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Effect of different types of superplasticizer on fresh, rheological and strength properties of self-consolidating concrete ☆

Ali Mardani-Aghabaglou [a,*], Murat Tuyan [a], Gökhan Yılmaz [b], Ömer Arıöz [c], Kambiz Ramyar [a]

[a] Department of Civil Engineering, Ege University, Bornova-İzmir, Turkey
[b] Draco Construction Chemicals Company, Izmir, Turkey
[c] Çimbeton, Cementır Holding, Izmir, Turkey

HIGHLIGHTS

- Four mixtures containing different superplasticizer types were prepared.
- The admixtures had same main chain and same polymer structure.
- Different molecular weight and side chain density of carboxylic acid groups were used.
- Slump-flow, V-funnel, slump-flow loss and L-box of SCC were determined.
- Rheological parameters were measured by using a concrete rheometer.

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ABSTRACT

The effect of different types of superplasticizer on fresh, rheological and strength properties of self-consolidating concrete (SCC) was investigated. The admixtures had same main chain and same polymer structure but different molecular weight and different side chain density of carboxylic acid groups. Fresh concrete properties were determined by using the slump-flow, V-funnel, slump-flow loss and L-box tests. Besides, the rheological parameters including apparent yield stress and plastic viscosity were measured by using a concrete rheometer. The compressive strength, ultrasonic pulse velocity and dynamic elastic modulus of SCC mixtures were determined at 1, 3, 7 and 28 day ages. Test results indicated that V-funnel flow time, plastic viscosity and slump retention of SCC mixtures were affected by the side chains density of polymer considerably. It was observed that the compressive strength of SCC mixtures was also influenced slightly with the incorporation of different types of superplasticizers. The effect was more pronounced at early ages.

1. Introduction

Self-consolidating concrete (SCC) is a special type of highly flowable concrete that does not require vibration for placing and compaction. It is able to flow under its own weight, completely fill formwork and achieve full compaction, even in the presence of congested reinforcement. SCC is a new variety of high performance concrete with superior deformability and segregation resistance. The mechanical properties and durability of SCC are highly affected by its fresh properties, such as flowability, filling ability etc. [1–3]. The high flowablity of SCC mixtures is achieved by using superplasticizer which influences many fresh and hardened properties of SCC mixtures [4,5].

Nippon Shokubai and Nippon Master Builder Technology invented the polycarboxylate based superplasticizer (PC) in the middle of the 1980's in Japan [6]. PC is synthesized from petrochemical products and widely used in concrete in recent years, especially in SCC mixtures. It is composed of three essential parts: a backbone of polyethylene, grafted chains of polyoxyethylene (POE) and carboxylic groups as adsorbing functional groups. The dispersion mechanism of PC-based superplasticizers is more related to a steric hindrance effect (produced by the presence of neutral side long 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 [6]. The chemical structure modifications of PC-based superplasticizers include charge density differentiation, side chain length, main backbone length, degree of backbone polymerization and composition of functional groups [7–9].

The effect of type of new generation superplasticizer, air-entraining, viscosity modifying and anti-foaming admixtures on the air content and workability of high performance SCC have

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* Corresponding author. Tel.: +90 232 3886026; fax: +90 232 3425629.
E-mail address: ali.mardani16@gmail.com (A. Mardani-Aghabaglou).

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been investigated by Łaźniewska-Piekarczyk [10]. The test results showed that admixtures from different sources cannot be used interchangeably, even if they appear to have a similar chemical composition.

The effect of molecular weight of a superplasticizer on the adsorption on cement surface was investigated by Andersen and Roy [11]. For this purpose, four superplasticizer admixtures with different molecular weight (4000, 16,000, 31,000 and 70,000 g/mole) were used. The test results showed that the superplasticizer with the largest molecular weight gave the largest negative zeta potential, indicating its higher ability to prevent flocculation of cement particles.

