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Development of new age cost effective superplasticizer for ready mixed concrete: A study on physico-chemical and mechanical property

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ABSTRACT

A superplasticizer, methylmeth acrylate has been prepared by triphenyl stibonium 1,2,3,4-tetraphenyl cyclopentadienylide as radical initiator by free radical polymerization in dioxane at 60 ± 1 ^oC for 1 hour, under atmosphere of nitrogen. Polymethyl methacrylate as a superplasticizer and fly ash as a mineral admixture are used in ready mixed concrete and properties of RMC has been studied. The superplasticizer extents the setting time of cement, without loss in properties of concrete. The concrete is workable, plastic and flowable. 20-30% substitution of cement by fly ash, increases the strength and reduces the cost of concrete, making it environment friendly. The bulk density is maintained between 2345-2446 kg/m^3. The w/c ratio is between 0.38 to 0.49. The slump is in between 110-130.

Key words: Triphenyl stibonium 1,2,3,4-tetraphenylcyclo- pentadienylide, Poly(methylmeth acrylate), Ready-Mixed Concrete (RMC), w/c ratio, Fly ash.

INTRODUCTION

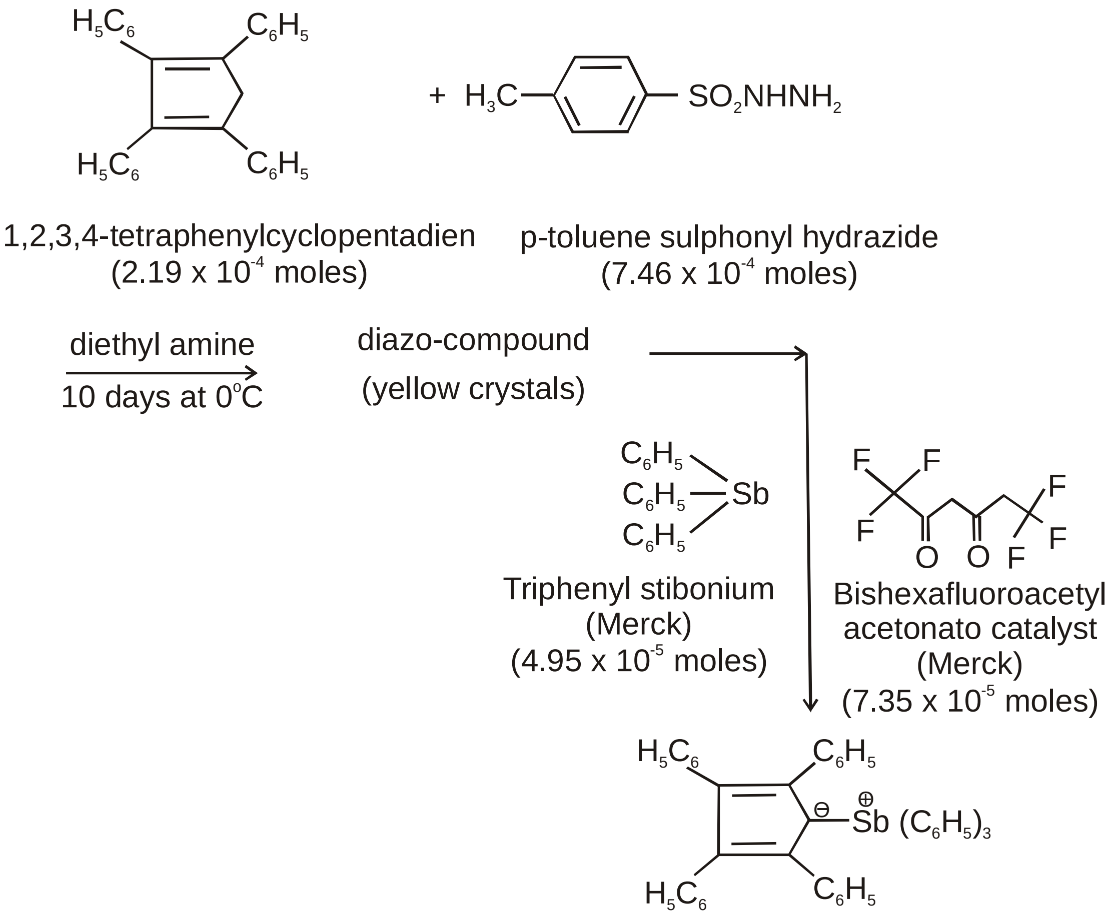
Ready mix concrete is generally transported to different construction sites and delivered with the help of revolving type transits mixers. These sites are located at long distances and the concrete delivered has to be workable and flowable. Recent developments in admixture technology have produced superplasticizer which can extend the setting time of concrete beyond the typical retardation time achieved with conventional retarding mixtures.

For labour saving building techniques and in developing efficient and economical working methods to reduce cement consumption without increasing cost of construction and imparting any loss to the properties of concrete[1,2] Thus, plasticisers of different properties as an ingredient in concrete mix have to be developed. These superplasticizers when used, within limits, impart extreme workability without adversely affecting the hydration and cohesion characteristic of cement in concrete. The aim of present study is to study the application of ylide[3-6] initiated polymerization of methylmethacrylate, to get polymethylmethacrylate as superplasticizer in the ready mix concrete.

MATERIALS AND METHODS

Methyl methacrylate was purified[7-8] with alkali and distilled water followed by vacuum distillation. Triphenyl stibonium 1,2,3,4-tetraphenylcyclopentadienylide was prepared by the method given in literature[9]. Triphenyl stibonium (Merck) and dioxane was used without further purification.

Synthesis may be summarized as follows:



Triphenyl stibonium 1,2,3,4-tetraphenylcyclopentadienylide

Polymerization procedure-

Polymerization[10] was carried out in 1-4-dioxane at 60 ± 1°C for 1 hour under the atmosphere of nitrogen. The polymer was precipitated with methanol.

