowledgement

The authors wish to thank Derek Brown, senior petrographer at the Grace Research Laboratories, for the characterization of the sand samples.

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Table 1. Location and Type of Sands

Manufactured Sands (HS)	Natural Sand (NS)	Location
	EN	Standard Sand - Europe
GC-HS	HC-NS	Central California
HSLO-HS	HSLO-NS	Central California
MARI-HS	NS	Arizona
CP-HS	CP-NS	Arizona
BARGE-HS	HV-NS	Southern California
S-HS	DUR-HS	Southern California
D-HS	--	Illinois
FL-HS	FL-NS	Florida

Table 2. Mortar compositions with increased paste contents

	Control	Control w/ VMA	Control + 10% Paste	Control + 20 % Paste	Control + 30% Paste	Control + 40% paste
Cement	400	400	440	480	520	560
Sand	800	800	800	800	800	800
Water	188	188	207	225	244	263
VMA, % s/s	-	0.0035	-	-	-	-

Table 3. Chemical Composition of Cement

#170
ASTM C 150
SiO ₂
Al ₂ O ₃
Fe ₂ O ₃
CaO
MgO
SO ₃
Total Alkali as Na ₂ O
LOI
Bogue Compounds
C ₃ S
C ₂ S
C ₃ A
C ₄ AF
C ₃ A/SO ₃
Fineness, Blaine m ² /g

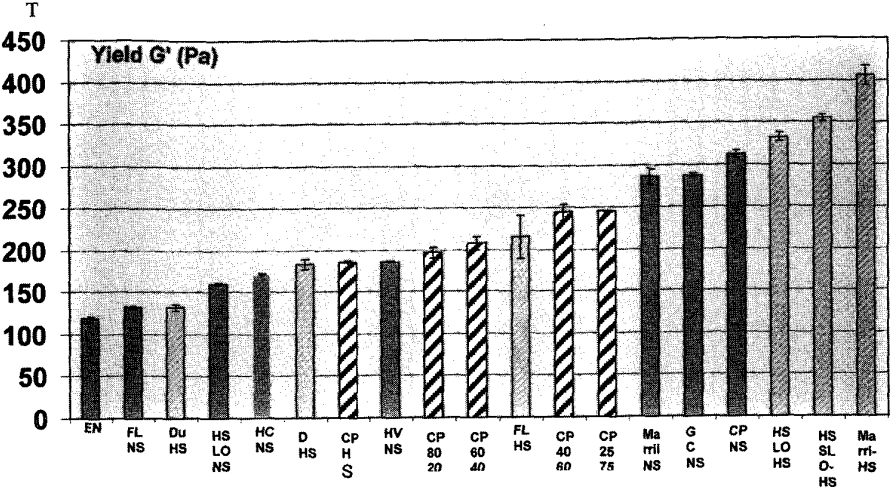


Figure 1. Yield measurement of mortar mixtures prepared with natural and manufactured sands as well as blends of both sands.

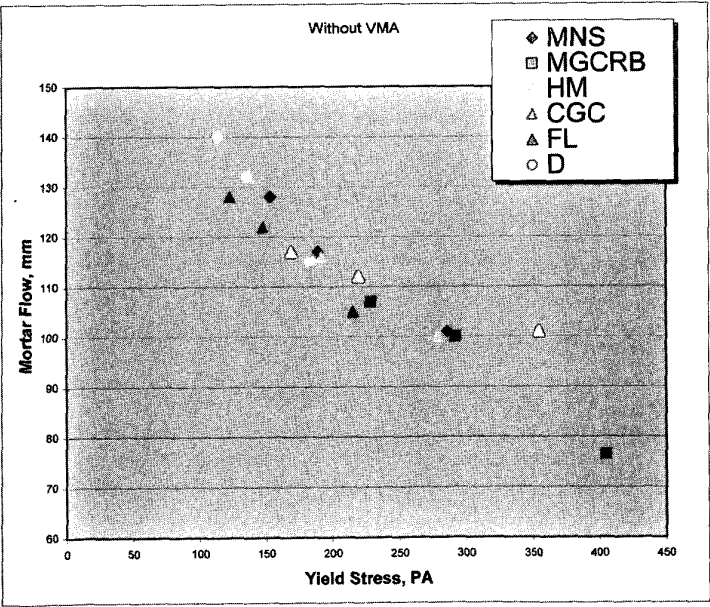


Figure 2. Correlation of mortar flow with yield stress.