In another research, effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties of concentrated cement suspensions was investigated by Rana et al. [12]. The results demonstrated that the polymer with long side chain had higher dispersion power than that of the polymers having shorter ones due to the stronger steric hindrance effect of the former.

The effect of some properties of superplasticizers such as origin, molecular weight, side chain length, degree of sulfonation and polymerization on the fresh properties, mechanical properties and durability of concrete mixtures was investigated by many researchers [13–19]. However, in the literature, there is no study related with the effect of side chain density of carboxylic acid groups of superplasticizer admixture on the fresh, rheological and compressive strength of either conventional concrete or SCC.

In this study, the effects of four types of polycarboxylate ether-based superplasticizers having various characteristics on the fresh and rheological properties as well as compressive strength of SCC were investigated.

2. Experimental details

2.1. Materials

In this study, a CEM II B-M (L/W) 42.5 R type cement conforming to EN 197-1 standard [20], crushed limestone aggregate with maximum size of 15 mm, limestone powder as filler and four different types of polycarboxylic ether-based superplasticizer admixtures (SP) were used. The admixture used in this study had same main chain and same polymer structure but different molecular weight and different side chain density of carboxylic acid groups. The chemical composition, as well as some mechanical and physical properties of the cement and some characteristics of SP, obtained from their manufacturers are given in Tables 1 and 2, respectively.

The specific gravity and water absorption capacity of the crushed aggregate limestone with two different particle sizes, e.g. 0–5 mm and 5–15 mm used in the experiments, were determined in accordance with EN 1097-6 standard [21]. The physical properties of aggregates are presented in Table 3. The gradation of the combined aggregate obtained by mixing 50% 0–5 mm and 50% 5–15 mm aggregate size fractions as well as standard gradation limits [22] are shown in Fig. 1.

Table 1
Chemical and physical properties of cement.

Oxide	(%)	Physical properties	
SiO_2	20.52	Specific gravity	2.97
Al_2O_3	6.46	Lechatelier soundness (mm)	0.5
Fe_2O_3	3.31	*Setting time (min)*	
CaO	57.45	Initial	180
MgO	1.54	Final	275
K_2O	0.88	*Fineness*	
Na_2O	0.44	Blaine specific surface (cm^2/g)	4590
SO_3	3.13	Residual on 0.090 mm sieve (%)	0.3
Cl-	0.01	Residual on 0.032 mm sieve (%)	9.2
Free CaO	2.02	*Mechanical properties*	
LOI	3.8	Compressive strength (MPa)	
Total	99.56	2-day	32.1
		7-day	46.3
		28-day	55.2

Table 2
Properties of polycarboxylate ether based superplasticizer admixtures.

Appearance	A Slightly yellowish liquid	B Slightly yellowish liquid	C Slightly yellowish liquid	D Slightly yellowish liquid
pH , 25 °C	6.2	6.03	6.0	6.86
Density (g/cm^3)	1.116	1.097	1.073	1.116
Mass average molecular weight	50,000	42,000	48,000	42,000
Side chain density of carboxylic acid groups	1:5	1:3	1:4.5	1:6
Viscosity cP, impeller rotational velocity (rpm)	896 cP, 20	265 cP, 100	256 cP, 100	940 cP, 30

Table 3
Physical properties of aggregates.

Aggregate		Bulk SSD specific gravity	Absorption capacity (%)	Loose bulk density (kg/m^3)
Type	Size (mm)			
Limestone	0–5	2.60	0.21	1740
	5–15	2.65	0.67	1505

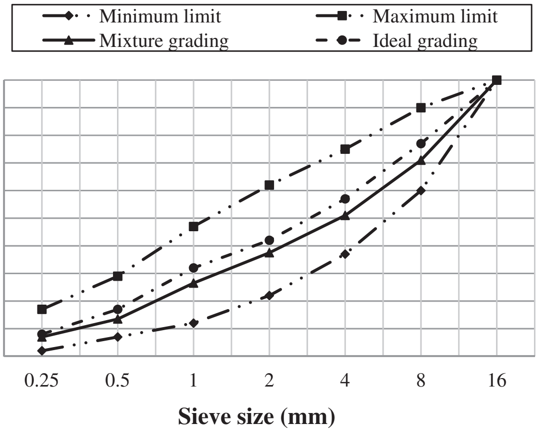

Fig. 1. Gradation curve of combined aggregate and TS 802 [22] standard limits.

