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Physicochemical Studies on Single and Combined Effects of Latex and Superplasticiser on Portland Cement Mortar

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Abstract

This article reports on the compressive strength, rate of hydration at 3, 7, 28 and 90 days; by thermogravimetry (TG), differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), mercury intrusion porosimetry (MIP) of unmodified, latex-modified, superplasticiser-modified, and superplasticised latex-modified mortars. Two commercial superplasticisers and three copolymer type latexes (selected from an earlier compatibility study) have been used with a uniform flow range. It has been observed that addition of superplasticiser in three latexes had increased both the rate of hydration and the compressive strength up to 28 days. Formation of a comparatively lower quantity of $Ca(OH)_2$ *was observed at a higher latex content. The addition of superplasticiser in a latex-modified mortar further reduced the quantity of* $Ca(OH)_2$*. This was confirmed by both XRD and DSC observations. In all modified samples the peak temperature for* $Ca(OH)_2$ *decomposition was at least equal to or higher than the unmodified one. Appearance of two maxima for exotherm of latex in superplasticised latex-modified mortar was indicative of a possible change in emulsion character in the presence superplasticiser. MIP revealed that addition of latex caused the pore size distribution to become more even in character. The presence of superplasticiser in latex-modified mortar reduced the total pore volume significantly. © 1996 Published by Elsevier Science Limited.*

Keywords: cement, mortar, latex, superplasticiser, combined effect, X-ray diffraction, thermal analysis, mercury intrusion porosimetry, degree of hydration.

INTRODUCTION

A large amount of technical literature is available on the behaviour of portland cement mortar modified with either latex emulsions or chemical admixtures such as water reducing agents, superplasticisers etc. There are, however, limited data available on the combined effect of latex and superplasticiser on the behaviour of portland cement mortar.[1–3] In the course of their continuing research on modifications of mortar by polymeric latexes, the present authors have studied consistency, setting time of cement paste, air content, bleeding, water reduction capacity, flow-time relationship of mortar modified with four types of latexes and five types of superplasticisers. Out of these, three latexes and two superplasticisers were found to have satisfactory performance and compatibility when applied simultaneously in mortar.[17] Compressive strength, deformations, and water absorptions were determined using these compatible sets of superplasticisers and latex and are reported elsewhere.[18]

In order to understand the true physicochemical behaviour, it is necessary to study the influence of the binary admixture system (latex and superplasticiser) on the rate of hydration, phase formation, thermal stability, pore distribution and microstructure of the composite system. Early work[4–8] in this area has been concerned with either pure compounds of hydraulic cements or portland cement itself. Some recent published results are available[9,10] on mortar modified with latex only. However, systematic studies to evaluate the effect of a binary admixture system on the physicochemical and microstructural properties of mortar are limited.

This article is intended to highlight the compressive strength, rate of hydration (of various ages), thermogravimetry (TG), differential scanning calorimetry (DSC), powder X-ray diffraction (XRD), mercury intrusion porosimetry (MIP) of unmodified, latex-modified, superplasticiser-modified, and superplasticised latex-modified mortars. Specifically, two commercial superplasticisers and three latexes selected from an earlier compatibility study,[17] have been used with a uniform flow range of 155 ± 5 mm (25 strokes) measured in accordance with ASTM C430, flow table test.

MATERIALS

Cement and fine aggregate

The cement used was ordinary portland cement (according to IS 269) marketed by Larsen & Toubro Co., India. The aggregate used was standard 'Ennore Sand' (according to IS 650) obtained from Madras, India. Some physical properties of the cement and sand are shown in Tables 1 and 2, respectively.

LATEX

Three commercial varieties of copolymer type latexes were used. They were vinylacetate Veova (VAV), methylmethacrylate–butylacrylate-2 ethylhexylacrylate (MBE) and styrene butadiene rubber (SBR) latexes. Technical specifications as declared by the manufacturer are furnished in Table 3. Before mixing the latex to mortar, a silicone-emulsion type of defoamer was added to the latex in a weight ratio of 0.7% of silicone solids in the defoamer to the total solids in the latex.

SUPERPLASTICISER

Two commercial superplasticisers were selected out of an initial five, based on their compatibility with the latexes used. They were sulfonated melamine formaldehyde type (SMF) and sulfonated melamine and naphthalene formaldehyde type (SMNF). The superplasticisers were used without any accelerator, retarder or air entraining agents. Table 4 shows some technical specifications.

Table 1. Some properties of cement used

Type	*Specific gravity at 32°C*	*Blaine specific surface area (cm^2/gm)*	*Standard consistency (%)*	*Setting time (min)*	
				Initial	*Final*
Ordinary portland cement	3.16	2750	30	155	305

Table 2. Some properties of aggregate used

		Particle size		
Type	*Specific gravity*	*Passing sieve (mm)*	*Retained sieve (mm)*	*Percentage by weight*
Ennore Sand	2.65	2	1	33.3
		1	0.5	33.3
		0.5	0.09	33.3

Table 3. Latex Specifications*

Sl No.	*Symbol used*	*Basic ingredients*	*Solid content*	*Specific gravity*	*Appearance*
1	VAV	Vinylacetate veova	55%	1.077	Opaque, milky white aqueous dispersion
2	MBE	Methylmethacrylate–butylacrylate-2-ethylhexylacrylate	49%	1.05	Milky white aqueous dispersion
3	SBR	Styrenebutadiene rubber	45%	1.02	Milky white liquid

* Supplied by M/S, Vam Organic Chemicals Ltd., Caltech India Ltd., Sika Qualcrete Pvt. Ltd., India.

EXPERIMENTAL PROGRAMME

Preparation of mortar

Mortar specimens of size 70.7 mm cube were prepared in accordance with IS 4031 in four groups. The first group was unmodified mortar with cement:sand = 1:3 (by weight), water–cement ratio = 0.5 (UM). In the second group two types of superplasticisers, SMF and SMNF were added to 2 wt% of cement to form superplasticised mortar mix (SM). In the third group three latexes (VAV, MBE and SBR) were used in 5%, 15% and 20% (as solid polymer content by weight of cement) to make latex-modified mortar (LM). In the last group, combinations of superplasticisers and latexes were used (SLM). In all cases of modified mortar, variable water–cement ratios (Table 5) were used to adjust a flow range of 155 ± 5 mm as obtained in unmodified mixes. UM and SM specimens were subjected to moist curing (by covering with wet hessian cloths) for 7 days at 32–36°C and subsequent air curing at relative humidity 85–90% whilst LM and SLM specimens were subjected to a similar type of moist curing for 2 days at 32–36°C and subsequent air curing at relative humidity 85–90%. All the specimens were hand mixed for a batch of three cubes, the time of mixing being restricted to 3–4 min measured from the instant of mixing gauging water. Superplasticisers and latexes were added to the gauging water before mixing it with cement and aggregate. Moulded specimens were vibrated in a mortar vibrator. Table 5 gives details of percentages of latex and superplasticiser content for each type of specimen.

Compressive strength test

Mortar specimens, UM, SM, LM and SLM were tested at age 3, 7 , 28 and 90 days under uniaxial compression until failure by a compression testing machine (Mohr & Federhaff, Germany). For each type, the average of three specimens was considered. Results are shown in Table 5 for unmodified and 20 modified samples.