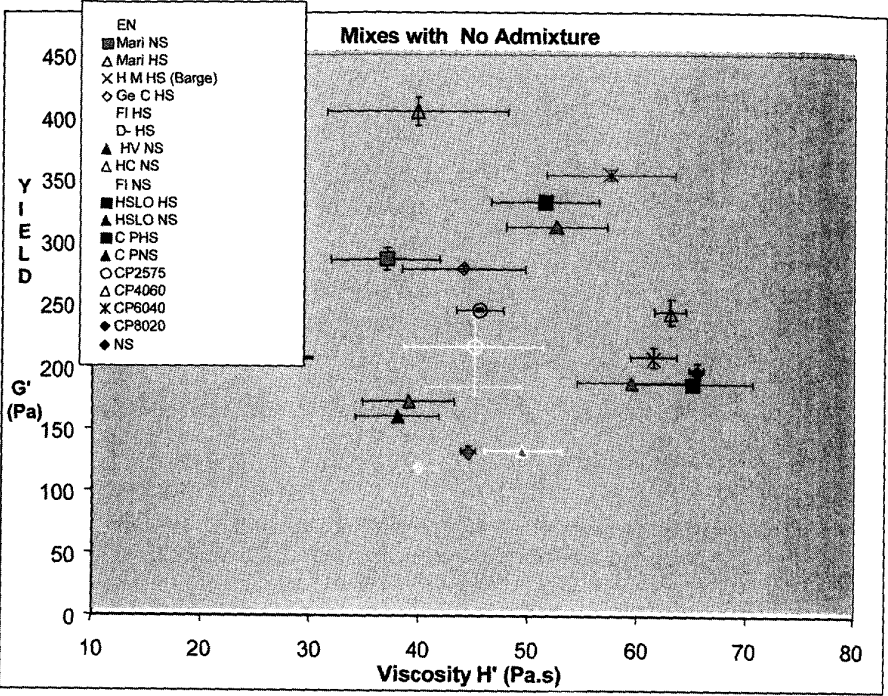


Figure 3. Mortar rheology as a function of yield stress versus viscosity.

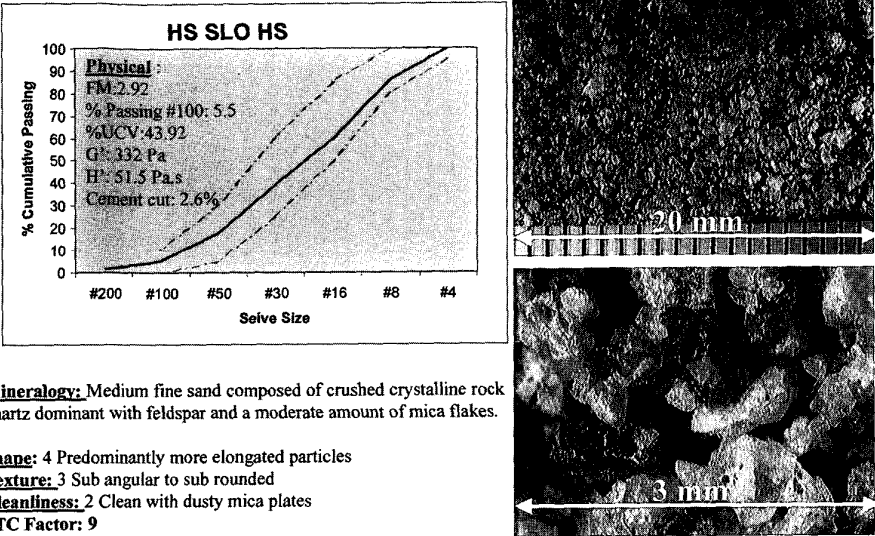


Figure 4. Petrographic analysis of harsh sand HSLO.