2.2. Mixture proportions

Four SCC mixtures (incorporating four different types of superplasticizers) with same water/cement ratio of 0.4 were prepared. In all of the mixtures 450 kg/m^3 CEM II B-M (L/W) 42.5 R type cement was used. The slump flow of the mixtures was kept constant at 730 ± 10 mm. In order to achieve the required slump flow, the superplasticizer content of the mixtures was adjusted in the range of 5.5–7.5 kg/m^3. The corrected mix proportions of SCC mixtures are listed in Table 4.

2.3. Test procedures

2.3.1. Fresh concrete tests

Fresh concrete properties of SCC mixtures were determined by using the slump-flow, V-funnel and L-box tests in accordance with EFNARC [23] as well as slump-flow loss after 15 and 30 min. Besides, the rheological parameters including apparent yield strength and plastic viscosity were measured by an impeller type rheometer suitable for SCC mixtures.

2.3.2. Hardened concrete tests

The batch was placed in 150 mm cubic specimens. The specimens were demolded after 24 h and were stored in a moist room in water at 23 ± 2 °C until the testing day. For each mix, twelve specimens were prepared and tested at 1, 3, 7 and 28-day ages for compressive strength in accordance with EN 12390-3 [24] standard. The ultrasonic pulse velocity (UPV) values of the concrete mixtures were determined in accordance with the ASTM C 597 [25] standard at the same ages. The dynamic elastic modulus of the concrete mixture was calculated using the following equation [26,27]:

Table 4
Corrected mix proportions of the SCC mixtures (kg/m^3).

	Cement	Water	LP[b]	Aggregate		SP[c]	Unit weight	
			0–0.125(mm)	0–5 (mm)	5–15 (mm)		Theoretical	Measured
Mix A[a]	465	186	173	793	793	6.6	2338.4	2416.6
Mix B[a]	459	183	171	783	783	6.1	2338.0	2385.1
Mix C[a]	461	184	172	786	786	5.7	2337.6	2394.7
Mix D[a]	442	177	165	754	754	7.4	2339.5	2299.4

[a] Each mixture contains a different type of superplasticizer admixture having modified polymer chain and structures.
[b] LP: limestone powder as filler.
[c] SP: superplasticizer admixture.

$$E_{dn} = \rho c^2 \frac{(1+v)(1-2v)}{(1-v)} \tag{1}$$

where E_{dn} is the dynamic elastic modulus of concrete (MPa), ρ is the hardened concrete density (kg/m^3), c is the UPV (km/s) and v is the Poisson's ratio. Poisson's ratio was assumed as 0.22 for all of the SCC mixtures.

3. Test results and discussion

Fresh properties of the SCC mixtures are summarized in Table 5. Each value presented is the average of three measurements. In terms of slump flow value, all of the SCC mixtures belong to SF2 class in accordance with EFNARC [23]. It was found that, for the desired slump flow value (730 ± 10 mm), Mix C and Mix D required the minimum and maximum superplasticizer dosages, respectively. The V-funnel flow times were determined in the range of 27–47 s. It is known that the V-funnel flow time is related to the viscosity and cohesiveness of the mixtures [23]. As expected, V-funnel flow times decreased with increasing superplasticizer dosage. This may be in part due to the difference between side chain density of carboxylic acid groups of admixtures and in part due to the admixture dosage. For example, Mix D containing the admixture with the highest side chain density of carboxylic acid groups and the highest dosage among the other mixtures showed the lowest V-funnel flow time. V-funnel flow time increased with decreasing side chain density of carboxylic acid groups. Houst et al. [28] stated that steric hindrance influenced by backbone chain length, side chain length and spacing of side chains. The V-funnel flow times of Mix A, B and C, decreased with increasing the molecular weight of the superplasticizer. Uchikawa et al. [29] found similar results.