Degree of hydration

The degree of hydration was determined from the water contents of the hydrated cement paste at 3, 7, 28, 90 and 180 days by the method described by Mikhail[11] and Su[12] with the assumption that the chemically bound water for fully hydrated cement was 0.24 and loss on ignition of cement at 1000°C was 2 wt%. The degree of hydration was determined for unmodified and 20 other modified samples.

Table 4. Superplasticiser specifications*

Sl No.	*Symbol*	*Basic ingredients*	*Sp. gravity*	*Appearance*
1	SMF	Sulphonated melamine formaldehyde condensate	1.24	Liquid, brown colour
2	SMNF	Sulphonated melamine formaldehyde and Naphthalene formaldehyde condensate	1.16	Liquid, brown colour

* Supplied by M/S, Sika Qualcrete Pvt. Ltd., India.

Table 5. Mix type, compressive strength (MPa) and strength age factors*

SI No.	*Latex % and type*	*Super % and type*	*Water cement ratio (by weight)*	*Compressive strength (MPa)*				*Strength age factors*			
				3 days	*7 days*	*28 days*	*90 days*	*3 days*	*7 days*	*28 days*	*90 days*
1	—	—	0.500	6.20	15.6	25.2	31.6	0.246	0.619	1.00	1.253
2	5% VAV	—	0.400	7.60	19.2	26.6	34.4	0.286	0.722	1.00	1.278
3	10% VAV	—	0.357	6.80	17.2	25.6	34.0	0.265	0.672	1.00	1.343
4	5% MBE	—	0.410	6.60	16.4	25.4	33.8	0.260	0.645	1.00	1.330
5	10% MBE	—	0.365	6.40	16.0	26.0	34.4	0.246	0.615	1.00	1.323
6	5% SBR	—	0.420	6.00	15.8	26.4	33.8	0.227	0.598	1.00	1.280
7	10% SBR	—	0.370	6.80	16.6	25.6	34.8	0.265	0.648	1.00	1.360
8	—	2% SMF	0.390	10.0	22.8	28.0	34.0	0.357	0.814	1.00	1.214
9	5% VAV	2% SMF	0.310	8.20	19.4	27.6	36.4	0.297	0.703	1.00	1.320
10	10% VAV	2% SMF	0.272	9.40	21.4	27.0	35.2	0.348	0.792	1.00	1.304
11	5% MBE	2% SMF	0.320	8.00	18.2	27.0	36.0	0.296	0.674	1.00	1.333
12	10% MBE	2% SMF	0.290	7.60	16.8	27.2	35.6	0.279	0.617	1.00	1.309
13	5% SBR	2% SMF	0.350	8.60	19.2	27.6	37.0	0.311	0.696	1.00	1.341
14	10% SBR	2% SMF	0.320	7.60	17.6	27.8	37.2	0.273	0.633	1.00	1.338
15	—	2% SMNF	0.400	10.4	24.0	28.4	34.8	0.366	0.845	1.00	1.225
16	5% VAV	2% SMNF	0.300	9.80	22.4	28.2	37.6	0.347	0.794	1.00	1.333
17	10% VAV	2% SMNF	0.273	10.2	22.2	28.6	38.6	0.356	0.776	1.00	1.350
18	5% MBE	2% SMNF	0.320	7.2	16.4	26.8	35.6	0.268	0.612	1.00	1.328
19	10% MBE	2% SMNF	0.300	7.40	16.8	27.2	36.4	0.272	0.617	1.00	1.338
20	5% SBR	2% SMNF	0.350	7.40	17.4	26.8	35.8	0.276	0.650	1.00	1.336
21	10% SBR	2% SMNF	0.300	7.60	17.6	27.0	35.6	0.281	0.652	1.00	1.318

* Flow for all mixes: 155 ± 5 mm (25 strokes) by ASTM C430 flow table test.

Powder X-ray diffraction

The broken pieces of mortar specimens from the compressive strength specimens at 90 days were crushed and samples were taken from them. The samples were made into powder passing a 75 μm sieve by mortar and pestle for unmodified and 20 modified samples. The XRD patterns were recorded by a PW 1840 diffractometer by Philips. $CuK\alpha$ radiation was used with a Bragg angle range of $2\theta = 15°–35°$. Other conditions were: goniometer speed = 3°/min, chart speed = 10 mm/2θ, range = 5000 counts/s, time constant = 1 s, slit angle = 0.2°. The X-ray tube was operated at 40 kV, 20 mA. Tests were carried out during the ages 90–95 days.

Thermal analysis

DSC and TG were conducted to recognise the phases of cement and weight losses at different stages of temperature rise for the unmodified and 20 modified samples. The samples used were the same as for the XRD records. Tests were carried out by Stanton Redcroft STA 625 instrument for the age of sample between 90 and 95 days. Simultaneous TG and DSC were recorded from ambient temperature to 580°C with 11.5 mg of sample, heated in air with 'no reference' at a rate of 10°C/min.

Mercury intrusion porosimetry

MIP was conducted on unmodified and eight modified samples taken from fragments (passing 10 mm and retained on 4.75 mm sieve) after compressive strength tests. Tests were carried out during the ages 90–95 days by a model Autoscan 60 Mercury porosimeter (Quantachrome, USA) with contact angle $\theta = 140$°C, surface tension $S = 0.480$ N/m. The samples were dried in a vacuum of 0.05 mm Hg at 25°C before intrusion. The pore distribution was recorded from 17.5 to 75000 Å pore radius. The shape of the pores was assumed to be cylindrical.

TEST RESULTS AND DISCUSSION

Compressive strength and degree of hydration

In Table 5, compressive strengths for 3 , 7 , 28 and 90 days specimens are presented for LM and SLM mixes with 5% and 10% latex addition only, because beyond 10% of latex,

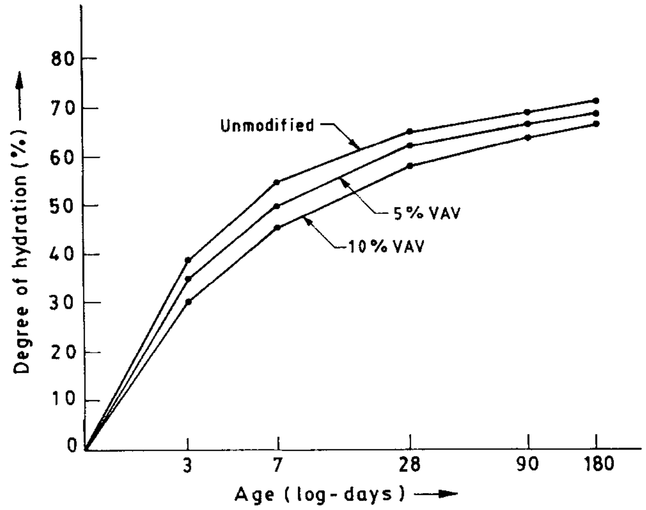

Fig. 1. Degree of hydration vs age (log-days).

