



EFFECT OF NOVEL SUPERPLASTICIZER ON WORKABILITY AND STRENGTH OF READY MIXED CONCRETE

Anuradha Varshney^[a], Pratibha Singh^[b] and Kiran Prajapati^[c]

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With the advent of superplasticizers, dream to discover method of making ready mixed concrete at the lowest possible water cement ratio while maintaining a high workability has achieved. In addition, these concrete material are also suitable for use with other cementations materials like fly ash. Poly(styrene-co-acrylonitrile) prepared with the help of p-acetyl benzylidene triphenyl arsonium ylide had made it possible, the production of concrete at low water cement ratio. Many waste materials of today become the useful by products of tomorrow water cement ratio was maintained between 0.38-0.47. Use of fly ash in concrete improves the penetration rate of CO₂ or chloride ions. The result have shown substantial improvement in the properties of concrete after use of copolymer of styrene and acrylonitrile as superplasticizer.

* Corresponding Authors

E-Mail: anurmc@gmail.com

[a] Department of Chemistry, D.G. (P.G.) College, Kanpur, India

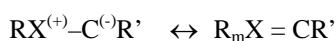
[b] Research Scholar Singhanian University, Rajasthan, India

[c] Department of Chemistry, G.G.I.C., Singhpur, Kanpur, India

chapter as attempt has been made to synthesis¹³ copolymer of styrene and acrylonitrile with p-acetylbenzylidene triphenyl arsonium ylide and study the effect of the copolymer as novel superplasticizer on workability and strength of ready mix concrete.

Introduction

Polymer chemistry is emerging as one of the fastest growing field in science and technology. Polymerization dates back to the beginning of DNA based life, as both DNA and proteins are polymers. However, it was not until the industrial revolution that the modern polymer chemistry began to flourish. The advent of new technique has created a boom in the growth of polymer science. Modern methods of polymerization like atom transfer radical polymerisation,¹ group transfer polymerisation,² liquid crystal polymerisation,³ star polymerisation,⁴ polymerization by ylide⁵ have proven to be effective in controlling the properties of the polymers. The ylides⁶ are 1,2 dipolar compounds in which a carbon atom is attached directly to a heteroatom X⁺ carrying a positive formal charge.



(I)

(II)

X⁺ = (nitrogen, phosphorus, sulphur, arsenic, antimony, bismuth, selenium or tellurium)

The ylides give mostly alternating copolymers as well as syndiotactic homopolymers unlike the conventional initiators like azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) otherwise Lewis acids are used to obtain stereo regular polymers. Ylides^{5,7-9} are found to be more economical than conventional initiators.

Concrete, a composite material made with cement, aggregates, admixtures and water comprises in quantity the largest of all man-made materials. Superplasticizers¹⁰⁻¹² in concrete confer some beneficial effects such as acceleration, retardation, air entrainment, water reduction, plasticity etc. and these effect are due to their action on cement. In this

Experimental

Purification of monomers and solvents¹⁴⁻¹⁵ were carried out by standard methods. P-acetylbenzylidene triphenyl arsonium ylide (p-ABTAY) was prepared¹⁶ using triphenyl arsine (Merck) and dioxane. They were used without purification.

Polymerization procedure

Styrene acrylonitrile copolymer was prepared in dioxane flushed with nitrogen gas at 60 ± 0.1°C for 1 hour using p-ABTAY as radical initiator. The copolymer were precipitated with acidified methanol and dried under vacuum. The copolymers were refluxed with cyclohexane and DMF to remove homopolymers of styrene and acrylonitrile respectively. The structure of the copolymer was confirmed by (FTIR, ¹H-NMR and ¹³C-NMR (Fig. 1, 2, 3).

Materials used

Cement (OPC -43 grade) and its properties

Specific gravity (G _c)	3.16
Normal consistency	30%
Initial setting time	120 minutes
Final setting time	370 minutes
Compressive strength	54.46 N mm ⁻²
Fineness	97.80

Fly ash from Thermal Power Station, Kanpur

Specific gravity (G _f)	2.1
Fineness (Blaine's)	380 m ² kg ⁻¹

Lime reactivity	5.4 N mm ⁻²
Loss on ignition	3.4 %

Fine Aggregate river sand

Specific gravity (G_{fa})	: 2.53
Unit mass (W_{fa})	1420 kg m ⁻³
Fineness modulus	
by sieve analysis (Table 1)	2.78
Water absorption	0.32 %