From passing-ability view point, obtained from L-box test, Mix A and Mix C belong to PA2 class in accordance with EFNARC [23]. However, passing ratios of Mix B and Mix D were lower than 0.80 (the lower limit of EFNARC Guideline [23]).

Shear stress–shear rate curves of the SCC mixtures are shown in Fig. 2, indicating a strong linear relationship between shear stress and shear rate. Therefore, all of the mixtures correspond to Bingham body model. The Bingham body model can be written as follows:

$$\tau = \tau_0 + \lambda t \tag{2}$$

where τ is shear stress, τ_0 is yield stress, λ is plastic viscosity and t is time.

Table 5
Fresh properties of concrete mixtures.

Mix	Slump flow (mm)	L-Box			V-funnel (s)	SP (w% of cement)
		20 cm (s)	40 cm (s)	H2/H1		
Mix A	730	2	5.5	0.95	40	1.42
Mix B	720	2.5	6.5	0.76	47	1.33
Mix C	740	1.5	5	0.90	44	1.24
Mix D	720	1	3	0.58	27	1.67

Two rheological parameters (apparent yield stress and plastic viscosity) of SCC mixtures were determined using Eq. (2). Apparent yield stress and plastic viscosity values of the mixtures were in the range of 5–44 Pa and 210–354 Pa s, respectively. Generally, the plastic viscosity of SCC mixtures should not exceed 150 Pa s [30]. The higher plastic viscosity values obtained in this study may be attributed to increasing both the molecular weight and side chain density of carboxylic acid groups of superplasticizer admixture.

In this study, apparent yield stress values of SCC mixtures increased with increasing superplasticizer dosage. The other properties of superplasticizers such as molecular weight and side chain density seem to have no significant effect on the apparent yield stress values.

As emphasized in the V-funnel flow time test results, as side chain density of carboxylic acid groups increased, causing an increase in steric hindrance, plastic viscosity values of the mixtures decreased. For example, the superplasticizer admixture used in Mix B had the minimum side chain density, thus, this mixture showed the greatest plastic viscosity compared to that of other mixtures.

The relationship between V-funnel flow time and plastic viscosity of the mixtures are shown in Fig. 3. Test results indicated that there was a strong relationship ($r = 0.9714$) between the values obtained from rheometer and the values obtained from V-funnel flow test. It seems that it is possible to have an idea about the plastic viscosity of SCC mixtures by measuring the V-funnel flow time of them.

The slump values of the SCC mixtures at 0, 15 and 30 min are shown in Fig. 4. When the slump loss values of Mix A, B and C are compared, it becomes obvious that Mix C showed roughly no slump loss within 30 min. This may be attributed to the lower side chain density of carboxylic acid groups of the SP. However, there was a slightly reduction in slump flow values of the Mix A and Mix B within this period. Mix D had no slump retention at the end of 15 min. This indicates that the superplasticizer and cement used in this mixture are incompatible. The incompatibility may be arisen from the higher amount of side chains of the polymer which may in turn increase the risk of flocculation of cement particles. Similar results are reported in the case of admixtures having extremely long side chains [31].