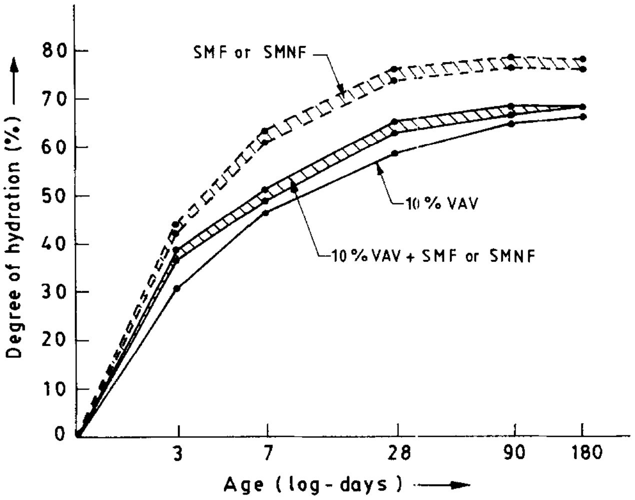

Fig. 2. Degree of hydration vs age (log-days).

compressive strengths fell below that of the unmodified mix in almost all cases.[18] In the case of VAV, 5% addition developed more strength than 10% addition at all ages. This is evident from the rate of hydration (Fig. 1) where 5% VAV mortar has hydrated more than 10% VAV up to 180 days. This higher rate of hydration was also shown by Su[12] with other latexes. For MBE and SBR, there is no definite trend with relation to latex percentage. For all cases of addition of superplasticiser, SMF or SMNF, the increase in compressive strength was maintained in all modified specimens with age. This is in agreement with Beaudoin *et al.*[1] and Atzeni.[2] In the case of VAV latex, for 10% VAV + SMF/SMNF combination the 7 day strength was about 78–80% of the 28 day strength whilst for only VAV the corresponding value was 67% (Table 5). Beyond 28 days also, the rate of increase of compressive strength of VAV + superplasticiser was greater than only VAV except 10% VAV + SMF. Figure 2 is consistent with this observation, where mortar containing VAV plus superplasticiser (SMF or SMNF) has a higher rate of hydration compared to only VAV up to 180 days. For MBE and SBR latexes, the addition of superplasticisers improved the rate of compressive strength up to 28 days and the rate of hydration up to 180 days for all cases (Table 5, Figs 3 and 4). However beyond 28 days, the rate of gain in compressive strength due to addition of superplasticiser was noticed for 5% MBE + SMF, 10% MBE + SMNF and 5% SBR + SMF/SMNF (Table 5). Addition of only superplasticiser SMF or SMNF to mortar increased both the rate of compressive strength

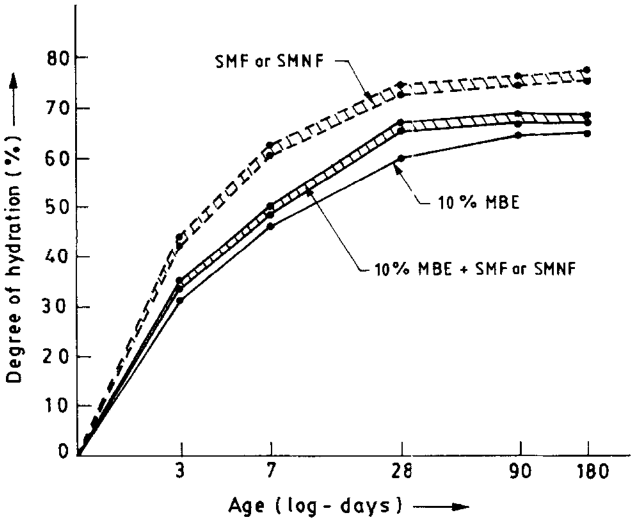

Fig. 3. Degree of hydration vs age (log-days).

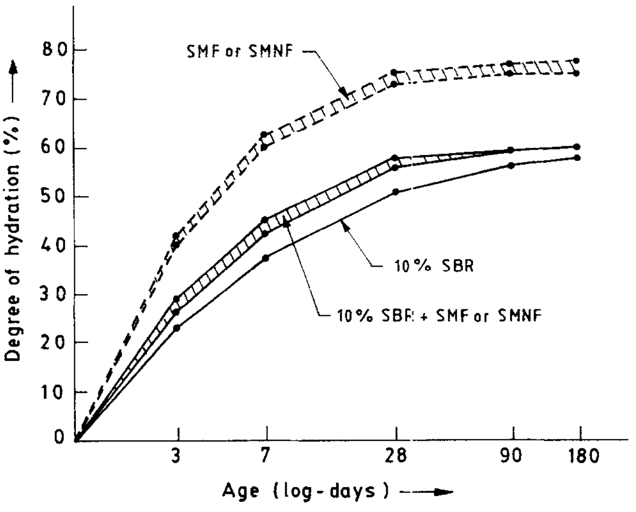

Fig. 4. Degree of hydration vs age (log-days).

(up to 28 days) and rate of hydration up to 180 days (Figs 2–5). The values are also higher than the corresponding SLM specimens. The presence of latex, therefore, had a negative influence on both short term strength and degree of hydration of SM specimens. From Fig. 6, it is evident that rate of hydration of 10% SBR is much less than 10% VAV or 10% MBE, the last two being comparable.

Powder X-ray diffraction analysis

For qualitative assessment, X-ray intensity for various phases of different mixes are shown in Table 6. Figures 7 and 8 also show some test results. It is evident that addition of either latex or superplasticiser to the mortar, has reduced the amount of calcium hydroxide crystals at $2\theta = 34.1°$ for all cases and at $2\theta = 18.1°$ for all cases except mortar with 5% VAV, 5% MBE

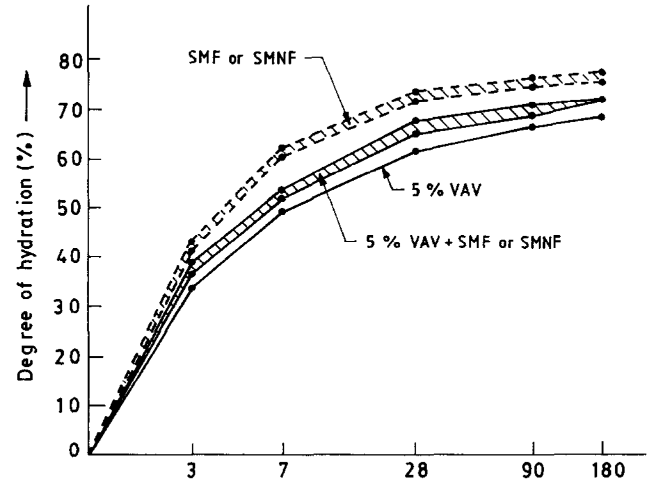

Fig. 5. Degree of hydration vs age (log-days).

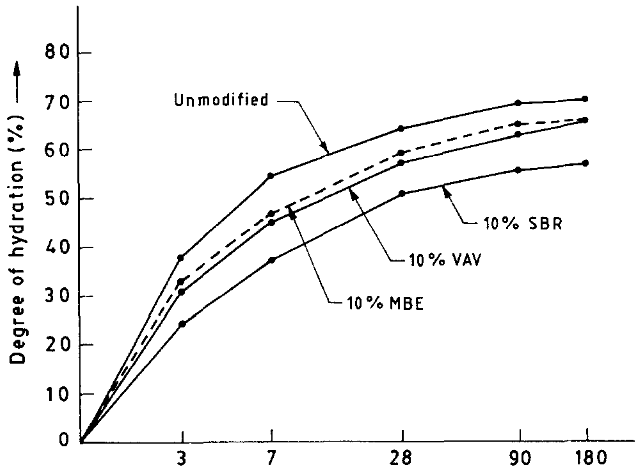

Fig. 6. Degree of hydration vs age (log-days).