Coarse aggregate–

Grit	10 - 20 mm
Specific gravity (G_{ca})	2.64-2.73
Unit mass (W_{ca})	1360-1375 kg m ⁻³
Fineness modulus	6.91

Water

Tap water

Polymer Admixture

Copolymer of styrene and acrylonitrile prepared by (p-ABTAY)

Result and Discussion

The copolymer of styrene and acrylonitrile prepared initiated by p-ABTAY. The properties of copolymer are studied which are as follows:

Properties of polymer admixture

Polymer	styrene-co-acrylonitrile
Colour	yellowish
Activation energy	
by Arrhenius equation	55 KJ mol ⁻¹
Polydispersity index	
by GPC M_w/M_n	12

Characterization of copolymer(s)**Fourier Transform Infrared Spectroscopy**

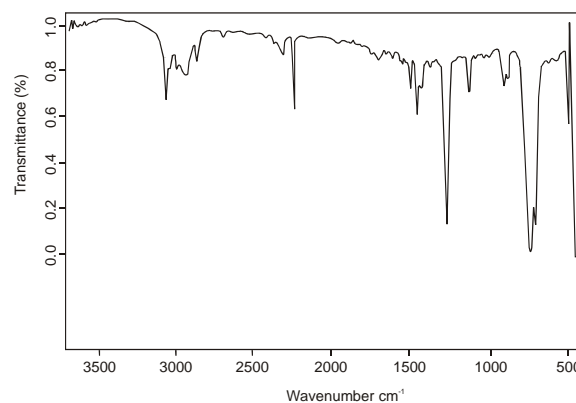
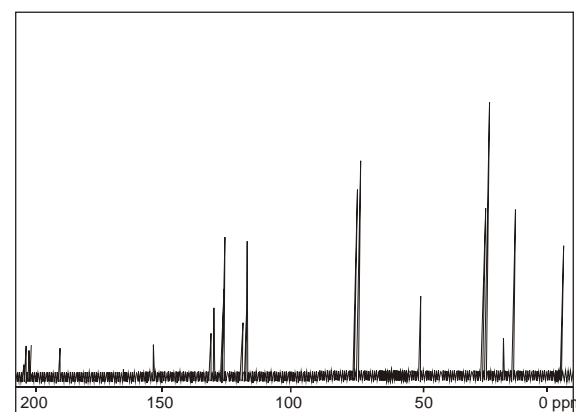
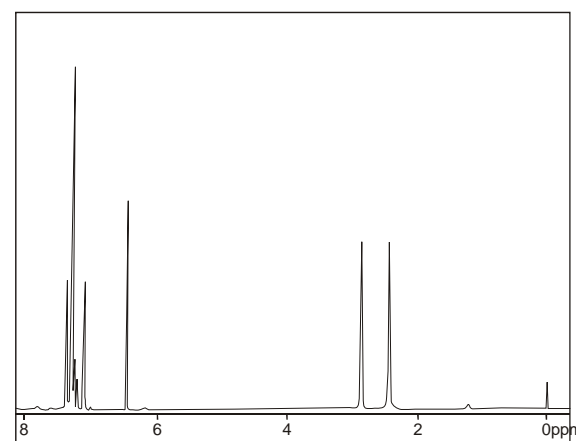
The FTIR spectrum¹⁷ of the copolymers (Fig. 1) shows bands at 3053 cm⁻¹ and 2237 cm⁻¹ due to aromatic C–H stretching of phenyl protons of styrene and –CN group of acrylonitrile respectively.

¹H-Nuclear Magnetic Resonance Spectroscopy

The ¹H-NMR spectra¹⁸ of the copolymers (Fig.2) shows peak at 6.1-7.4 δ ppm due to phenyl group of styrene.

¹³C-Nuclear Magnetic Resonance Spectroscopy

The ¹³C-NMR spectrum of the copolymers (Fig.3) shows peaks at 122-124 δ ppm and at 128-133 δ ppm due to –CN group of AN and –C₆H₅ carbon of styrene respectively.

**Figure 1.** FTIR spectrum of the prepared (Sty-co-AN).**Figure 2.** ¹H-NMR spectrum of the prepared (Sty-co-AN).**Figure 3.** ¹³C-NMR spectrum of the prepared (Sty-co-AN).