The compressive strengths of SCC mixtures at different ages are shown in Fig. 5. Each value presented is the average of three measurements. Test results revealed that, as the slump loss of the concrete mixture increased the rate of stiffening and consequently the rate of hardening and early strength of the mixtures increased. However, although Mix D had the highest slump loss among the mixtures, it showed the lowest compressive strength. This may be due to the fact that the Mix D lost its self compacting property with in the time of placing in the molds. In addition, UPV values showed that Mix D had the highest wave travel time indicating its highest porosity. The same observation was made regarding the unit weights of the hardened mixtures. Mix D with 2299 kg/m^3 showed the lowest unit weight value among the mixtures. However, except for Mix D, the effect of superplasticizer type on

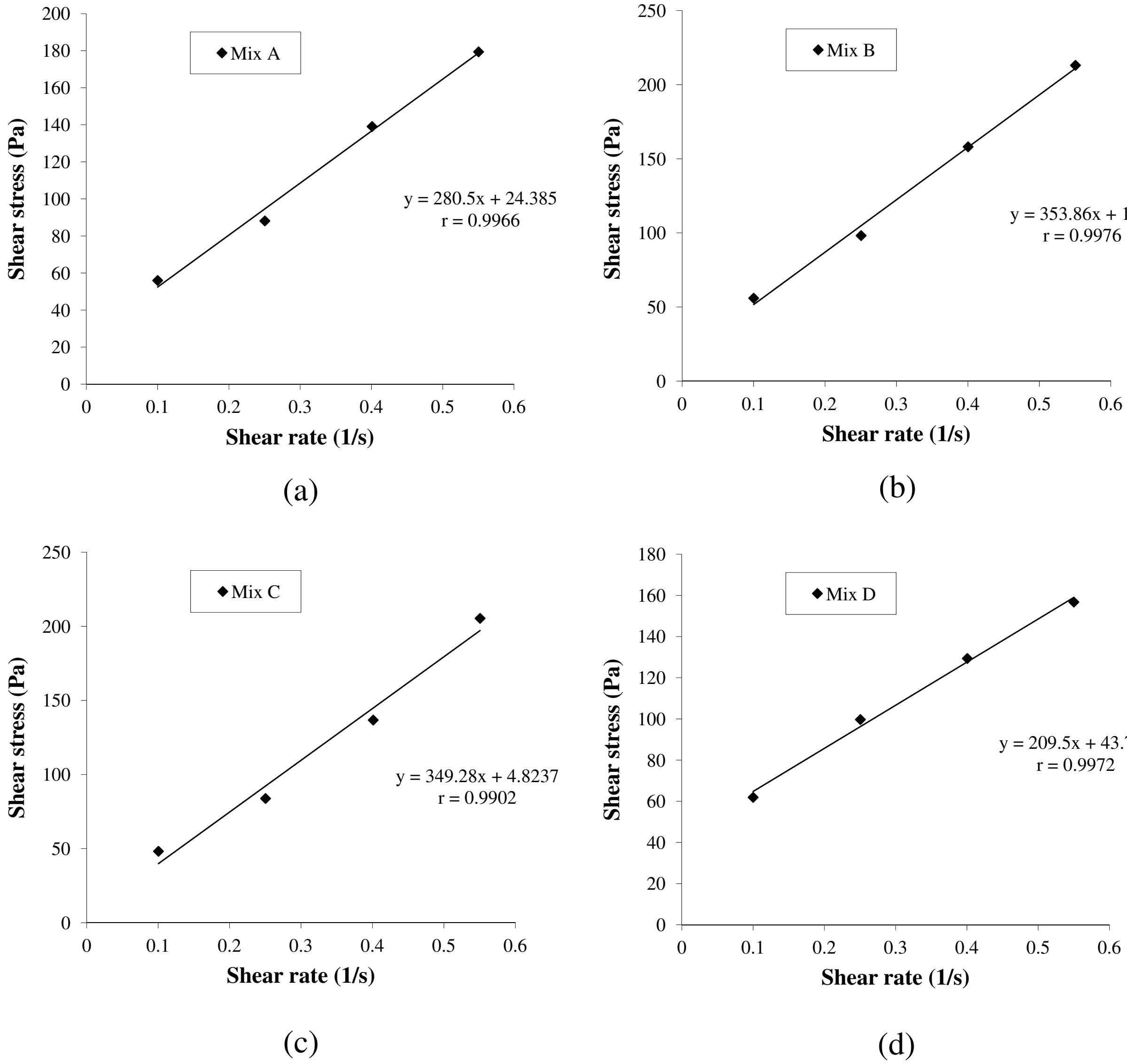

Fig. 2. Shear stress-shear rate curves: (a) Mix A, (b) Mix B, (c) Mix C, and (d) Mix D.