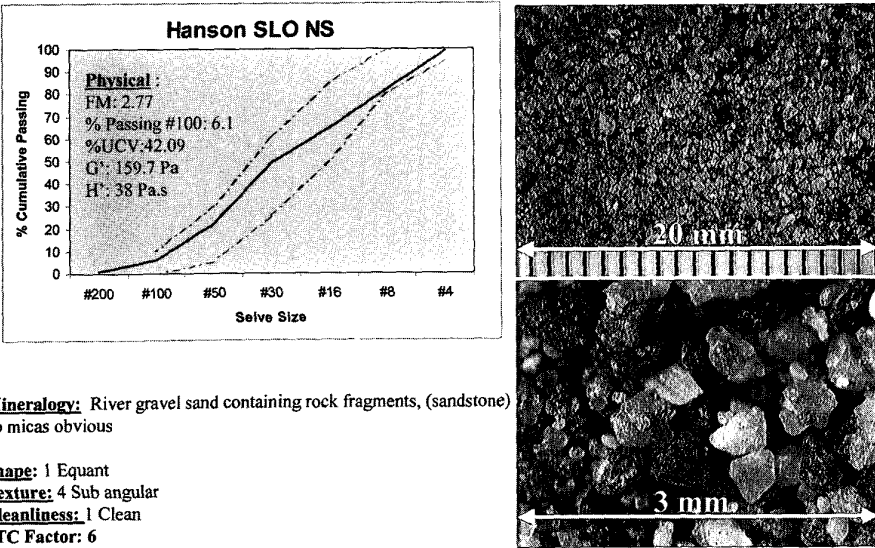
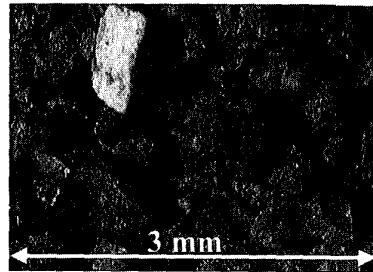
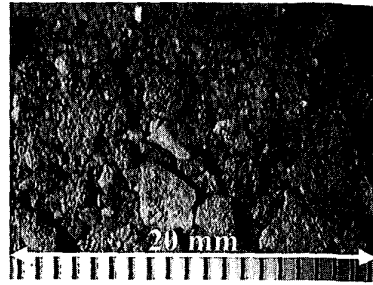
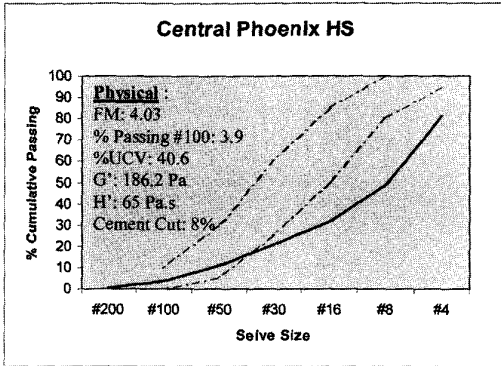


Figure 5. Petrographic analysis of natural sand HSLO.



Mineralogy: : Medium to fine well graded sand of mixed lithology with little to no micas.

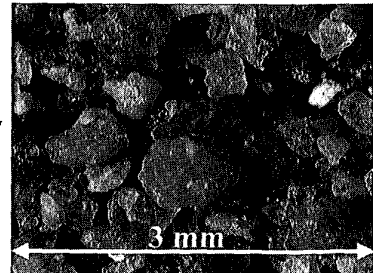
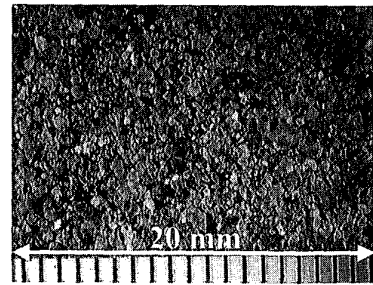
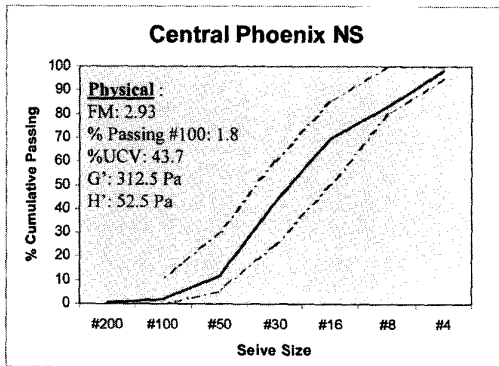
Shape: 3 Elongated and Equant

Texture: 3 Sub Angular to sub rounded

Cleanliness: 4 Dirty

STC Factor: 10

Figure 6. Petrographic and sieve analysis of harsh sand CP.



Mineralogy: : Medium to fine river gravel / sand of mixed lithology with some micas

Shape: 3 Elongated and Equant

Texture: 4 Sub Angular

Cleanliness: 1 Clean

STC Factor: 8

Figure 7. Petrographic and sieve analysis of natural sand CP.