Table 6. X-ray data (Cuka) for powdered mortar (typical)*

Mix	Intensity of crystalline phases (arbitrary scale)						
	001 plane $Ca(OH)_2$ $2\theta = 18.1°$	SiO_2 $2\theta = 26.7°$	Alite2 $\theta = 29.5°$	Alite + BC_2S $2\theta = 32.3°$	Alite + BC_2S $2\theta = 32.7°$	101 plane $Ca(OH)_2$ $2\theta = 34.1°$	Reference (12) OI = I(001)/I(101) 0.74
Anhydrous cement: sand = 1:3	0	12	20	28	20	0	
Unmodified	21	15	6	2	2	25	1.14
5% VAV	33	30	10	5	3	17	2.62
10% VAV	18	52	5	6	4	18	1.35
5% MBE	29	28	7	4	4	18	2.18
10% MBE	17	78	9	4	3	13	1.76
5% SBR	7	19	9	6	6	12	0.79
10% SBR	5	20	8	5	5	10	0.68
SMF	29	31	8	2	1	17	2.30
5% VAV + SMF	5	14	6	9	7	9	0.75
10% VAV + SMF	4	22	5	7	7	11	0.50
5% MBE + SMF	9	28	8	5	6	12	1.01
10% MBE + SMF	7	33	5	8	5	12	0.79
5% SBR + SMF	8	29	10	7	8	10	1.08
10% SBR + SMF	4	49	8	7	7	9	0.60
SMNF	17	36	8	4	3	17	1.35
5% VAV + SMNF	5	31	5	6	7	9	0.75
10% VAV + SMNF	4	19	5	7	7	10	0.54
5% MBE + SMNF	7	14	10	6	8	12	0.67
10% MBE + SMNF	4	40	7	7	7	8	0.79
5% SBR + SMNF	9	35	10	6	7	15	0.81
10% SBR + SMNF	4	19	8	7	6	7	0.77

* Considering the inhomogeneity in the ratio of cement and sand in powdered mortar sample, the tests were repeated three times for each sample and the maximum coeff. of variation from mean was found to be 5.0.

and SMF. This may be attributed to the 'saponification' reaction by which Ca^{2+} ions from the liquid phase are trapped by the carboxylate group of the polymer dispersion in water. This phenomena was adequately described by Larbi *et al.*[13] The addition of both superplasticiser and latex further reduced the amount of $Ca(OH)_2$ crytalline phase. However, since the strength and rate of hydration of SLM mortar, even with the reduced $Ca(OH)_2$, was higher than corresponding LM mortars (Table 5), it appears that estimation of the quantity of $Ca(OH)_2$ alone does not provide sufficient means for predicting the strength. This fact was also reported by Afridi.[9] X-ray data shows that for the latexes VAV, MBE and SBR, the increase in percentage of latex decreased the quantity of $Ca(OH)_2$ crystals. This was pronounced for $2\theta = 18.1°$. This reduction in quantity was also apparent in SLM mixes with both SMF and SMNF superplasticisers. Among the latexes, the mortars with 5% and 10% SBR addition were found to have a lower quantity of $Ca(OH)_2$, and the condition did not alter even with the inclusion of superplasticiser SMF or SMNF. The anhydrous crystalline phases of the cement compound, the alite and alite + βC_2S were found to be reduced for all hydrated samples (both unmodified and modified) with respect to anhydrous cement. The addition of latex or latex plus superplasticiser, therefore, also allows the formation of nearly amorphous or poorly crytalline C–S–H gel, which plays a vital role in contributing the strength. However, the formation was lower in comparison to unmodified or SMF- or SMNF- modified samples. The type of superplasticiser SMF or SMNF had no definite effect on the formation of $Ca(OH)_2$ or C–S–H gel.

It is known that the presence of latex has a marked influence on morphology and orientation of $Ca(OH)_2$.[9,14] The orientation index (OI) was estimated using the relation described by Su.[12] It has been found from Table 6, that OI

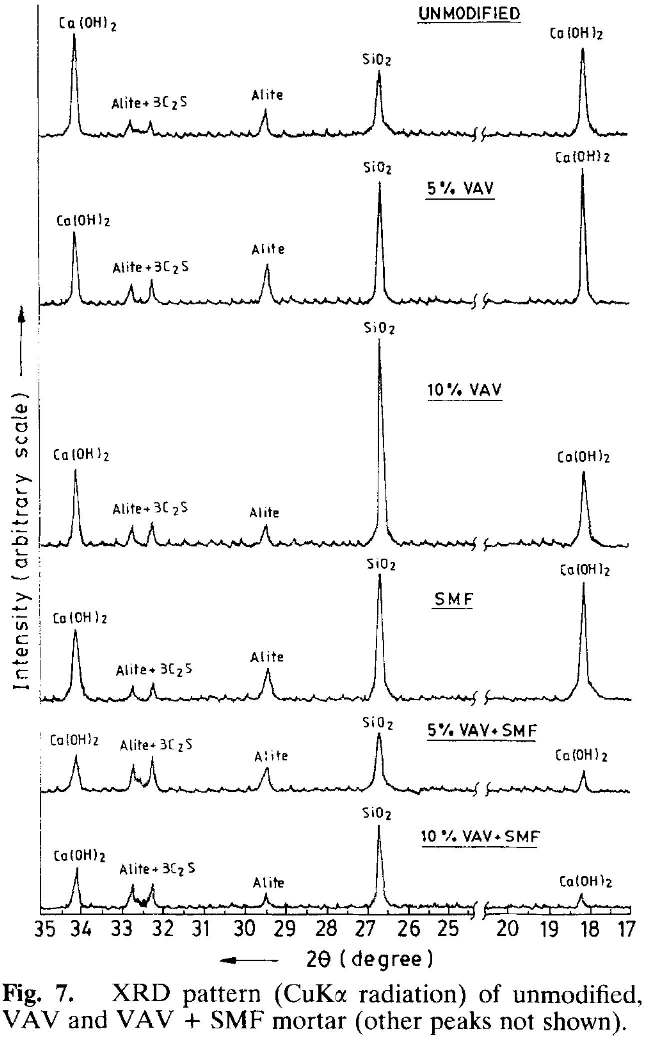

Fig. 7. XRD pattern (CuKα radiation) of unmodified, VAV and VAV + SMF mortar (other peaks not shown).