Different grades of concrete, M-20, M-25, M-30, M-35, M-40 and M-45 (Table 2 and 3) were used to study the effect of ready mixed concrete in presence of absence of polymer admixture and fly ash to get low cost environment friendly concrete. Bulk density was maintained between 2350 to 2441 as per specification (Fig. 4). The water cement ratio was maintained between 0.38 - 0.47 with slump 120-130. Low strength¹⁹ on 7th day is due to the pozzolanic reaction between fly ash and cement it lags behind cement hydration.

Table 1. Sieve Analysis of sand

S. No.	Bis sieve size	Weight retained g (I)	% ge retained (1)/10 (II)	Cumulative of retained (III)	Cumulative of passing (100) (IV)	Silt content
1.	4.75 mm	102	10.2	10.2	89.8	7.50%
2.	2.36 mm	110	11	21.2	78.8	
3.	1.18 mm	107	10.7	31.9	68.1	
4.	600 μ	184	18.4	50.3	49.7	
5.	800 μ	200	20	40.3	29.7	
6.	150 μ	244	24.4	94.7	5.3	
7.	Passing 150 μ	-	0	94.7	5.3	
	Wt. of sample cumulative	1000		278.8		

Table 2. Effect of RMC without fly ash.

Material	M-20	M-25	M-30	M-35	M-40	M-45
Cement, kg m ⁻³	345	390	420	470	530	565
Sand, kg m ⁻³	771	770	764	738	683	679
20 mm grit, kg m ⁻³	720	700	695	685	684	660
10 mm grit, kg m ⁻³	350	340	320	310	305	300
Admixture, kg	2	2.5	3	4	5	6
Water, kg	162	177	185	198	215	220
w/c ratio	0.47	0.45	0.44	0.42	0.40	0.38
Density	2350	2379	2387	2405	2422	2430
Slump	130	120	125	120	120	120

Table 3. Effect of RMC with fly ash.

Material	M-20	M-25	M-30	M-35	M-40	M-45
Cement, kg m ⁻³	250	290	310	350	400	425
Fly ash, kg m ⁻³	95	100	110	120	130	140
Sand, kg m ⁻³	800	790	785	753	693	690
20 mm grit, kg m ⁻³	720	700	695	685	684	660
10 mm grit, kg m ⁻³	350	340	320	310	305	300
Admixture, kg	2	2.5	3.0	4	5	6
Water, kg	162	177	185	198	215	220
w/c Ratio	0.47	0.45	0.44	0.42	0.40	0.38
Density	2387	2400	2408	2420	2432	2441
Slump	130	120	120	120	130	125

Table 4. Cube test results showing strength of RMC without fly ash.

S. No.	Grade	Weight gms	7 days		28 days	
			Load (KN)	Characteristic strength, N mm ⁻²	Load (KN)	Characteristic strength, N mm ⁻²
1.	M-20	8180	519	23.11	55	28.44
2.	M-25	8135	580	25.78	639	31.52
3.	M-30	8125	644	28.65	866	38.51
4.	M-35	8165	730	32.45	933	41.50
5.	M-40	8225	862	38.32	975	43.35
6.	M-45	8390	935	41.56	1072	47.65

Table 5. Cube test results showing strength of RMC with fly ash.

S. No.	Grade	Weight gms	7 days		28 days	
			Load (KN)	Characteristic strength, N mm ⁻²	Load (KN)	Characteristic strength, N mm ⁻²
1.	M-20	8265	485	21.56	710	31.56
2.	M-25	8120	522	23.23	812	36.11
3.	M-30	8365	602	26.78	959	42.65
4.	M-35	8450	686	30.51	1091	48.51
5.	M-40	8620	794	35.33	1229	54.65
6.	M-45	8320	893	39.71	1388	61.72

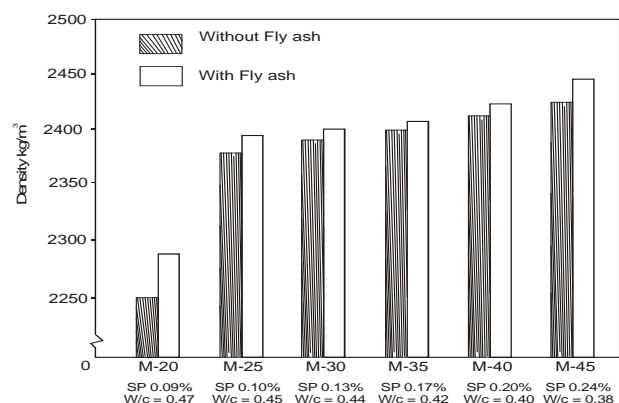
Table 6. Study of strength of ready mixed concrete M-20 in presence and absence of polymer admixture.