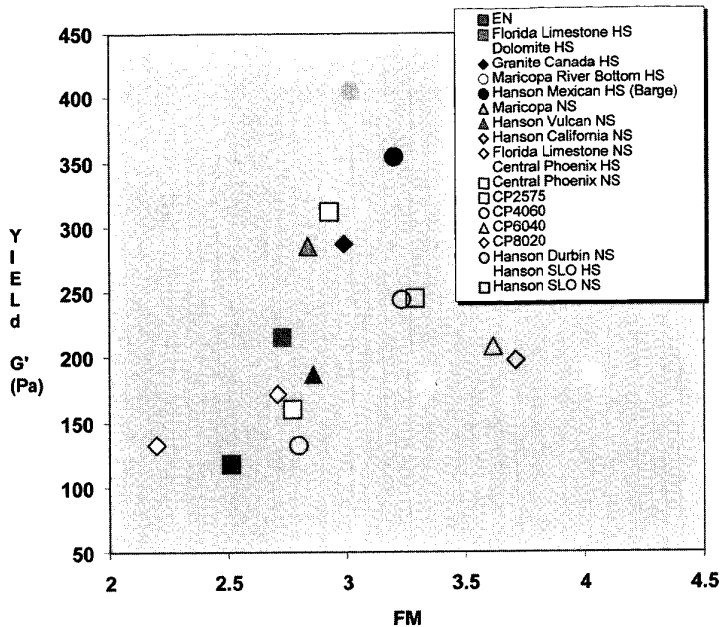


Figure 8. Correlation of yield stress versus fineness modulus (FM).

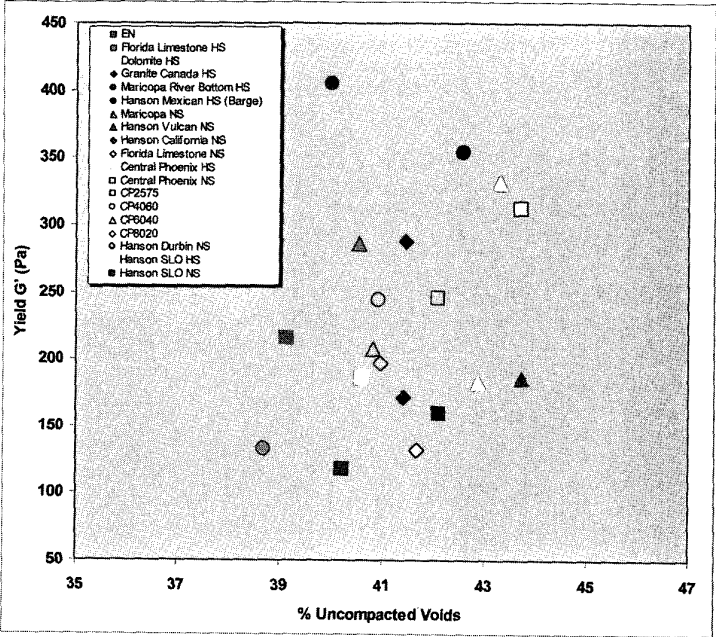


Figure 9. Correlation of yield stress versus % uncompacted voids.

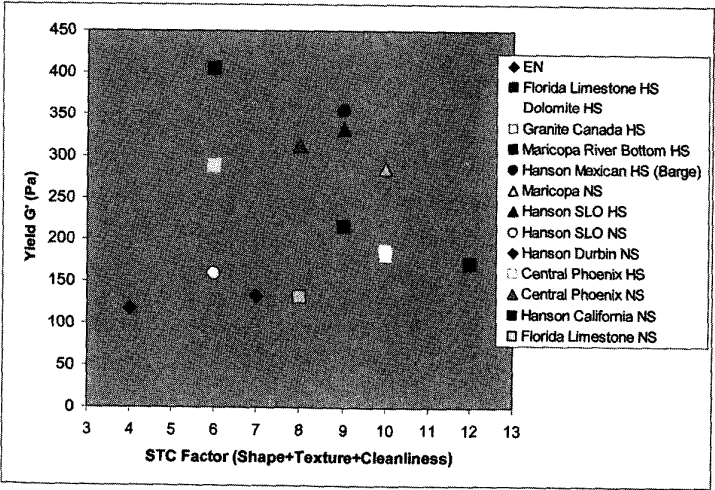


Figure 10. Correlation of yield stress with combined aggregate properties of shape, texture, and cleanliness.

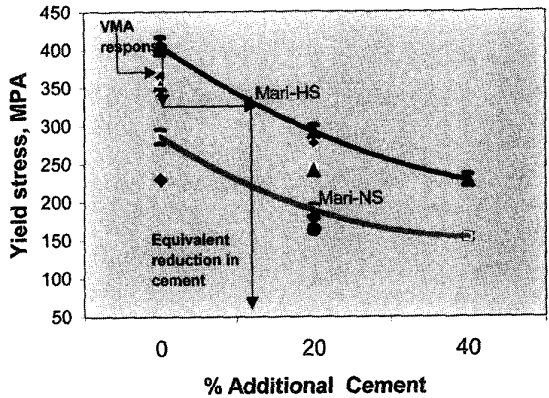


Figure 11. Change in mortar yield as a function of VMA and cement paste addition for mortar mixtures prepared with natural and manufactured sands.