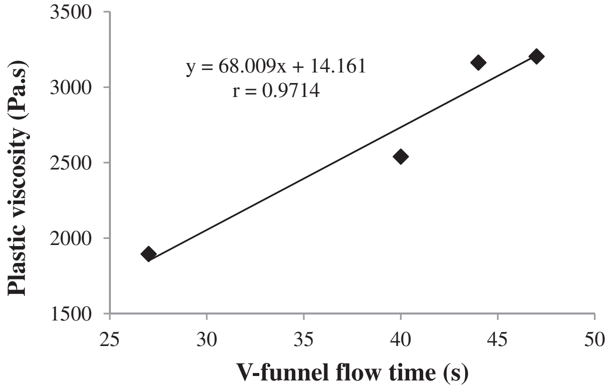

Fig. 3. Relationship between V-funnel flow time and plastic viscosity.

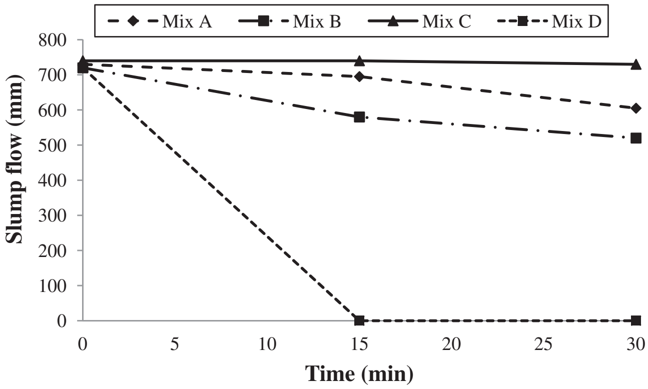

Fig. 4. Slump flow values at different times.

the compressive strength of SCC mixture diminished at the ages beyond 7 days.

The 1, 3, 7 and 28-day UPV test results of SCC mixtures are presented in Fig. 6. Each value presented is the average of three measurements. The UPV of concrete is affected by a number of parameters e.g., age, moisture condition, concrete porosity, aggregate type and ITZ characteristics [32]. As expected, the UPV of SCC mixtures increased with age. The increase in UPV values of the mixtures was noticeable at first 7 days. Beyond this age the rate of UPV increment was negligible. It can be seen that the UPV values

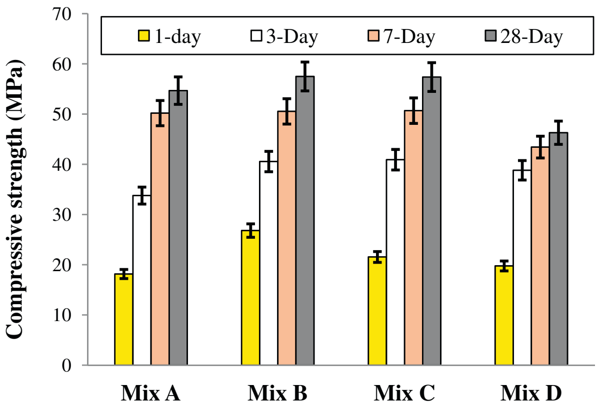

Fig. 5. Compressive strength of SCC at different ages.