Admixture	3 h	8 h	12 h	24 h	7 day	28 day
0%	2.8	5.8	9.1	13.2	17.2	21.2
1%	2.7	5.1	8.9	12.7	16.5	21.0
2%	1.9	4.7	7.8	11.7	15.1	20.9
3%	1.7	3.8	6.5	10.9	14.7	20.7
4%	1.6	3.0	6.1	9.2	14.6	20.0
5%	1.4	2.7	6.2	8.6	14.2	19.9

Table 7. TG studies showing rate of hydration with different percentage of polymer admixture.

Polymer Admixture	Cement	w/c	Slump, (mm)	Characteristic strength of RMC, N mm ⁻²			
				1 day	3 days	7 days	28 days
Without polymer admixture	345	0.47	60	15.35	17.62	19.56	28.51
With polymer admixture	345	0.47	130	16.71	20.11	21.56	31.56

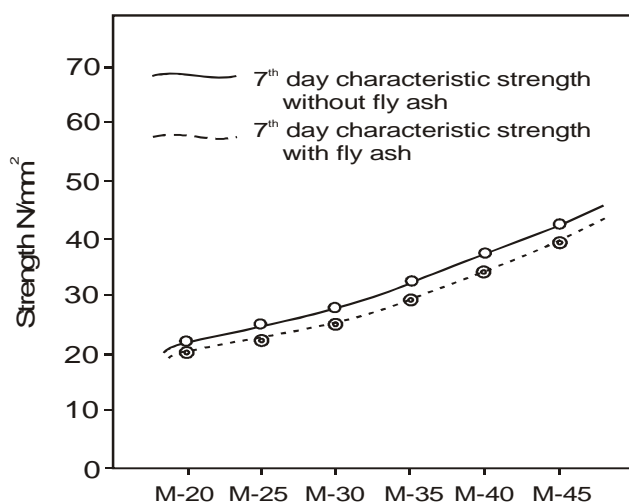
Memon²⁰ studied the effect of superplasticiser and extra water on workability and comprehensive strength of self compacting geopolymer concrete by incorporating fly ash in the design mix. They varied the superplasticiser from 3 to 7 % and extra water ranging from 10-20 % of the mass of fly ash. The test results indicated that extra water and superplasticizer are key parameters and play an important role in the development of self compacting geopolymer concrete with the increase in amount of water and superplasticizer the workability was improved.

**Figure 4.** Effect of the density of ready mix concrete in absence and presence of fly ash.

Niral Desai²¹, have developed a new age superplasticizer Fairflo S. It is high range water reducer, excellent slump retainer and it is very much cost effective. The slump obtained by them using w/c ratio 0.45 and 0.8% superplasticizer was between 105-135 mm.

It was observed that the effect of 20-30% substitution of cement by fly ash using different quantities of polymer admixture gives better density of concrete (Fig. 5 and 6), more pumpability and less strength on 7th day but higher on 28th day as analysed cube testing reports (Table 4 and 5). Krishnamoorthy²² has pointed out that fly ash should regarded more as a durability enhancer and void blocker than as a cement economizer.

The role of polymer admixture on compressive strength of ready mixed concrete on 1, 3, 7 and 28 days keeping cement, water cement ratio constant was studied.

**Figure 5.** Comparative study of 7th day characteristic strength of the specimen of RMC with and without fly ash.

It was observed that it is higher than the blank at early stages of hydration (1-3 days) but at later stage it is slightly higher (Fig. 7 and Table 6). Cube testing results on 28th day of R.M.C. with fly ash shows greater strength of design mix concrete. Hence we can conclude that strength of design mix concrete with fly ash increases drastically and there by reducing the cost of ready mix concrete and making it economical. Similar results were obtained by Ahmad *et al.*²³ they studied the effect of superplasticizer on workability and strength of concrete, superplasticizer used was Rheobuild 561 and 1100.

Mechanism

The principal role in the mechanism of water reduction and set retardation of the admixtures can be explained as follows. These substances are usually composed of long chain organic molecules that are hydrophobic (non wetting) at one end and hydrophilic at the other.