2.1 Materials and specimens preparation

2.1.1 Cement - (OPC -43 grade)

Properties

Specific gravity (G_c)	:	3.21
Normal consistency	:	31%
Initial setting time	:	125 minutes
Final setting time	:	380 minutes
Compressive strength	:	55.12 N/mm^2
Fineness	:	78.10

2.1.2 Fly ash - from Thermal Power Station, Kanpur

Specific gravity (G_f)	:	2.1
Fineness (Blaine's)	:	382 m^2/kg
Lime reactivity	:	5.3 N/mm^2
Loss on ignition	:	3.2%

2.1.3 Fine Aggregate -River sand

Specific gravity (G_{fa})	:	2.52
Unit mass(W_{fa})	:	1425 kg/m^3
Fineness modulus	:	2.80 By Sieve Analysis
Water absorption	:	0.32%

2.1.4 Coarse aggregate - Grit	:	20 mm	10 mm
Specific gravity (G_{ca})	:	2.73	2.64
Unit mass (W_{ca})	:	1375 kg/m^3	1360
Fineness modulus	:	6.91	

2.1.5 Water - Tap water

2.1.6. Polymer Admixture :
Polymethyl methacrylate prepared by triphenyl stibonium 1,2,3,4-tetraphenylcyclopentadieneylide.

Experimental:
To evaluate the compressive strength and workability, cube and slump tests were carried out.

Cube Test:- The concrete was prepared using different composition of materials. The concrete moulds/cubes were oiled (Lubricated) to prevent the concrete from sticking to them and for easy demoulding, the size of the cube is (150 x 150 x 150 mm). The concrete was poured into the cube and placed on the compacting machine, which when switched on vibrated the cubes, making the concrete to lose the trapped air in the mix. This was allowed for 2 minutes before the switching off. The excess concrete was cleared from the surface with the aid of the travel and the cubes were marked for easy identification to prevent mix-up. After casting of the cubes, they were allowed to set and harden before de-moulding. The cubes were then covered with polythene sheets to prevent excess evaporation.

After de-moulding the cubes were placed in a curing tank for specified days i.e. (1-28 days). At each specified period of days, the cubes were crushed to determine the compressive strength of the concretes. Test cubes were placed for the load to be applied to the opposite side of the cube as casted. Also the axes of the cubes were carefully aligned in the centre of the plates.

Slump Test:- A means of evaluating workability of concrete is the slump test. Slump is the distance through which a cone full of concrete drops when the cone is lifted. The apparatus used for the slump test are tamping rod, a cone, measuring rule, scoop, straight edge and a clean platform. The mould for the slump test is a frustum or cone whose inside was moistened. It was placed on a smooth surface with the smaller opening at the top, and filled with concrete in three layers. The mould was firmly held against its base during the test, this was facilitated by handles or foot-rest brazed to the mould. Immediately after filling, the cone was slowly lifted and the unsupported concrete then slumped. The decrease in the height of the concrete was then measured. Concrete which incidentally dropped immediately around the base of the cone was cleaned off.

RESULTS AND DISCUSSION

The homopolymer, Methyl meth acrylate was prepared initiated by Stibonium ylide. The properties of homo polymer is studied which are as follows:

Properties of polymer admixture

Polymer	Colour	Activation energy by Arrhenius equation	Polydispersity index by GPC $\bar{M}_w / \bar{M}_n$
(PMMA)	yellowish white	35 KJ mol–1	13

Characterization of the polymer
(i) Fourier Transform Infrared Spectroscopy
The FTIR spectrum[11-12] of PMMA (Fig.1) shows the following bands:
2994 cm^{-1} – aliphatic C-H stretching
1734 cm^{-1} – >C=O stretching in acrylate group
1151-1276 cm^{-1} – ester (C-O-C) stretching

The presence of band at 1061 cm^{-1} indicates the syndiotactic nature of the polymer.

(ii) ^{1}H Nuclear Magnetic Spectroscopy
The ^{1}HNMR spectrum of PMMA (Fig.2) shows the following peaks:
0.85 δ ppm – due to $–CH_3$ group
1.7 δ ppm – due to $–CH_2$ group
3.9 δ ppm – due to $–OCH_3$ group

(iii) ^{13}C Nuclear Magnetic Spectroscopy

The ^{13}CNMR spectrum of PMMA (Fig.3) shows the following peaks:
12 δ ppm – $-CH_3$
23 δ ppm – $-CH_2$
33 δ ppm – >C –
51 δ ppm – $-OCH_3$
170 δ ppm – >C=O

Table-I : Effect of RMC in absence of fly ash

Material	M-20	M-25	M-30	M-35	M-40	M-45
Cement (kg/m^3)	330	375	400	475	510	570
Sand (kg/m^3)	771	753	747	691	690	688
20 mm grit (kg/m^3)	540	525	520	510	493	460
10 mm grit (kg/m^3)	540	525	520	510	493	460
Admixture (kg)	2	3	3.5	4.5	5	6
Water (kg)	162	172	180	2.00	205	220
W/c Ratio	0.49	0.46	0.45	0.42	0.40	0.38
Density (kg/m^3)	2345	2353	2370	2390	2396	2404
Slump	120	120	130	110	120	115

Table-II : Effect of RMC in the presence of fly ash

Material	M-20	M-25	M-30	M-35	M-40	M-45
Cement (kg/m^3)	250	280	300	335	385	425
Fly ash (kg/m^3)	80	95	100	120	125	145
Sand (kg/m^3)	781	768	761	701	700	690
20 mm grit (kg/m^3)	540	525	520	510	498	480
10 mm grit (kg/m^3)	540	525	520	510	498	480
Admixture (kg)	2	3	3.5	4	5	6
Water (kg)	162	172	180	200	205	220
W/c Ratio	0.49	0.46	0.45	0.42	0.40	0.38
Density	2355	2368	2384	2400	2416	2446
Slump	120	130	115	125	125	120

Table-III : 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	8265	397	17.66	498	22.15
2.	M-25	8130	425	18.91	679	30.21
3.	M-30	8125	467	20.76	776	34.51
4.	M-35	8096	551	24.52	866	38.52
5.	M-40	8300	600	26.71	914	40.65
6.	M-45	8126	662	29.45	1080	48.00

Table-IV : 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	364	16.22	640	28.45
2.	M-25	8102	396	17.61	801	35.62
3.	M-30	8056	443	19.71	869	38.65
4.	M-35	8092	497	22.11	978	43.51
5.	M-40	8215	547	24.32	1051	46.72
6.	M-45	8116	596	26.52	1186	52.75

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

Polymer Admixture	Cement	W/c	Slump (mm)	Strength N/mm^2			
				1 day	3 days	7 days	28 days
Without polymer admixture	330	0.49	75	13.22	15.72	16.12	20.75
With polymer admixture	330	0.49	120	14.10	16.72	17.66	22.15

The extra peaks may be accounted to the small amount of isotactic and atactic PMMA formed along with syndiotactic PMMA during polymerization process.