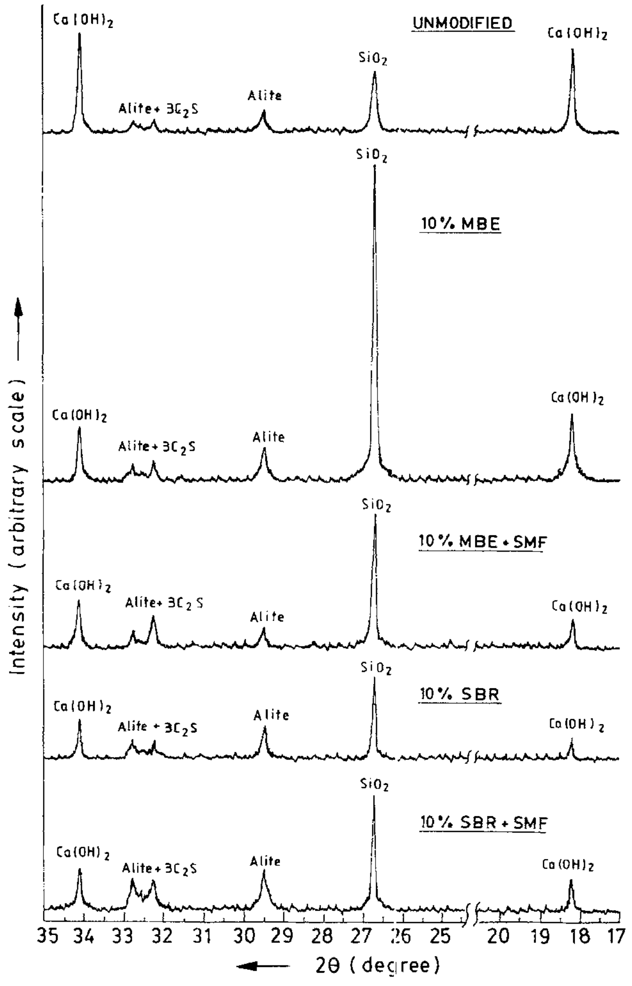

Fig. 8. XRD pattern (CuKα radiation) of unmodified, MBE, MBE + SMF, SBR and SBR + SMF mortar (other peaks not shown).

values for all SBR samples whether superplasticised or not, were consistently low (between 1.08 and 0.68), whereas the OI for 5% and 10% VAV were 2.62 and 1.35, respectively and became 0.75 and 0.50 only when superplasticised by SMF. Addition of SMNF modified the values to 0.75 and 0.54, respectively. This characteristic reduction in OI values, due to inclusion of either SMF or SMNF in latex–mortar, had also occurred in case of mortar with MBE. It is also evident from Table 6 that in all cases of LM and SLM samples, the OI values got reduced with the increase in latex percentage from 5% to 10%. This reduction in OI values indicates that the quantity of $Ca(OH)_2$ crystals having C-axis perpendicular to the plane of sample got reduced due to addition of superplasticiser and increase in latex percentage.

X-ray analysis also shows that scattering from crystalline SiO_2 in sand increased due to the presence of latex. The maximum scattering was obtained for 10% MBE and 10% VAV. Inclusion of superplasticiser maintained this high profile of reflection by crystals. This phenomena may possibly be due to the favourable orientation of crystalline SiO_2 in the presence of latex and latex with superplasticiser.

TG and DSC analysis of powdered mortar

The results of TG and DSC which were performed simultaneously are tabulated in Table 7. Figures 9, 10 and 11 are presented for comparison of unmodified and modified samples. Total weight loss up to 550°C from TG shows that unmodified samples had undergone a maximum loss of 18%, whereas the values for LM, SM or SLM samples were between 12% to 17%. In the case of SM specimens losses for SMF and SMNF were 14% and 12.5%, respectively. It has been found that among the latexes, mortar with SBR was the most stable against heating up to 550°C, undergoing only 13% and 14% loss for addition of 5% SBR and 10% SBR, respectively. The corresponding values of losses for VAV were 16% and 17%, respectively, and for MBE (5% and 10%) it was 17%. Addition of superplasticiser (SMF or SMNF type) in the latex-modified system had reduced weight loss for mortar with VAV by up to 4.5% (for 10% VAV + SMF). This indicates an enhanced stability for SLM samples with VAV. For MBE or SBR, no such consistent improvement was noticed. This may be due to the higher decomposition loss of MBE and SBR compared to VAV in the presence of superplasticiser.

The initial endotherms due to free moisture loss were noticed at 54°C for unmodified and at 50–55°C for SM samples, whilst the corresponding values for LM and SLM samples were in the range of 80–87°C and 76–86°C, respectively (Table 7). This shows that the capability for retaining free moisture was more in the case of LM or SLM samples compared to UM or SM. This may be due to the film formation of latex which helped to retain the moisture of LM or SLM samples up to a higher temperature. Among the latexes 10% VAV could hold the moisture up to 87°C, whilst MBE and SBR showed lower temperatures. Inclusion of superplasticiser in the latex did not significantly alter the situation.

The calcium hydroxide endotherm was indentified from previous works.[9,10] From the values of heat energy in the DSC curve (Table 7), it is evident that the quantity of $Ca(OH)_2$ formation in UM samples was a maximum, with an endotherm heat energy of 32 mcal/mg. The SMF or SMNF samples allowed lower values of 24 mcal/mg and 16 mcal/mg, respectively. For all LM specimens, the increase in percentage of latex from 5% to 10% reduced the $Ca(OH)_2$ formation. This reduction was a maximum for MBE, intermediate for VAV and least for SBR. This phenomenon of reduction of $Ca(OH)_2$ in modified samples was reported by Afridi *et al.*[9] and Chandra and Flodin.[16] Samples with both superplasticiser and latex had further reduced the $Ca(OH)_2$ formation than corresponding LM mortars (Figs 9, 10 and 11). This observation was true for both types of superplasticiser and all latexes. There was a drastic lowering of $Ca(OH)_2$ endotherm heat energy for 10% VAV + SMF (by 90%), 10% SBR + SMF (by 67%), 10% VAV + SMNF (by 80%) and 10% SBR + SMNF (by 100%) with respect to corresponding LM mortar samples. Formation of $Ca(OH)_2$ was not significantly affected when MBE latex was added with SMF and SMNF.

The overall tendency to inhibit the formation of $Ca(OH)_2$ was in agreement with the results from XRD analysis. A possible explanation for this is the capturing of Ca^{2+} ions within the carboxylate anions of polymer dispersions (VAV and MBE type) and subsequent lowering of $Ca(OH)_2$ formation in latex-modified samples. For SBR type, it was possibly due to

Table 7. DSC and TG analysis of unmodified and modified mortar (up to 550°C)