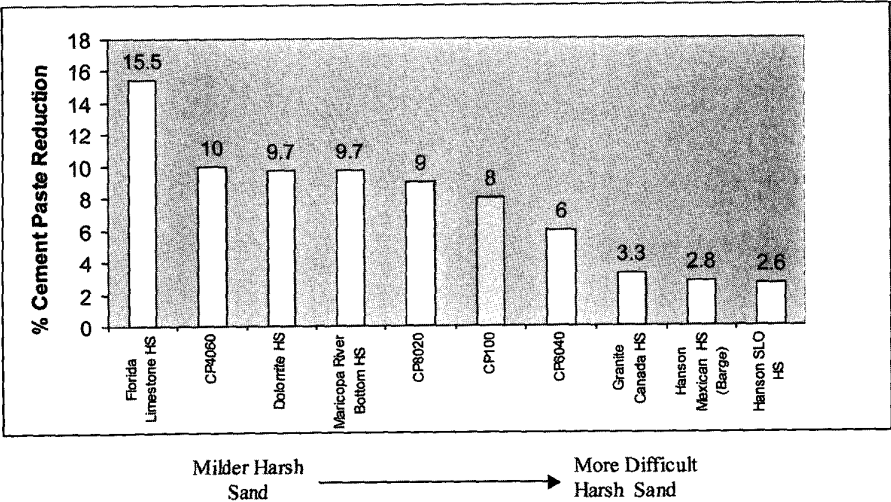


Figure 12. Reduction in cement paste content with 0.003% VMA s/s at constant yield stress.

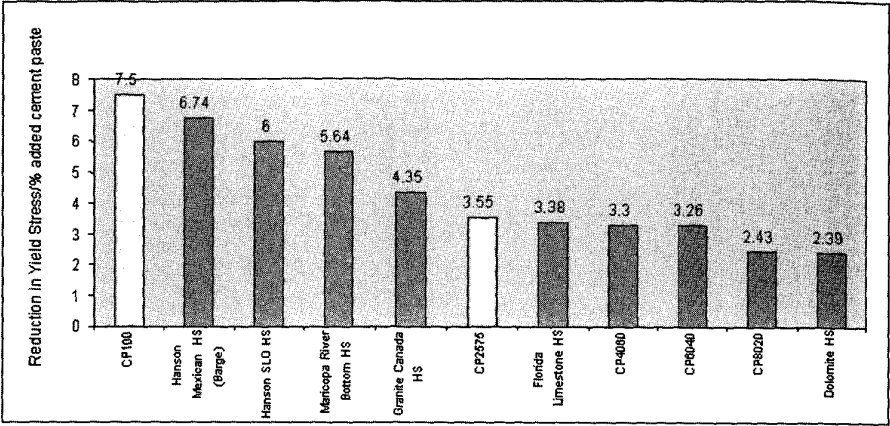


Figure 13. Reduction in yield stress as a function of added cement paste.

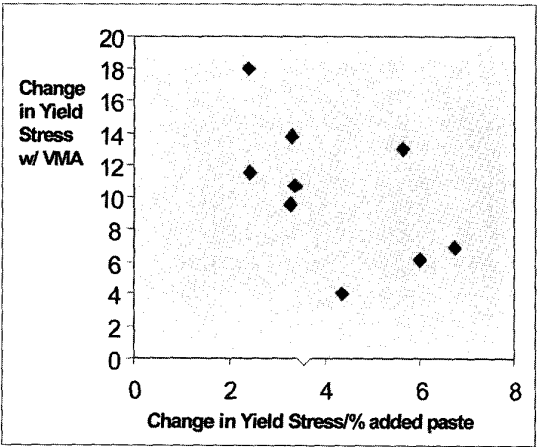


Figure 14. Correlation of VMA and cement paste additions on yield stress of mortar with various harsh sands. Sands with low response to VMA appear to respond well to added cement paste.