Different grades of concrete, M-20, M-25, M-30, M-35, M-40 and M-45 (Table I and II) were used to study the effect of fly ash and superplasticizer viz. polymethyl methacrylate on the strength of cement to get low cost and environment friendly concrete (Fig.4). Bulk density was maintained between 2345 to 2416 as per specification. To get pumpable concrete water cement ratio was kept between 0.38 to 0.49 with slump between 110 to 130.

Table-VI : T.G. studies showing rate of hydration with different percentage of polymer admixture

Admixture	3 h	8 h	12 h	24 h	7 day	28 day
0%	2.7	5.40	9.7	15.1	19.6	21.5
1%	2.4	5.1	8.1	14.9	18.5	21.0
2%	2.1	4.8	7.3	13.7	17.2	20.5
3%	1.9	3.7	6.9	13.1	16.9	20.0
4%	1.7	3.1	5.4	12.4	16.5	19.8
5%	1.5	2.5	4.1	11.0	16.0	19.7

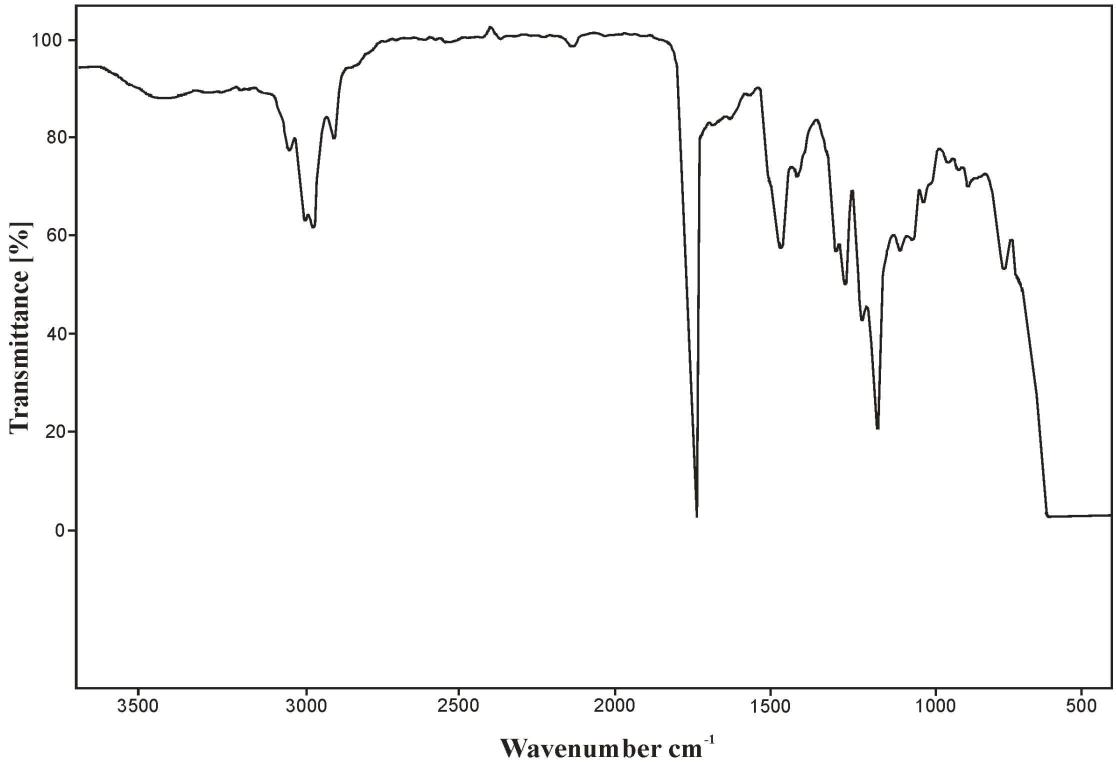


Fig. 1: FTIR spectrum of PMMA

It was observed that when 20-30% substitution of cement by fly ash, using polymer admixture, polymethyl methacrylate gives better density of RMC, more pumpablity and less strength on 7th day and more strength on 28th day (Table III & IV) Fig.5,6 as tested by cube test reports. Low strength[13] on 7th day is due to the pozzolanic reaction between fly ash and cement, it lags behind cement hydration. Krishnamoorthy[14] has pointed out that fly ash should be regarded, more as a durability enhancer and void blocker than as a cement economizer. Memon[15], 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 superplasticisor 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.

The role of polymer admixture on compressive strength of RMC on 1st, 3rd, 7th & 28th day was studied (Table V & Fig.7). It was observed that the strength increased drastically on addition of polymer admixture in RMC. T.G. studies shows the reduction in hydration by polymer admixture upto 24 hours (Table VI & Fig.8). After 24 hours the rate of hydration shows only marginal difference.