Such molecules tend to become concentrated and form a film at the interface between two immiscible phases such as water and cement and alter the physio-chemical forces acting at this interface. The poly(Sty-co-AN) get absorbed on the cement particles giving them a negative charge that

then orients the water dipoles around each particle²⁴ hence it results in (a) Reduction of the interfacial tension. (b) An increase in electro kinetic potential (c) A protective sheet of oriented water dipoles around each particle.

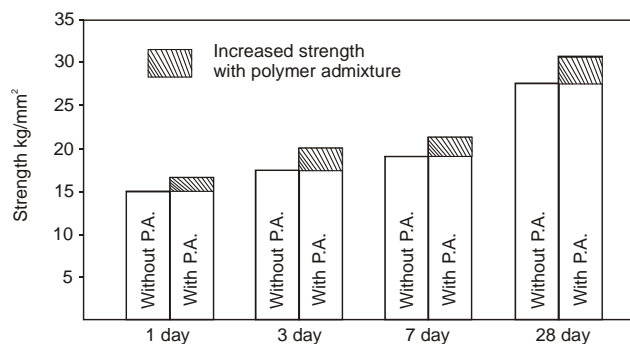


Figure 6: Comparative study of 28th day characteristic strength of the specimen of RMC with and without fly ash.

Hence we can conclude that the mobility of the fresh mix becomes greater partly because of a reduction in the inter particle forces and partly because water is freed from the restraining influence of the highly flocculated system which is now available to lubricate the mixture. Less water is therefore, required to achieve given consistency.

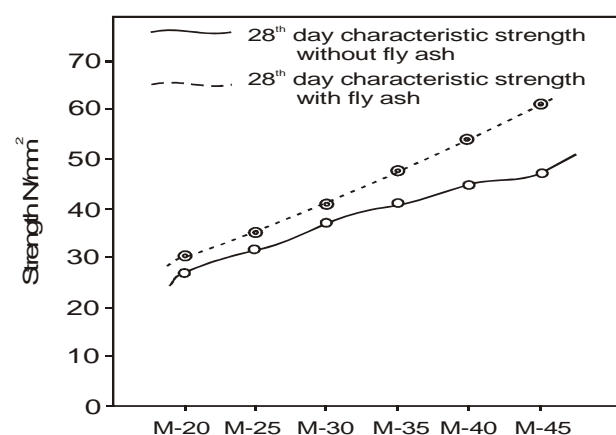
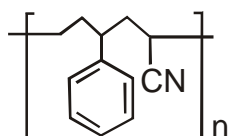


Figure 7: Comparative study of M-20 sample of RMC with and without polymer admixture

Mechanism as retarding admixture

The mechanism of set retardation^{25,26} is based on adsorption. The large admixture anions and molecules are adsorbed on the surface of the cement particles, which hinders further reactions between cement and water i.e. it retards the setting. Experiments performed showed the setting time of superplasticizer increased by 3-5 hours. In one formulation, an alkalinized sulfite liquor was mixed with ethylene oxide-propylene oxide copolymer to extend the setting time of cements by 2½ to 5 hrs.²⁷



Organic group for poly(styrene-co-acrylonitrile) as retarding admixture.

Kinetics of hydration

The hydration is a process in which Portland cement mixed with sand gravel and water and produces the synthetic rock, called concrete. As the reaction proceed, the products of the hydration process gradually bond together the individual sand and gravel particles, and other compounds of the concrete to form a solid mass.

In the anhydrous state, four main types of minerals are normally present, alite, belite, aluminate (C_3A) and a ferrite phase (C_4AF) when water is added the reaction is exothermic and generate heat. The conduction calorimetry shows the rate at which the minerals are reacting by monitoring the rate at which the heat is evolved (Fig. 8). The principal reaction^{28,29} that occur are as follows:

Stage I: On adding water some of the clinker sulphates and gypsum dissolve producing an alkaline, sulfate-rich, solution after mixing the C_3A phase react with water to form an aluminate rich gel. The gel reacts with sulfate in solution to form small rod-like crystals of ettringite.

Stage-II: Stage II is called dormant or induction period. In this stage C_3A reaction with water is strongly exothermic but does not last long typically only a few minutes, and is followed by a period of a few hours of relatively low heat evolution.