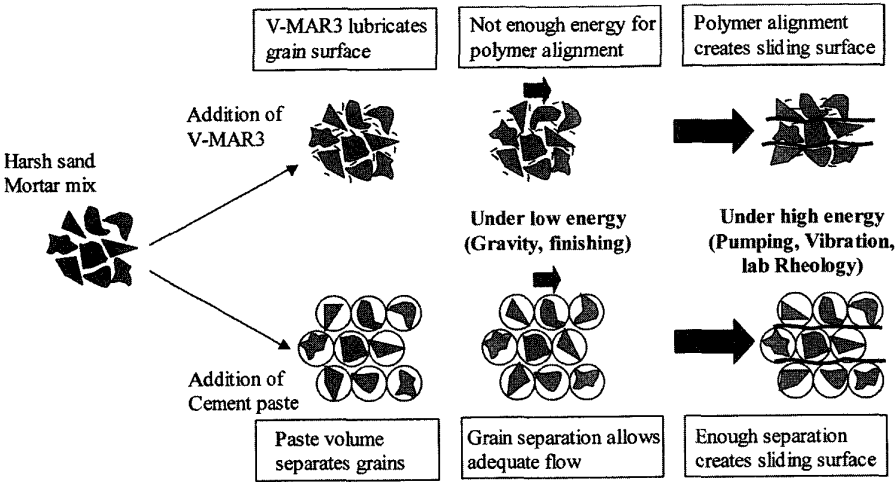


Figure 15. Mechanism of yield stress reduction as a function of VMA and cement paste additions.

Development of New Superplasticizer Providing Ultimate Workability

by D. Hamada, T. Hamai, M. Shimoda, M. Shonaka,
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Synopsis: Recently, the concrete workability has become regarded as much more important due to large demands for high durable concrete with low water content and unstable quality of concrete ingredients. The new superplasticizer was found to provide better workability controlling the rheological properties of the fresh concrete than the previous polycarboxylate type superplasticizers regardless of the quality of concrete ingredients. The framework structure of the new superplasticizer was a hyper-branched polymer in which specific function monomers were co-polymerized. The new polymer of the hyper-branched structure was more condensed than that of polycarboxylate type polymers and was highly adsorptive to cement particles, which made a higher density of the polymer adsorption onto cement surfaces possible. This dense and strong adsorption of the superplasticizer polymer molecules provided the unique rheological properties of the concrete or the mortar such as the lower viscosity of the concrete giving much easier handling. This new superplasticizer also provided the robustness against varieties of the concrete ingredients qualities. This superplasticizer for new generations has already been made practicable successfully for several constructions, and this technology will bring various possibilities and merits in concrete construction fields such as shortening the construction period thanks to better workability.

Keywords: adsorption; cement; EO chain; hyper-branched polymer; plastic viscosity; rheology; superplasticizer; yield value; workability

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INTRODUCTION

The rheological property of fresh concrete or mortar is one of the most important parameters to determine the workability in pumping, placing, and filling in a concrete framework. The fresh concrete has been generally treated as a Bingham fluid [1] according to the following equation (1) and Fig.1

$$\dot{\gamma} = (\tau - \tau_y) / \eta_{pl} \quad (1)$$

where $\dot{\gamma}$ is the shear rates of the Bingham fluid; τ is the shear stress; τ_y is the yield value; η_{pl} is the plastic viscosity.

The shear rate $\dot{\gamma}$ which is determined by the plastic viscosity η_{pl} and the yield value τ_y represents the mobility of the fluid when the shear stress τ is imparted. Therefore, $\dot{\gamma}$ can be considered as the representative of a fresh concrete workability. τ_y and η_{pl} can be controlled by the mixture proportions of the concrete and the superplasticizer, while τ depends on the working condition at the construction site. Thus, the dispersion state of the cement particles by the superplasticizer in the concrete would affect on the rheological parameter τ_y and η_{pl} . The dispersion state is controlled by the adsorptive states that are determined by the chemical features of the superplasticizers.

In recent years, there is an increasing trend toward higher durability of concrete and, for

example, concrete is endowed with high strength by reduction of the amount of water used therein, and this trend is estimated to increase in the future as well. The reduction of the amount of water is effected mainly by using a polycarboxylate-based superplasticizer excellent in water-reducing properties and fluidity-retaining properties [2, 3, 4, 5, 6, 7]. As the amount of water is reduced, however, the plastic viscosity η_{pl} and the yield value τ_y of the fresh concrete is increased, and thus there is a problem of reduction in workability. This problem of an increase in the plastic viscosity η_{pl} and the yield value τ_y is not completely solved even by the polycarboxylate-based superplasticizer and there is a need for a new superplasticizer having a higher effect of reducing the plastic viscosity η_{pl} and the yield value τ_y of concrete for the better workability.