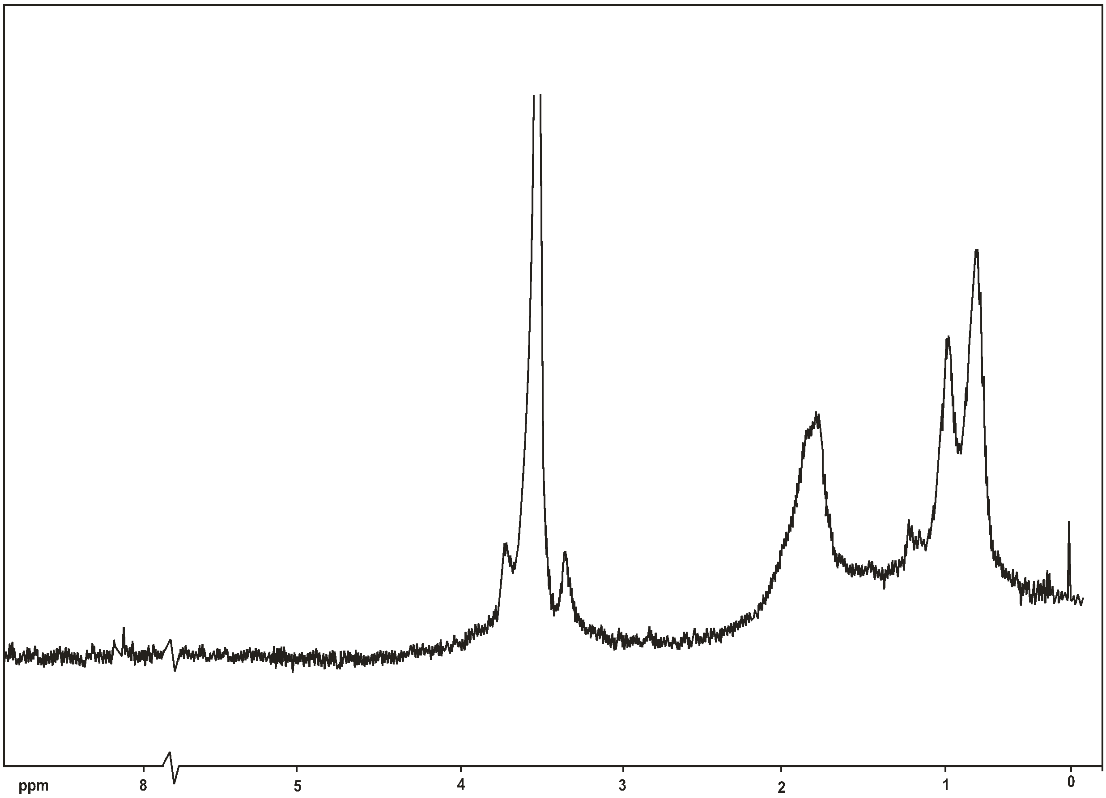


Fig. 2: ^{1}HNMR spectrum of PMMA

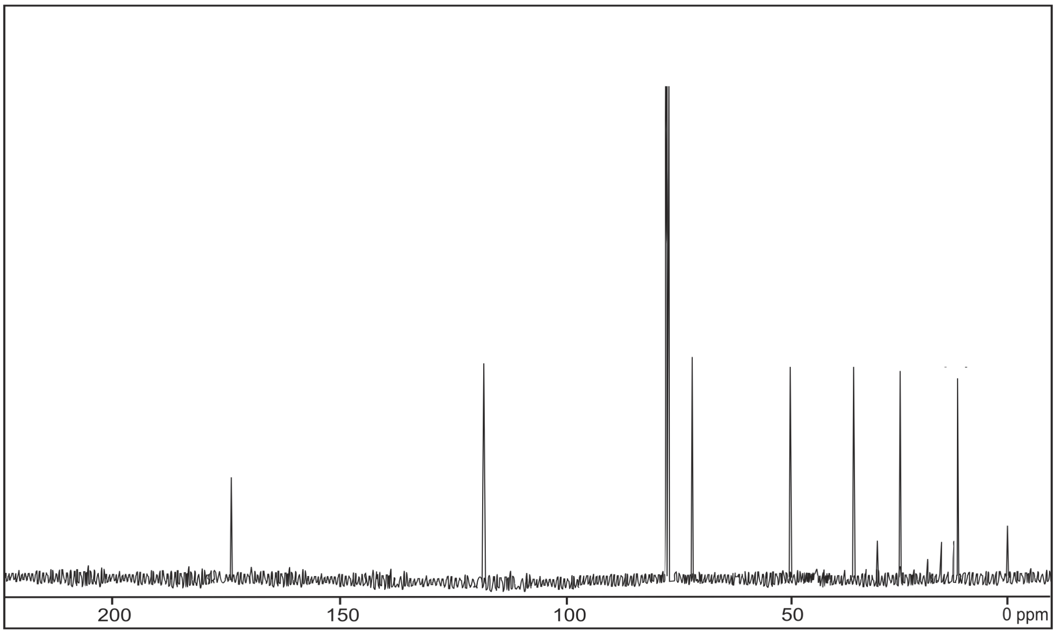


Fig. 3 : ^{13}C-NMR spectrum of PMMA

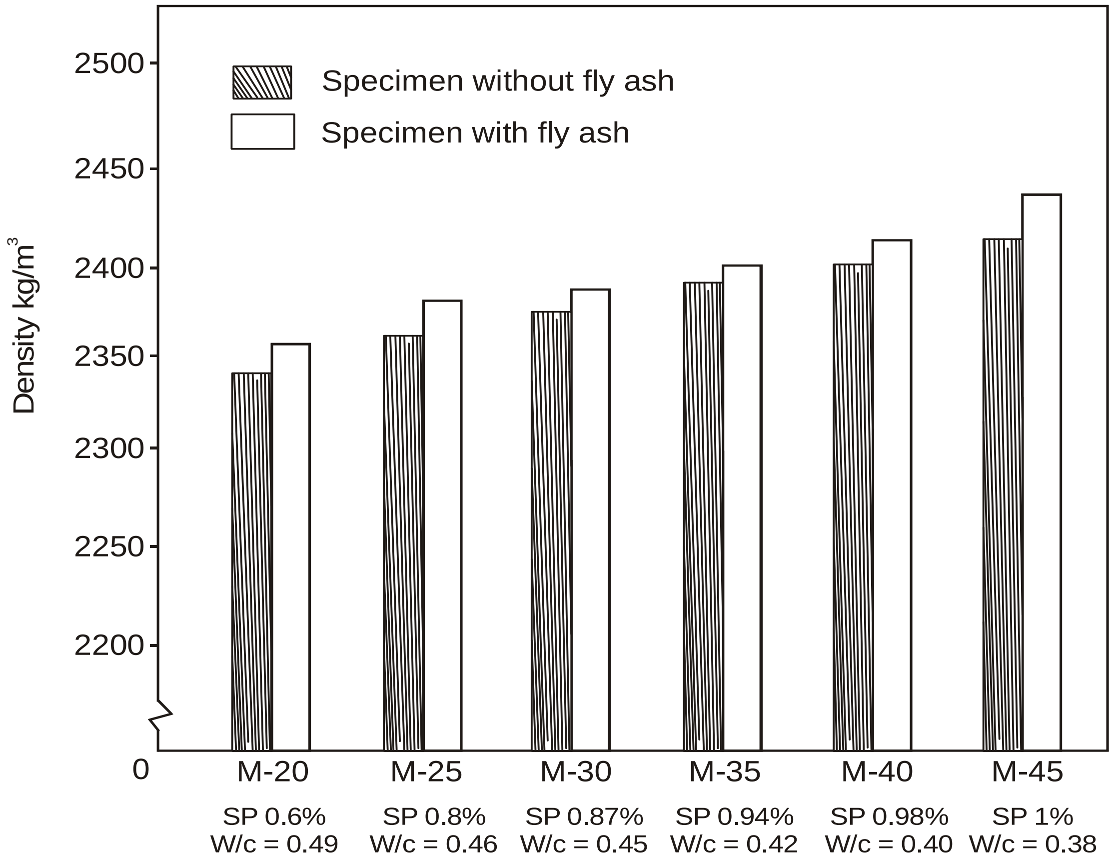


Fig. 4: Effect of density of the ready mix concrete in presence and absence of fly ash