Mix	*Temp range/ onset temp (°C)*	*Peak temp (°C)*	*Nature of peak*	*Weight loss in % (DTg)*	*Heat energy (mcal/mg) of $Ca(OH)_2$*	*Total weight loss up to 550°*
Unmodified	40–70	54	Moderate(Endo)	3%	—	18%
	437–464	448	Sharp(Endo)	2.9%	32	
5% VAV	66–100	85	Sharp(Endo)	2%		
	225(onset)	300	Broad(Exo)	—		16%
	439–458	450	Sharp(Endo)	2%	21	
10% VAV	65–110	87	Sharp(Endo)	3%	—	
	233(onset)	311	Broad(Exo)	—	—	17%
		386	Weak(Exo)	—	—	
	448–471	472	Sharp(Endo)	1.5%	15	
5% MBE	67–97	80	Sharp(Endo)	2%	—	
	300(onset)	360	Moderate(Exo)	—	—	17%
	438–459	450	Sharp(Endo)	1.8%	20	
10% MBE	66–100	83	Sharp(Endo)	1.8%	—	
	300(onset)	360	Sharp(Exo)	—	—	17%
	439–459	448	Sharp(Endo)	1.3%	12	
5% SBR	63–100	81	Sharp(Endo)	1.4	—	
	253(onset)	373	Moderate(Exo)	—	—	13%
	441–458	450	Sharp(Endo)	1.1	11	
10% SBR	63–96	80	Sharp(Endo)	1.6	—	
	270(onset)	363	Moderate(Exo)	—	—	14%
	440–459	448	Sharp(Endo)	—	10	
SMF	36–73	55	Sharp(Endo)	3%	—	
	442–466	454	Sharp(Endo)	2.4%	24	14%
5% VAV + SMF	60–100	85	Sharp(Endo)	3.5%	—	
	220(onset)	306	Broad(Exo)			14%
	431–457	449	Sharp(Endo)	1%	8	
10% VAV + SMF	66–107	86	Sharp(Endo)	3.0%	—	
	256(onset)	300	Sharp(Exo)	—		12.8%
		386	Small(Exo)	—		
	450–472	463	Sharp(Endo)	0.5%	1.5	
5% MBE + SMF	56–93	80	Sharp(Endo)	2.6%		
	300(onset)	363	Broad(Exo)	—		19%
	442–468	450	Sharp(Endo)	2.1%	16	
10% MBE + SMF	60–100	76	Sharp(Endo)	2%	—	
	300(onset)	360	Sharp(Exo)	—	—	16%
	438–459	451	Sharp(Endo)	1.2%	9	
5% SBR + SMF	63–100	82	Sharp(Endo)	2.6%	—	
	200(onset)	228.5	Small(Exo)	—	—	17%
	310(onset)	363.5	Broad(Exo)	—	—	
	441–462	458	Sharp(Endo)	0.9%	8.3	
10% SBR + SMF	62–100	77	Sharp(Endo)	2.0%	—	
	200(onset)	223	Small(Exo)	—	—	15%
	300(onset)	364.5	Large(Exo)	—		
	432–456	448	Sharp(Endo)	<0.5%	3.3	
SMNF	40–70	50	Sharp(Endo)	2%	—	
	220(onset)	310	Broad(Exo)	—	—	12.5%
	439–460	448	Sharp(Endo)	1.4%	16	
5% VAV + SMNF	60–100	84	Sharp(Endo)	3.4%	—	
	233(onset)	312	Moderate(Exo)	—	—	13.5%
	436–454	448	Sharp(Endo)	0.8%	7.3	
10% VAV + SMNF	60–105	85	Sharp(Endo)	2.2	—	
	260(onset)	310	Sharp(Exo)	—	—	14.0%
		386	Small(Exo)	—	—	
	445–470	457	Small(Endo)	—	3.0	
5% MBE + SMNF	60–90	80.3	Sharp(Endo)	2%	—	
	300(onset)	363	Moderate(Exo)	—	—	17%
	442–458	453.5	Sharp(Endo)	1%	8.0	
10% MBE + SMNF	65–100	79	Sharp(Endo)	1.4%	—	
	230(onset)	265	Small(Exo)	—	—	14%
		350	Sharp(Exo)	—	—	
	439–459	449	Sharp(Endo)	0.8%	8.0	
5% SBR + SMNF	53–95	80	Sharp(Endo)	2.7%	—	
	200(onset)	230.8	Small(Exo)	—	—	13%
	320(onset)	366	Broad(Exo)	—	—	
	439–461	453	Sharp(Endo)	1.5%	9.2	
10% SBR + SMNF	60–90	85	Small(Endo)	—	—	
	200(onset)	223	Small(Exo)	—	—	15%
	320(onset)	361	Broad(Exo)	—	—	
	—	515	Small(Endo)	0		

adsorption of $Ca(OH)_2$ crystal on the polymer film. This was thoroughly discussed by Larbi[13] and Chandra[15,16] for the latex-modified system. However, the further lowering of $Ca(OH)_2$ in SLM samples increases the validity of their explanation for superplasticised latex-modified mortar also.

The unmodified sample had a peak temperature of $Ca(OH)_2$ decomposition at 448°C with an onset at 437°C (Fig. 9). For all modified samples this peak temperature was at least equal to or higher than this value (Table 7, Figs 10 and 11). For LM samples, this was explained by other workers as a change in the morphology and orientation[14] of $Ca(OH)_2$ in the presence of latex and a kind of bond among the crystal in presence of polymer[16] which requires higher temperature for the decomposition of $Ca(OH)_2$. It seems that for SLM specimens this explanation was also valid since the peak temperatures of $Ca(OH)_2$ endotherm of all SLM samples were higher than the unmodified one, in spite of the size of the endotherm being much smaller.

Exotherms, due to decomposition of latex in the mortar, were 300°C and 311°C for 5% VAV and 10% VAV, respectively. The corresponding values were 360°C for 5% MBE and 10% MBE, and 373°C and 363°C for 5% SBR and 10% SBR, respectively. The higher values of decom-

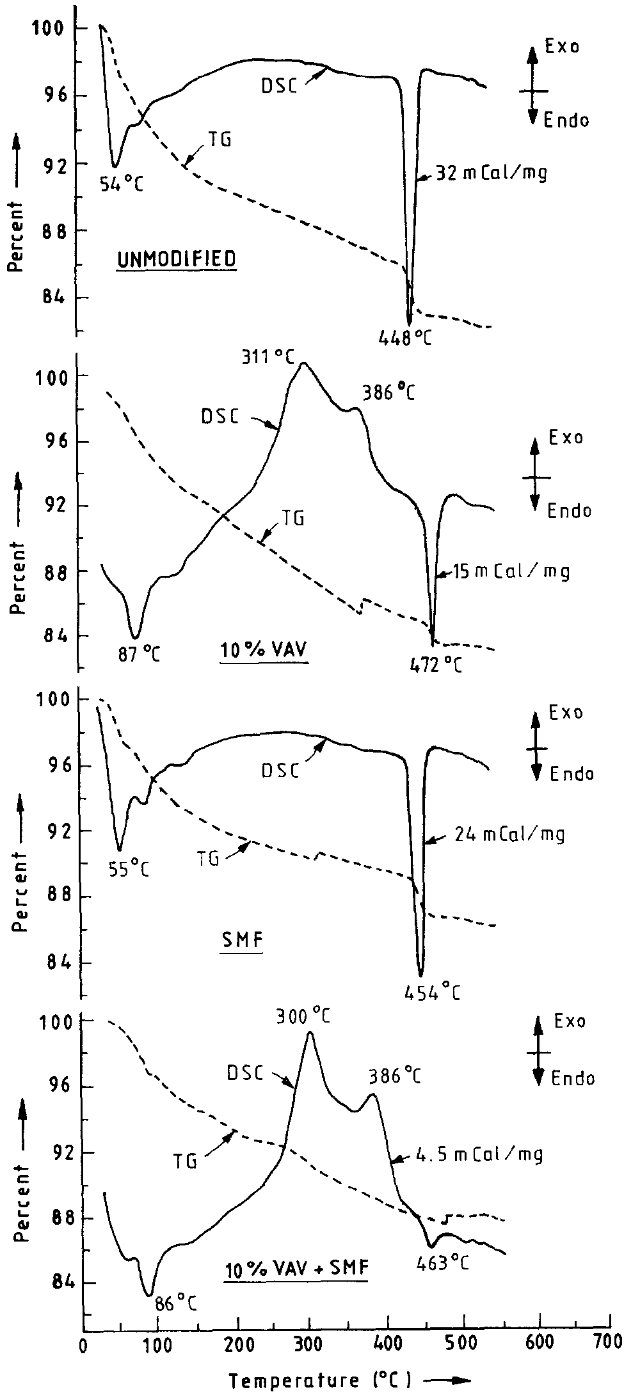

Fig. 9. Simultaneous TG and DSC curves of unmodified and modified samples.