Furthermore, various kinds of cements have tended to be used worldwide for ecological considerations in these days. Hence, the superplasticizers have been also required to meet the cement compatibilities. The adsorptive properties of polycarboxylate-based superplasticizers were reported to be effected by the concentration of SO_4^{2-} ions that was known as the representative affection by the cement variations on the dispersability [8]. Therefore a more robust, new superplasticizer, that is not affected by the SO_4^{2-} ions concentration and the cement variations, is desired to be developed in these days.

In this study, a new polymer was developed as a new superplasticizer to provide the ultimate workability with the lower plastic viscosity η_{pl} and the lower yield value τ_y , and also provide stable performance independently of cement variations.

MATERIALS AND EXPERIMENTAL METHODS

Molecular and Chemical Structure of Superplasticizers

The chemical structure and the molecular structure of the new superplasticizer polymer (NHBP) are shown in Fig. 2 and Fig. 3 in comparison with the conventional polycarboxylate based superplasticizer (PC). Polycarboxylate-based superplasticizers (PC) or polyether-based superplasticizers (PE) have carboxyl units and EO polymer units as the side chains, which are believed to impart electrostatic repulsion and steric repulsion, respectively [2, 3, 4, 5, 6, 7].

In the new superplasticizer molecule, the carboxyl units are chemically modified by the hydrophilic anionic groups (Z) to create a stronger adsorptive function. Moreover, the difunctional monomers are introduced in the structure, so that the molecular structure of the new superplasticizer is a hyper-branched polymer not like a linear polymer of a polycarboxylate based

superplasticizer shown in Fig. 3.

Figure 4 shows the relationship between the molecular weight and the intrinsic viscosity of the superplasticizer polymers with the side chain of EO 9 moles, measured by Tri-SEC RALLS System (Viscotek Model TDA 300) which was the integrative analysis system for the gel permeation chromatography (GPC) with a light-scattering detector, a differential pressure viscometer and a RI detector. The configuration of the polymer can be estimated by the coefficient α of Mark-Houwink-Sakurada's viscosity formula (2), the intrinsic viscosity dependence on the molecular weight.

$$[\eta] = KM^\alpha \quad (2)$$

where η is the intrinsic viscosity; M is the molecular weight; K , α are Mark-Houwink coefficients. The index α of PC (α_{PC}) and NHBP (α_{NHBP}) could be calculated by the approximation curve of Fig. 4 as follows.

$$\alpha_{PC} = 0.58 \quad \alpha_{NHBP} = 0.22$$

The smaller α value of the new polymer (α_{NHBP}) indicated more condensed structure of higher segment density. Generally, α becomes 0.5 ~ 1.0 for a linear polymer and α becomes ~ 0.5 for a hyper-branched polymer [9]. This result suggested that the new polymer structure is a hyper-branched one.

Cement Adsorption Test

Cement and water mixed with 3000 ppm of the superplasticizer were placed in a cylindrical vessel at W/C = 1.0. Mixing was carried out for 30 seconds. The supernatant liquid was separated centrifugally at 3000 rpm from the paste. The total organic carbon content of this liquid was then measured using Shimadzu TOC-5050A, and the concentration of the superplasticizer remaining in the supernatant liquid was obtained from a calibration curve prepared in advance. This yielded the amount of the superplasticizer adsorbed into the cement as the difference between the amount of superplasticizer added and that remaining in the liquid.

In an other set of tests, 2000 mol/L of Na_2SO_4 was added together with the superplasticizer solution. The adsorption amount of the superplasticizer with Na_2SO_4 was also measured to evaluate the effect of SO_4^{2-} ions, on the adsorption amount of the superplasticizers.

Mortar Preparation

Cement and sand and water mixed with the superplasticizer were placed in the stainless vessel of a capacity of 1000 ml (and of Ø 120 mm inside diameter). The mixture proportions and the ingredients of the mortar are listed in Table 1. Mixing was carried out for 3 minutes at the rotational speed of 200 rpm by the stirrer Z-2310 (of Ø 110 mm with six choppers of 30 mm height) manufactured by EYELA, measuring the electrical torque that corresponded to the mortar viscosity. The mortar preparation apparatus is shown in Fig. 5. The mortar fluidity was evaluated by the spread measured when a truncated cone (of Ø 100 mm and Ø 70 mm diameters, and 60 mm height) filled with the mortar was pulled away vertically.

Rheological Properties

The rheological properties of the mortar samples as referred to the above were measured by KMS Ball measuring system (where the ball diameter was 12 mm; the arm radius was 37 mm; the thickness of mortar sample was 50 mm; the vessel diameter was Ø 115 mm; the ball center position was 18 mm higher from the bottom) of MCR500 manufactured by Paar Physica (Fig. 6). The shear stress dependence of the shear rate was measured (from 10 Pa to 130 Pa for 40 seconds).