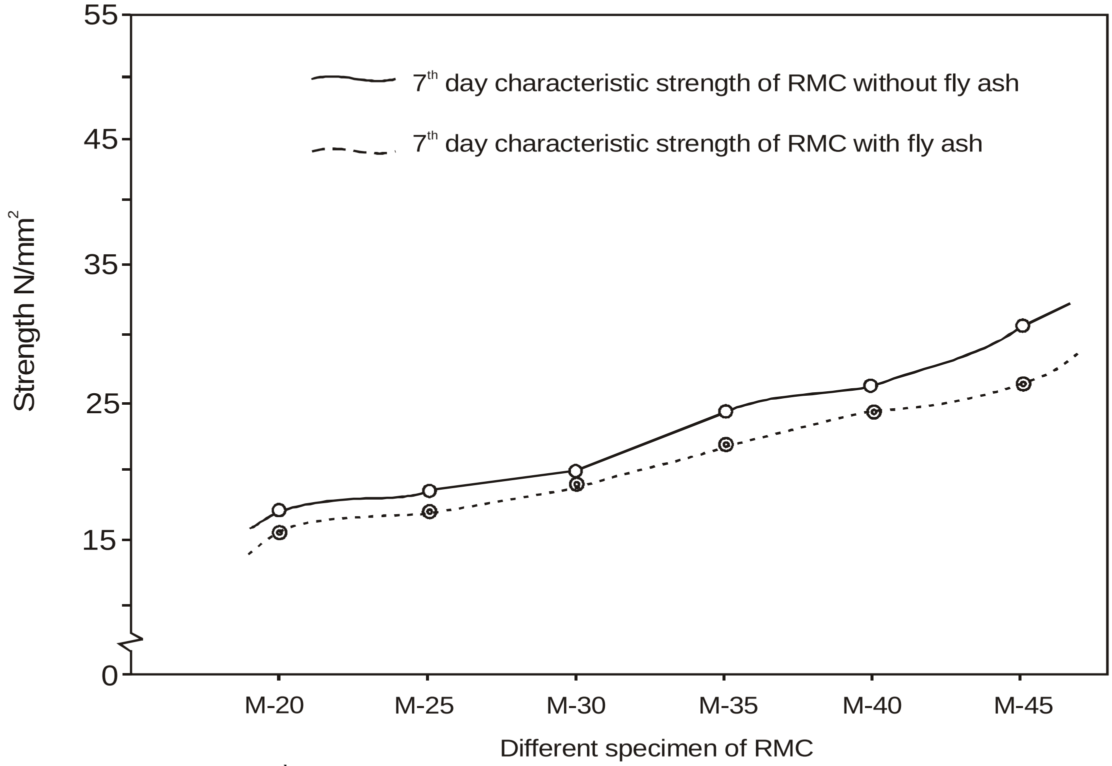


Fig. 5: Comparative study of 7th day characteristic strength of the specimen of ready mix concrete with and without fly ash

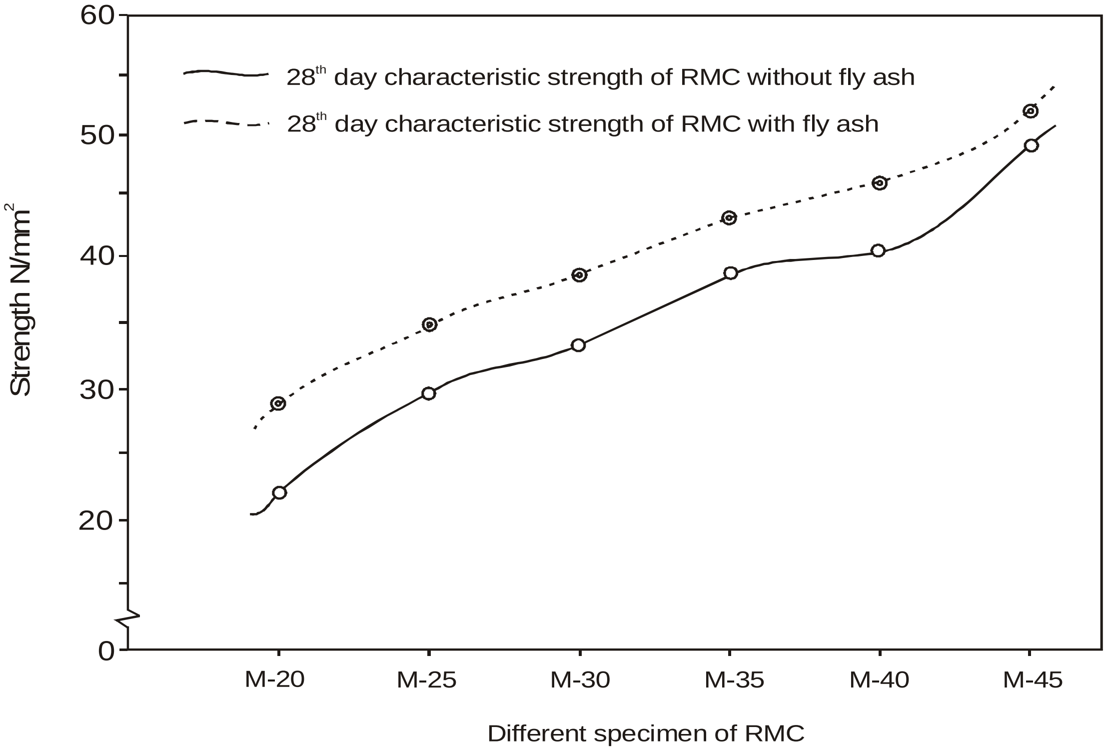


Fig. 6: Comparative study of 28th day characteristic strength of the specimen of ready mix concrete with and without fly ash