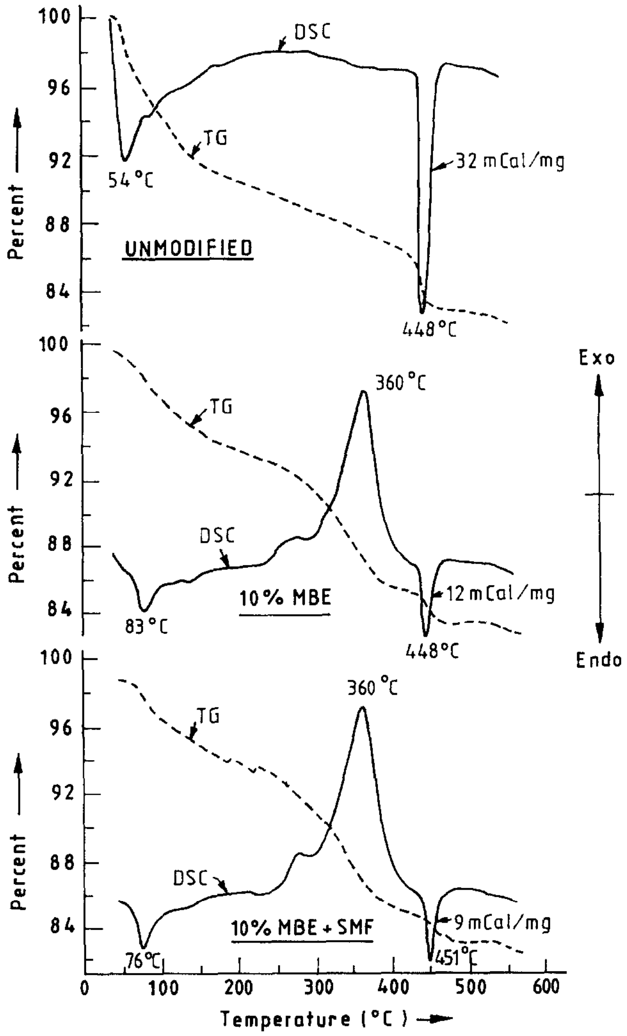

Fig. 10. Simultaneous TG and DSC curves of unmodified and modified samples.

position of MBE and SBR compared to VAV were characteristic of the latex type in hydrated cement medium. The increase of latex percentage from 5% to 10% had no definite effect on the exotherm peak temperature. For SM specimens, one distinguishing feature was that the mortar with SMNF superplasticiser had a broad exotherm with an onset temperature at 220°C and peak temperature at 312°C, whereas, in a mortar with SMF superplasticiser, this exotherm was absent. This may be explained by the fact that chemical interaction of superplasticisers SMNF and SMF with cement–sand mortar was different.

The addition of superplasticiser in latex mortars did not have much influence on the exothermic peak temperature due to decomposition of latex (Table 7 and Figs 9, 10 and 11). The trend as obtained in the case of LM samples was unchanged for SLM samples. For example, the higher peak temperatures for decomposition of MBE and SBR latex compared to VAV latex were also maintained when superplasticisers were added with them (Table 7). Appearance of more than one maxima for 5% SBR + SMF/SMNF and 10% SBR + SMF/SMNF was a special feature for SBR latex when used in combination with the superplasticisers (Table 7 and Fig. 11). This may be interpreted as a chemical interaction between SBR and SMF/SMNF in the hydrating cement medium and a subsequent change in the SBR emulsion character. The extra small peak for 10% VAV + SMF and 10% VAV + SMNF at around 386°C (Table 7 and Fig. 9) was also possibly due to a change in the emulsion character of VAV in the presence of SMF or SMNF type of superplasticisers. Montanaro[10] had observed such a phenomenon for mortars with ethylene–vinylacetate–vinyl chloride and acrylic polymers. Weak exotherms around 265°C for 5% MBE + SMNF and 10% MBE + SMNF were also the result of interaction between latex and superplasticiser (Table 7).

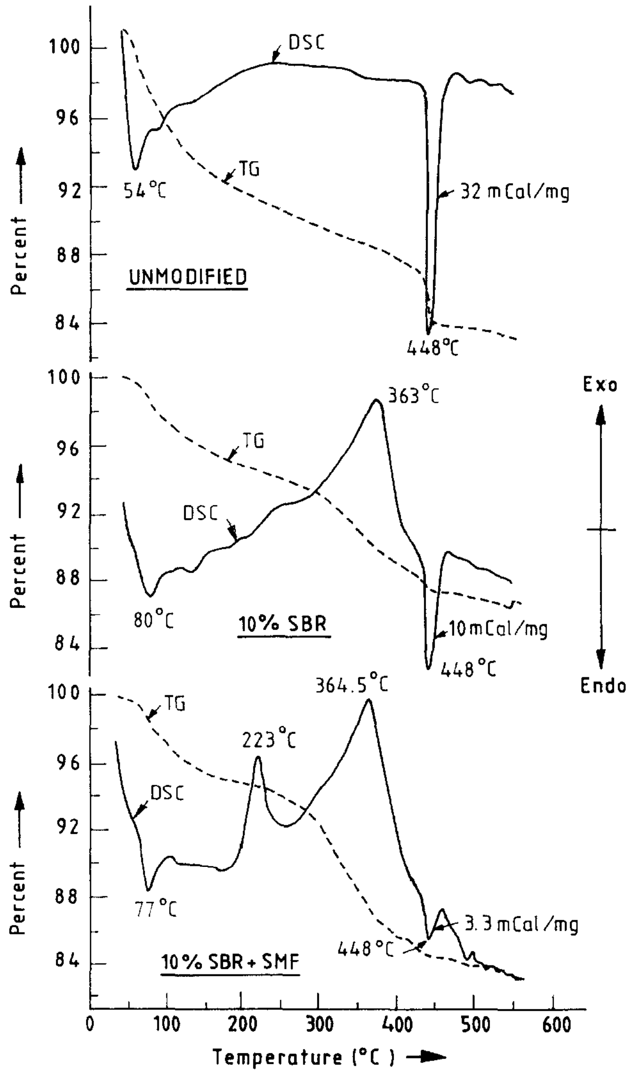

Fig. 11. Simultaneous TG and DSC curves of unmodified and modified samples.

Pore size distribution by MIP

For each sample, cumulative porosity in volume proportion of bulk volume (%) in ordinary scale were plotted against the pore radius (Å) in log scale. The plots are given in Figs 12–15. From the figures it is evident that total porosity of 10% VAV and 10% MBE mortars were almost of the same order as that of the unmodified mortar. The values were 11.06% for 10% VAV,

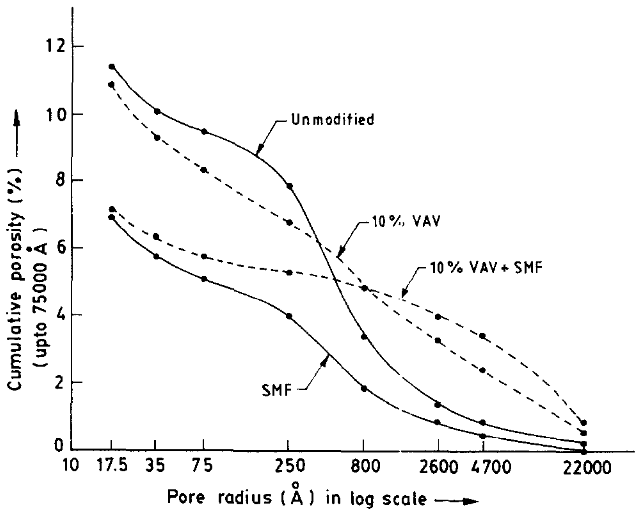

Fig. 12. Cumulative porosity in vol (%) vs pore radius (Å) curve.