Cement Compatibility Test

Cement and sand and water mixed with the superplasticizer were placed in a mortar mixer at $W/C = 0.5$. Four kinds of European cements were used for the evaluations. The mixture proportions and the used ingredients of the mortar are listed in Table 2. Mixing was carried out for 2 minutes at the low rotational speed of 62 rpm. The mortar fluidity was evaluated by the spread measured when a truncated cone (of Ø 100 mm and Ø 70 mm diameters, and 60 mm height) filled with the mortar was pulled away vertically.

Concrete Manufacturing

A biaxial-forced mixer with a capacity of 50 liters was used to mix 30 liters of concrete. The cement and both sand and gravel were placed in the mixer and mixed for 10 seconds, then

water containing the superplasticizer was added and the mixing continued for further 90 seconds. The mixture proportions and the ingredients of the concrete are listed in Table 3. The temperature of the concrete during mixing, and also the laboratory ambient temperature, were held at 20 ± 0.5 °C.

Flowing speed test (Workability)

The concrete flowing speed that was the characteristic index of the workability was measured when the concrete ran down the tilting lane (23°C) by *Tilting Flow Tester* manufactured by Newtech shown in Fig. 7.

RESULTS & DISCUSSION

Adsorptive properties

Figure 8 shows the adsorption amount of the superplasticizers (PC, NHBP) at W/C =1.0 with or without Na₂SO₄. The polymer samples for the evaluation were selected to fix the length of EO chains (p in Fig.2, p = 9, 23 moles) and the molar ratios of the EO chain units (m in Fig.2) in their polymer structures. The new hyper-branched polymer (NHBP) showed much larger adsorption amount and was less influenced by SO₄²⁻ ions than the polycarboxylate-based polymer (PC).

The higher adsorption amount of NHBP could be explained by the compactly arranged adsorption of the condensed hyper-branched structure on the cement particle surfaces.

The adsorptive force of PC was weaker than SO₄²⁻ ions so that the adsorption of PC was inhibited by SO₄²⁻ ions, as previously reported [8]. On the other hand, the adsorptive force of NHBP was thought to be so strong that the adsorption was not inhibited by SO₄²⁻ ions.

Mortar viscosity

Figure 9 shows the relationship between the mortar fluidity and the viscosity that was converted from the electrical torque during the mixing. NHBP showed much lower viscosity than PC at the same mortar fluidity. The lower viscosity meant that the amount of the committed water by the gathering cement particles was smaller, which suggested that NHBP dispersed the cement

particles more finely than PC.

Rheological properties of mortar

To investigate the difference of the rheological properties of PC and NHBP in details, their dynamic rheological properties were studied. Figure 10 shows the shear stress dependences of the shear rate of PC and NHBP at the same mortar fluidity of 200 mm. Both PC and NHBP exhibited the rheological behavior like Bingham fluids. Table 4 shows the plastic viscosity and the yield value for each mortar sample. As the paste volume in the mortar mixture for PC type was increased while W/C ratio was constant, both of the plastic viscosity and the yield value were decreased dramatically, which could be supported by the excess paste theory [10].

As can be seen from the figure, NHBP showed much lower plastic viscosity and lower yield value than PC though the mixture proportions and the mortar fluidity of them were same.

The lower plastic viscosity of NHBP than that of PC could be explained by the higher adsorption amount of the superplasticizer molecules, that lead to the denser adsorption state of EO chains on cement surfaces [11].

The lower yield value of NHBP might also be explained by the denser adsorption state of EO chains on cement surfaces. A yield value of a slurry is supposed to be reflected in the coagulation state of the particles. The dense adsorption state of EO chain on cement surfaces ($m\Gamma$) was considered to enhance the repulsive force (P_R) according to the following formula (3) [12,13], so that the dispersion state at the dynamic condition became stable and the coagulation state at the static condition became soft:

$$P_R(h) = kT\pi am\Gamma [(D_0/h)^{4/3} + 1] \quad (3)$$

where a is the particle radius (m); h is the distance between particles (m); D_0 is the thickness of adsorbed layer (m); K is Boltzmann constant; T is the absolute temperature (K); m is the number of EO chains in one molecule; Γ is the number of adsorbed molecule per unit area.

The lower plastic viscosity and the lower yield value of NHBP based superplasticizer would conduce to better workability in the concrete than PC based one. Furthermore, as can be seen in Table 4, the required cement paste volume in a concrete mixture design might be able to be reduced to get the predefined workability for NHBP compared to PC.