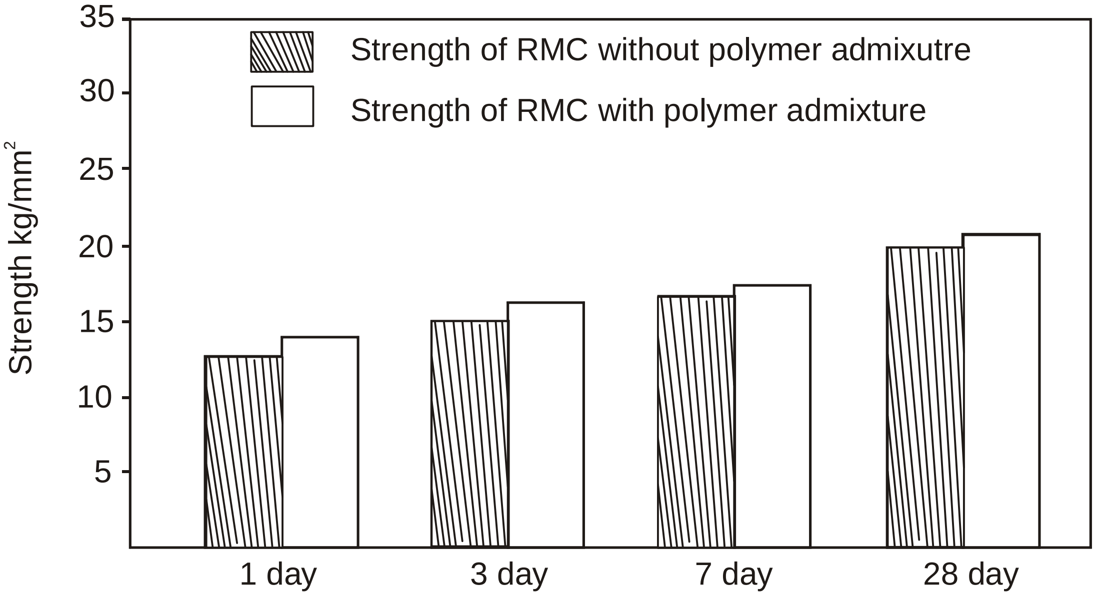


Fig. 7: Strength of M-20 sample of ready mix concrete on different days

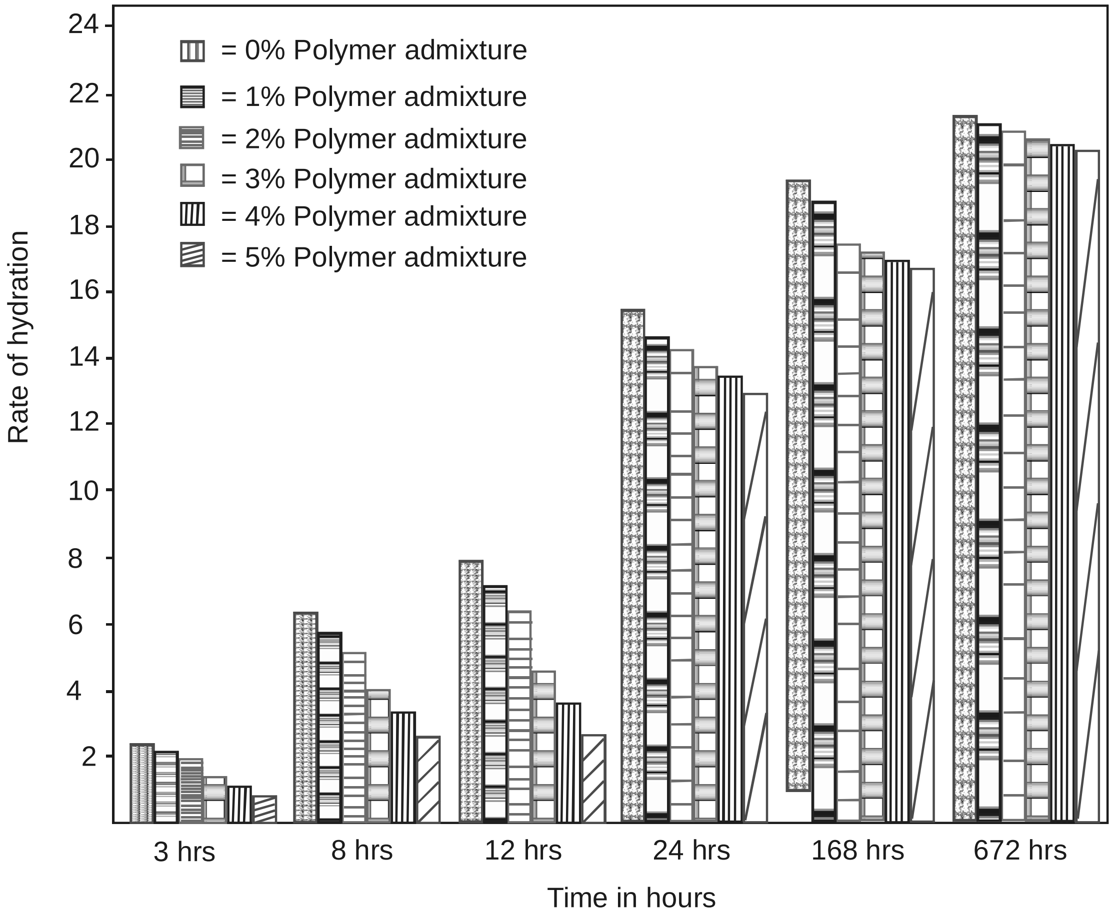


Fig.8: Studies showing rate of hydration with different percentage of polymer admixture