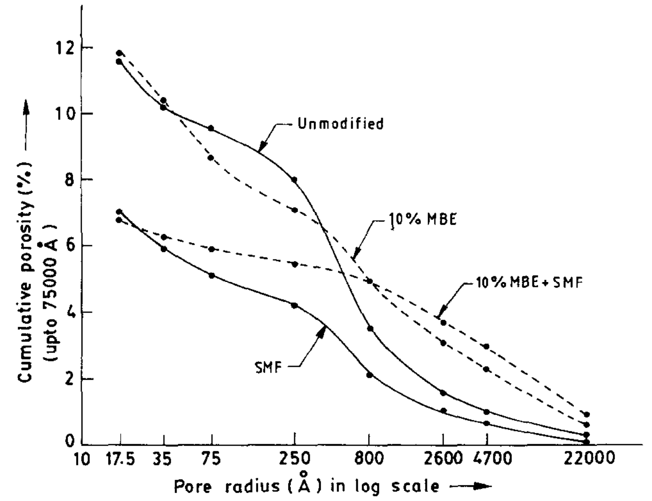

Fig. 13. Cumulative porosity in vol (%) vs pore radius (Å) curve.

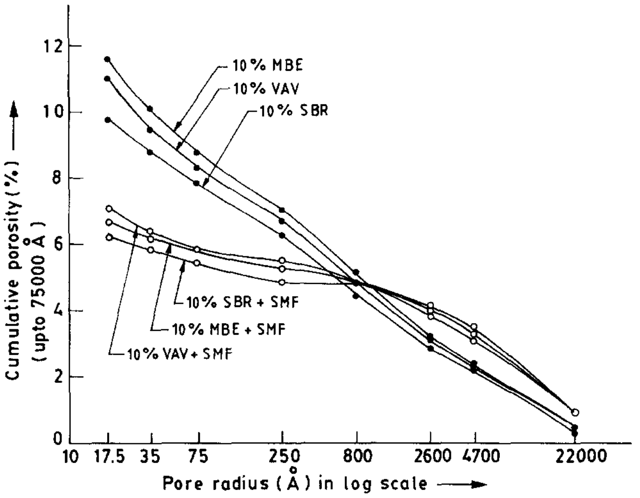

Fig. 15. Cumulative porosity in vol (%) vs pore radius (Å) curve.

11.61% for 10% MBE and 11.49% for the unmodified sample. The value of 10% SBR being 9.9% was about 1.6% less than the unmodified one. In the sample with only SMF, the total porosity decreased remarkably by 4.52% compared to unmodified mortar. For SLM specimens the values were 7.07%, 6.8% and 6.3% for 10% VAV + SMF, 10% MBE + SMF and 10% SBR + SMF, respectively. Addition of superplasticiser had decreased the porosity in all latex-modified mortars. This reduction in porosity was also reflected in higher compressive strength of SLM specimens over corresponding LM specimens (Table 5).

From Figs 12–15 it is evident that the pore distribution curves for all latex-modified samples were flatter than the UM sample. For SLM mix, this observation was still valid. For example, the curves for SLM mix with different latex addition were flat in nature compared to SM mix. Latex addition, therefore, made the pore distribution more uniform and evenly distributed in different pore size for both unmodified and superplasticiser-modified samples. In all LM specimens, the curves with 10% latex addition were lying under the UM up to about 450 Å pore radius, beyond which the LM curves swept over the UM curve. This is an indication that below about 450 Å pore radius, the pore volumes of LM samples were less than UM, whereas beyond 450 Å, the LM samples had larger volumes of pores than UM. A similar observation was made by Montanaro.[10] Addition of superplasticiser in LM samples made the curve flatter with respect to the corresponding LM curves. The curves of SLM were lying below LM groups up to about pore radius of 800 Å (Fig. 15). This signifies that inclusion of superplasticiser in latex-modified mortar helped to reduce the micropores of LM samples up to 800 Å. The statement is valid for SLM mixes with 10% VAV + SMF, 10% MBE + SMF and 10% SBR + SMF. From Fig. 15, it also appears that there was little variation of pore distribution among the latexes, viz. VAV, MBE, SBR. This variation, was also insignificant when superplasticiser SMF was mixed with each latex.

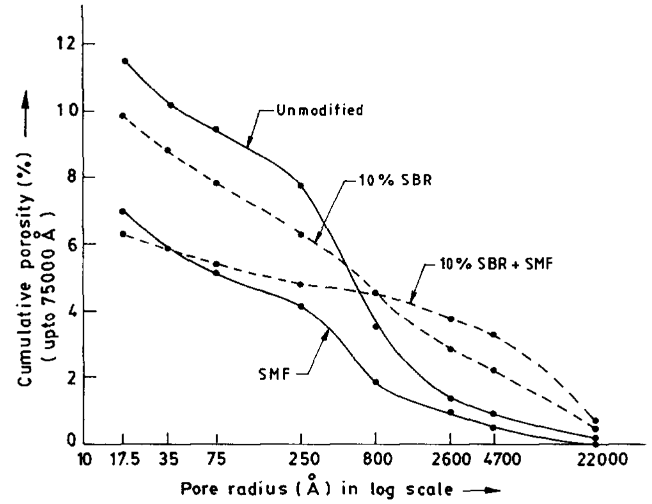

Fig. 14. Cumulative porosity in vol (%) vs pore radius (Å) curve.

CONCLUSIONS

Addition of superplasticiser to latex had increased the rate of hydration up to 180 days and the rate of compressive strength up to 28 days. Beyond 28 days, the improvement in rate of compressive strength was noticed for few selected combinations.

XRD data had revealed that lower quantity of $Ca(OH)_2$ had formed in presence of latex. Also, the increase in percentage from 5% to 10% had an inhibiting effect on $Ca(OH)_2$ formation. Addition of superplasticiser did not alter the situation. The quantity of $Ca(OH)_2$ crystals perpendicular to the *C*-axis had been found to be reduced with the increase in latex percentage from 5% to 10% for both LM and SLM samples.

Reduction in $Ca(OH)_2$ formation as obtained from XRD data was also confirmed by DSC curves. Addition of latex in UM or SM samples had raised the peak temperature for endotherm corresponding to free moisture loss.

For all modified samples, the peak temperature for $Ca(OH)_2$ decomposition was at least equal to or higher than the unmodified one.

The number of peaks for exotherm of latexes in SLM samples was indicative of some change in emulsion character in the presence of superplasticiser.

Mercury intrusion porosimetry tests of few samples revealed that the addition of latex to UM mixes caused a more even distribution of different pore size within the matrix.

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