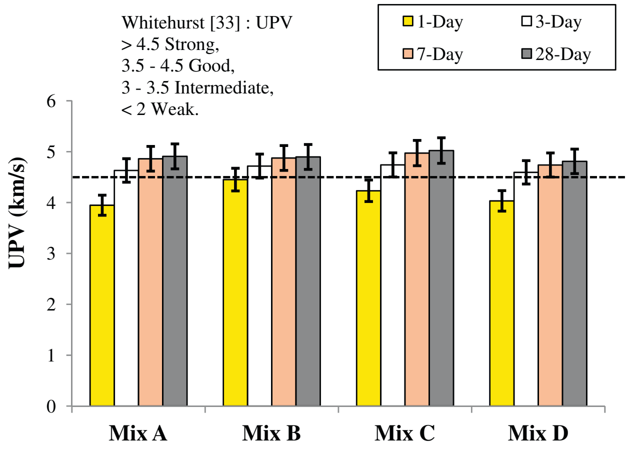

Fig. 6. UPV values of SCC at different ages.

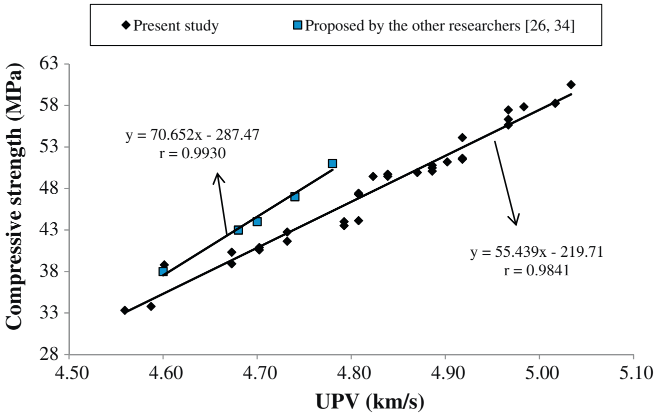

Fig. 7. The relationship between the UPV values and the compressive strengths of SCC mixtures beyond 1 day age.

of the SCC mixtures were higher than 4.5 km/s after 3 days, the limit specified for strong concrete by Whitehurst [33]. Mix D has minimum UPV values compared to other mixtures due to its poor compatibility.

Table 6
Dynamic elastic moduli of SCC (GPa).

	1-day	3-day	7-day	28-day
Mix A	25.6	34.9	40.0	41.1
Mix B	32.7	36.7	39.7	40.4
Mix C	29.5	37.0	41.5	42.3
Mix D	26.9	35.1	36.1	36.7

The relationship between the UPV values and the compressive strengths of the SCC mixtures are shown in Fig. 7. As it can be seen from the figure, a strong linear relationship between the UPV values and the compressive strengths of SCC mixtures were obtained. The UPV-strength relationship obtained in this study is compared with the UPV-strength relationship of conventional concrete mixture having similar aggregate cement ratio (3:1) proposed by the other researchers [26,34]. As it can be seen from the figure both linear relationships are very close to each other.

Dynamic elastic moduli of the SCC mixtures at different ages are summarized in Table 6. Dynamic elastic moduli of SCC mixtures are associated with unit weight and UPV value of the mixtures. As expected, the dynamic modulus of SCC mixtures increased with age. Due to lower unit weight and UPV value, which are indications of higher porosity, Mix D showed the lowest dynamic elastic modulus compared to the other mixtures.

4. Conclusions

In this experimental study, the effects of four types of polycarboxylate ether-based superplasticizer admixtures having same main chain and same polymer structure but different molecular weight and different side chain density of carboxylic acid groups on the fresh and rheological properties as well as compressive strength of SCC were investigated. The following conclusions were drawn:

V-funnel flow time as well as plastic viscosity of SCC mixtures decreased with increasing side chain density the superplasticizer admixture.

The apparent yield stress was affected by the superplasticizer dosage; however, the other properties of the admixture had no significant effect on the apparent yield stress of the SCC mixtures.

As the amount of side chains of the polymer increased, the slump retention of the cementitious system decreased. This may be due to the interlocking of the side chains.

When the admixture and the cement were compatible, the early strength was dependent on the type of admixture whereas at the ages beyond 7 days the strength became independent of the admixture type. The admixture causing the highest slump loss caused the highest concrete strength at early ages.

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