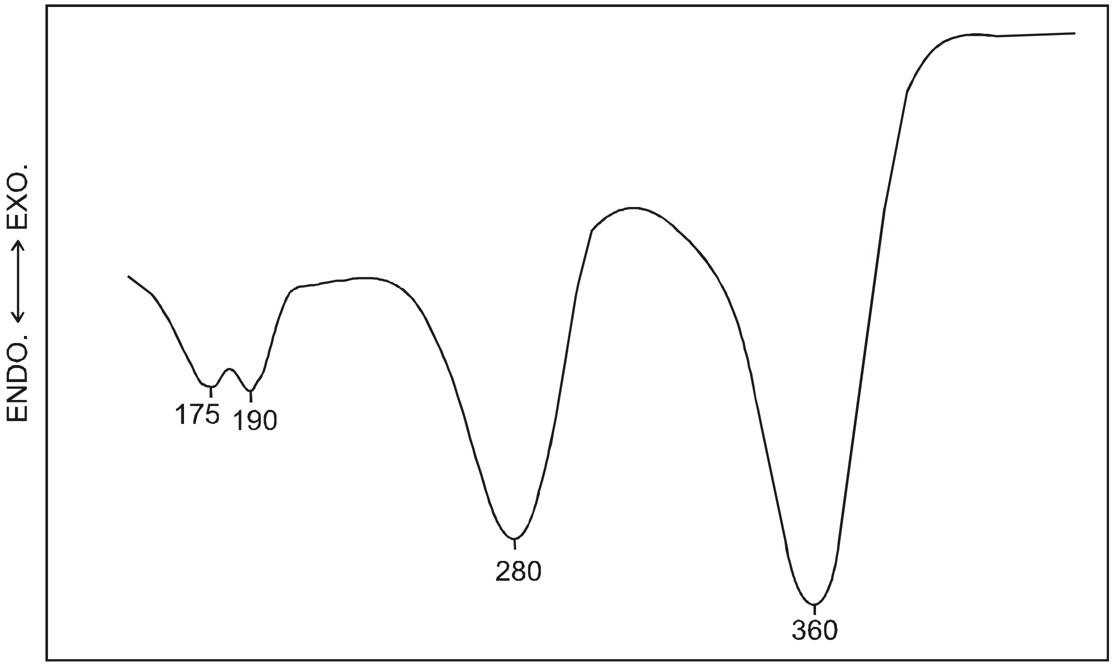


Fig. 9: Differential scanning calorimeter (DSC) thermogram of Bulk PMMA

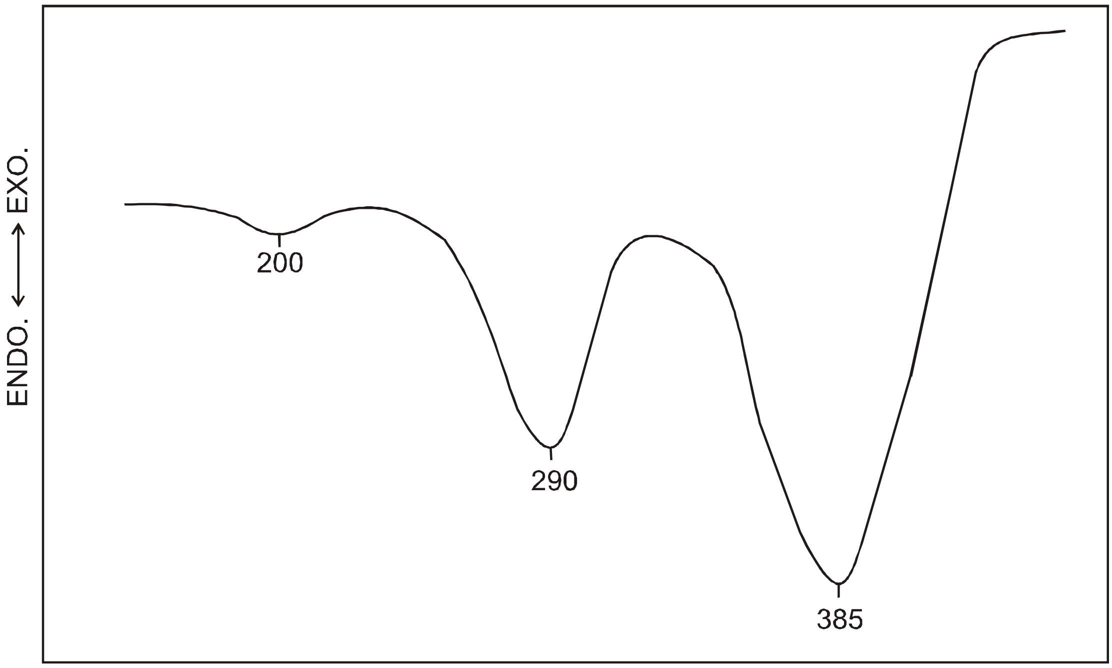
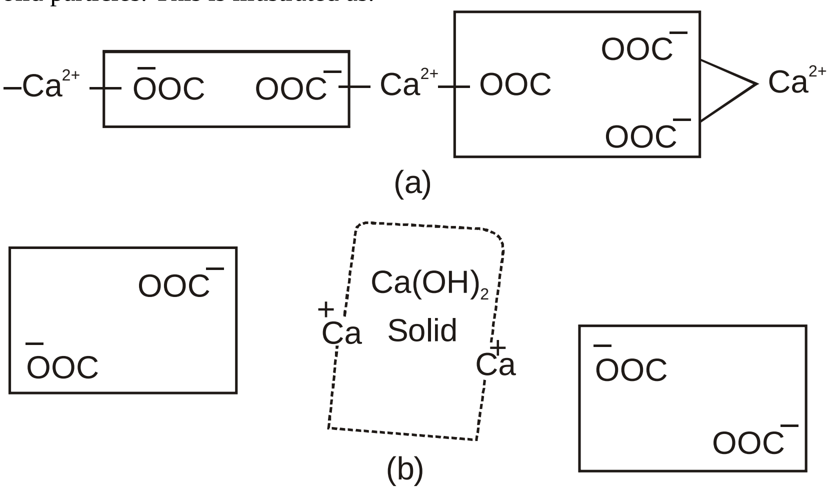


Fig. 10: Differential scanning calorimeter (DSC) thermogram of PMMA-CaO–SiO$_2$ system

Interaction between Ca(OH)$_2$ and methyl methacrylate polymer dispersion.