Stage-III: Stage III corresponds to main period of hydration during which time concrete strength increases. As the dominant period progresses, the paste becomes too stiff to be workable. At the end of dormant period, the alite and belite in the cement start to react, with the formation of calcium silicate and calcium hydroxide. The individual grains reacts from the surface inwards and the anhydrous particles become smaller, C_3A hydration continues as fresh crystals become accessible to water. The period of maximum heat evolution occurs typically between 10 and 20 hours after mixing and then gradually tails off. T.G. studies shows the reduction in hydration by superplasticizer upto 24 hours (Table 7 and Fig. 9). After 24 hours the rate of hydration shows only marginal difference.

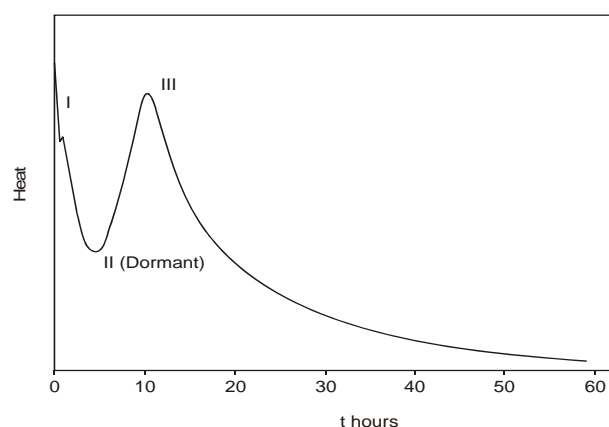


Figure 8: Conduction calorimetry showing different stages of hydration.

Mechanism of action of superplasticizers

Superplasticizers cause dispersion into smaller agglomerates of cement particles which predominate in the cement paste of the concrete mixture. Due to this dispersion effect, there

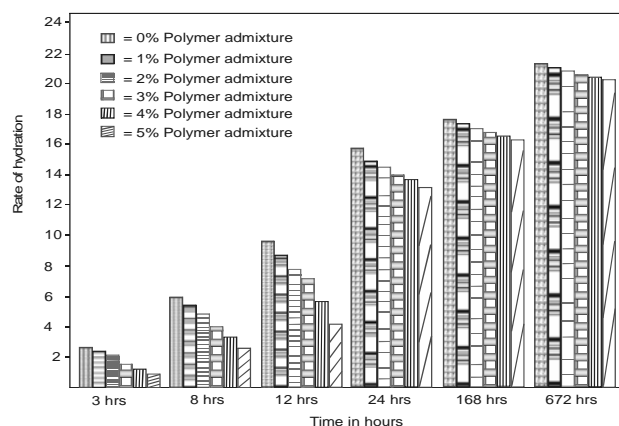


Figure 9. Studies showing rate of hydration with different percentage of polymer admixture.

is a fluidity increase in the cement mixture.³⁰ The dispersion mechanism performed by (Sty-co-AN) superplasticizers are related more to a steric hindrance effect (product by the presence of graft chain) rather than to the presence of negatively charged anionic groups.³¹ In other words we can say that, the graft chains of the polymer molecules on the cement would hinder by themselves from flocculating into large and granular agglomerates of cement particles (Fig.10).

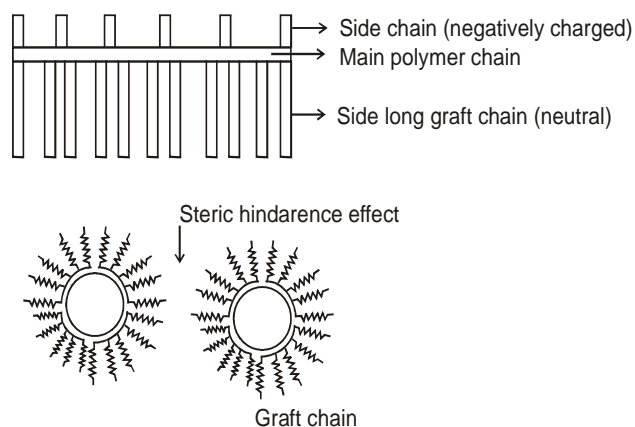


Figure 10. Schematic picture of (Sty-co-AN) copolymer and its steric hindrance effect on dispersion of cement particles.

This mechanism would be in the cement with the relating smaller number of negative anionic groups (COO^-) in the acrylic polymers products in comparison with those present as SO_3^- in the SEF and SNF polymers.³²

Conclusion

Superplasticizers are able to enhance the placement characteristics of concrete mixtures by increasing the workability level at a given w/c. concrete with higher characteristic strength and better durability was obtained with fly ash and admixture. Thereby replacing cement and reducing the cost of concrete and making it environment depends the time setting as the RMC is to be transported from the plant to the site so it is very useful.