During hydration of cement, Ca(OH)$_2$ is produced immediately after the addition of water to portland cement. Experiments were performed to study the interaction between Ca(OH)$_2$ and polymer. It was noticed that 5 g of Ca(OH)$_2$ powder has the capacity to digest 1 litre of dispersion containing 1 g of the solid polymer leaving the supernatant liquid transparent. When this limit exceeds the liquid becomes turbid again. The polymer dispersion used is composed of soft microparticles and has film forming ability. It was observed that, when small amount of Ca(OH)$_2$ is added to the polymer, film becomes translucent and gelation tendency was observed. When further Ca(OH)$_2$ is added, the film formation gradually reduces and finally no film is formed[16]. This no film formation can be attributed due to ionic bonding between calcium and carboxylate ions of the polymer, causing cross links and thereby inhibiting film formation.

Similarly we treated polymer dispersion with sodium hydroxide, no gelation tendency was observed and polymer formed the film. This showed that there is interaction between Ca^{2+} ions and the carboxylate groups of polymer dispersion and not the destabilization of polymer due to the alkalinity of the solution[17]. With solid calcium hydroxide, the carboxylate group of MMA particles interact with the free valencies of the calcium atoms on the surface of Ca(OH)$_2$ solid particles. This is illustrated as.

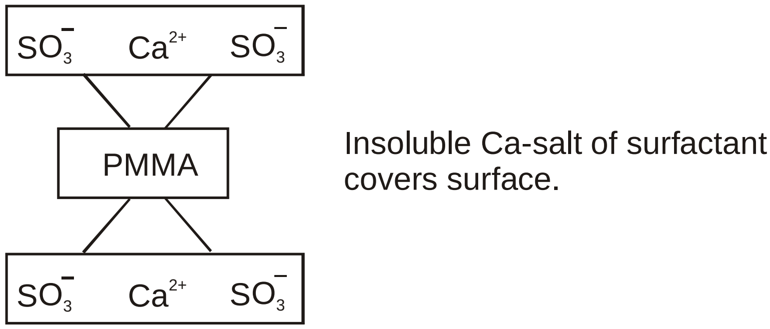


Schematic illustration of cross-linking of polymer particles by

(a) divalent Ca ions (b) Ca(OH)$_2$

Carboxylate groups are present all over the surface of the polymer particles, another crystal may be bonded to the particles which then act as a glue between solid $Ca(OH)_2$ particles as long as there are free bonding sites available on the $Ca(OH)_2$. Crystals diminishing peak of $Ca(OH)_2$ was observed by X-ray diffraction analysis[18], showing the complex not to be highly crystalline and confirming that the polymer has considerable influence on the cyrstallization of calcium hydroxide.

A decrease in the free calcium ion concentration was noticed[19] when tensides and a number of polymer dispersions made in the lab were mixed with $Ca(OH)_2$ saturated solution. Thus showing that, there is an interaction between the divalent Ca^{2+} ions and the anionic tensides.



Schematic diagram showing the interaction of Ca^{2+} with polymer dispersion containing tensides (SO_3 gp)

Differential scanning calorimeter

DSC of bulk PMMA and PMMA-CaO.SiO_2 was performed (Fig.9and 10). It was observed that bulk PMMA showed a peak which was attributed to the $-CH_2$ group. The second peak was attributed to the decomposition of a single $-CH_2-$ linkage[20-22]. Indicate that an apparent interaction between the $-CH_2-$ group of the PMMA and the calcium oxide of the calcium silicate system may take place.

CONCLUSION

Advantages of RMC for the supply of assured quality of concrete and services offered are known. Now the time has come to design and produce concrete mixes for delivery to project within few hours after the cement and water are mixed. Superplasticizer, polymethyl methacrylate extends the setting time of cement, without loss in the properties of the concrete. 20-30% substitution of cement by fly ash increased the density and strength of concrete. The concrete obtained was economical, environment friendly, pumpable and workable.

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REFERENCES

[1] Ambuja Technical Lecture Series "Concrete Admixture- Plasticizer, July **(1998).**

[2] Ambuja Cement Technical Lecture Series, "Ordinary Portland Cement (Physical and Chemical Properties), pp 1-6 January (**1999**).

[3] K. Prajapati, A. Varshney, *J. of Polym. Sci. A. Polym. Chem***. 2005**,43, 6524.

[4] K. Prajapati, A. Varshney, N.Jain, *Advances in Applied Science Research* ,**2011**,2(5)19.

[5] K. Prajapati, A. Varshney,N.Jain, *Der Chemica Sinica*,**2012**,3(1),10.

[6] A. Varshney, R. M. Mathur, K. Prajapati, *Advances in Applied Science Research*,**2012**, 3(5),2553.

[7] C.G. Overberger and N. J. Yamamoto, *J. Polym. Sci.*,***1966* 4**, 3101.

[8] A. I. Vogel, A Text Book of Practical Organic Chemistry, 5th Edn., Longman, London **(1994).**

[9] D. Lloyd, C. Glidewell, S. Metcaife, *Synthesis*, **1988**,319 .

[10] S. Saini, R. Vasishtha, P. Shukla, A. K. Srivastava, *Macromolecules*, **1989,22**, 1025 .

[11] S. Chandra, F. Flodin, L. Berntsson, 3rd Int. Cong. on Polymers in Concrete Koriyama, Japan, **1985**,125.

[12] M.R. Sylverstein and X. F. Webser, Spectromertic Identification of Organic Compounds, 6th edn. Wiley, New York, NY, 1965.
[13] J.R. Dyer, Application of Absorption of Organic Compounds, 10th edn. Prenctice-Hall, Englewood, New York, NY ,1998.
[14] S. Hinislioglu, O.U. Bayrak, *Civil Engg. and Environment System*, **2004**,1(2), 79.
[15] S. Krishnamoorthy, *ICI Journal*, Jan-Mar. p-10 **(2002).**
[16] F. A. Memon, M. F. Nuruddin, S. Demie and N. Shafiq, *Res. Journal of Applied Science Engg. and Tech*.,**2012** 45(2), 407.
[17] S. Chandra, L. Berntsson, P. Flodin, *Cem. Conc. Res*.**1981,** 11(1).
[18] S. Chandra, M. Addidsson, *Nord. Conc. Res*.**1982**,1 .
[19] S. Chandra, Report 83:5, Chalmers-Univ. of Technology **1983.**
[20] T. Sugama, L. E. Kukacka, *Cem. Conc. Res.* **1979**,9(1), 69.
[21] T. Sugama, L. E. Kukacka, *Cem. Conc. Res*.**1979,** 9(4), 461
[22] Sugama, L. E. Kukacka, *Cem. Conc. Res.* **1980**,10(2), 469.