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References

- Matyjaszewski, K., Tsarevsky, N. V., *Chem. Rev.*, **2007**, 107(6), 2270.
- Bugnon, L., Mortan, C. J., Novak, P., Velter, J., Nesvadba, P., *Chem. Mater.*, **2007**, 19(11), 2910.
- Mishra, G., Srivastava, A. K., *Polym. Bull.*, **2007**, 58(2), 351.
- Matyjaszewski, K., Gao, H., *Macromolecules*, **2006**, 39(15), 4960.
- Prajapati, K., Varshney, A. *J. Polym. Res.*, **2006**, 13(2), 97..
- Wittig, G., Felletschin, C. *Ann.* **1944**, 555, 133.
- Vasishtha, R., Srivastava, A. K., *J. Polym. Sci. Part-A: Polym. Chem.*, **1990**, 28, 1297.
- Tiwari, R. S., Awasthi, A., Kumar, M., Srivastava, A. K., *J. Polym. Chem. Ed.* **1984**, 22, 1875
- Saini, S. Srivastava, A. K., *J. Macromol. Sci. Chem. Part-A:* **1985**, 22(1), 43
- Phatak, T. C., Agarwal, S. K., Masood, I., 1992, 25, 355.
- Kantro, D. L., *Cem. Concr. Aggregates*, **1980**, 2, 95.
- Ramachandran, V.S. *Am. Concr. Inst.*, **1981**, SP-68, 393
- Srivastava, S. Varshney, A., *Design. Monomers Polym.*, **2005**, 8(1), 49 (2005).
- Overberger C. G. and Yamamoto, N. J., *J. Polym. Sci.*, **1966**, 4, 3101.
- Vogel, A. I., *A Text Book of Practical Organic Chemistry*, 5th Edn., Longman, London, **1994**.
- Tewari, R. S. Chaturvedi, S. C. *Synthesis*, **1979**, 616.
- Sylverstein M. R. and Webser, X. F. *Spectrometric Identification of Organic Compounds*, 6th edn. Wiley, New York, NY, **1965**.
- Dyer, J. R. *Application of Absorption of Organic Compounds*, 10th edn. Prentice-Hall, Englewood, New York, NY, **1998**.
- Hinislioglu, S. Bayrak, O. U., *Civil Eng. Environ. System*, **2004**, 21(2), 79.
- Memon, F. A. Nuruddin, M. F. Demie S. and Shafiq, N., *Res. J. Appl. Sci. Eng. Techn.*, **2012**, 45(2), 407.
- Desai, N., *Civil Eng. C. R.*, **2001**, 6, 55.
- Krishnamoorthy, S., *ICI Journal*, **2002**(1-3), 10
- Ahmad, S. Nawaz, M. Elahi, A., *30th Conf. World Concrete Struct.*, 23-24 August, Singapore, **2005**.
- Ramachandran, V. S. *Mater. Struct. Res. Testing*, **1971**, 4, No. 19.
- Diamond, S., *J. Am. Ceram. Soc.*, **1971**, 54(6), 273.
- Diamond, S., *J. Am. Ceram. Soc.*, **1972**, 55(4), 177.
- Stanik, V., Oltus, E., Vajner, J., Danis, L., *CS 254161 B1*, **1988**
- Ramachandran, V. S., Seeley, R. C., Polomark, G. M., *Mater. Struct.*, **1984**, 17, 285.

²⁹Singh, N. B., Ohja, P., *J. Mater. Sci.*, **1981**, 16, 2675.

³²Basete, F. Biagini, S. Ferrari, G. Collepardi, M., *Cement Concrete Res.*, **1987**, 805.

³⁰Collepardi, M. and Ramachandran, V. S., "Effect of Admixtures"
Proc. 9th Int. Congr. Chem. Cement, New Delhi, India, **1992**,
1, Theme IIID, 529-570.

³¹Collepardi, M., Coppola, T., Cerulli, T., Ferrari, G., Pistolesi, C.,
Zafforoni, P., "Zero slump loss superplasticized concrete",
Proc. Congr. "Our World in Concrete and Structures",
Singapore, **1993**, 73-80.

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