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Effects of metakaolin, water/binder ratio and interfacial transition zones on the microhardness of cement mortars

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Abstract

Variations in the microhardness of the hydrated cement matrix component of model mortars have been investigated as functions of the distance from the aggregate surfaces for specimens in which the binder was Portland cement or a blend of Portland cement and metakaolin. Microhardness measurements were made using a Knoop indenter at distances of up to 120 μm from the aggregate. The microhardnesses of the paste–aggregate interfacial transition zones (ITZs) were found to be between 14% and 22% lower than those of the corresponding bulk cement pastes at the lower water/binder ratios investigated, i.e. 0.4 and 0.5 for samples prepared with Portland cement and 0.4 for samples prepared with a binder comprising Portland cement and metakaolin. Metakaolin increased the mean microhardness of specimens prepared at the higher water/binder ratios of 0.5 and 0.6 by 13% and 54%, respectively. © 2002 Published by Elsevier Science Ltd.

Keywords: Interfacial transition zone; Microstructure; Metakaolin; Mortar; Microhardness

1. Introduction

Metakaolin is a pozzolan produced by the thermal activation of the mineral kaolinite. The effects of metakaolin on the durability and other properties of Portland cement composites have been widely reported [1–3].

Portland cement mortars and concrete consist of two principal components namely hydrated cement paste (HCP) and aggregate. However, it is widely acknowledged that there exists a third morphologically distinct constituent, often termed the interfacial transition zone (ITZ), at the HCP–aggregate boundary [4]. Wide, although not universal, agreement exists that the ITZ is characterised by higher porosity and differing chemical and mineralogical composition from the bulk HCP [5,6].

Microhardness testing provides a tool for quantifying microstructural gradients across the ITZ. Microhardness measurements can contribute to characterisation of the properties of the ITZ relative to the bulk cement paste matrix and also provide one means of estimating the width of the ITZ. As early as 1962, Lyubimova and Pinus [7] evaluated microhardness gradients across aggregate–paste interfaces and observed, over a range of water/binder ratios, that measured microhardness decreased within 100 μm of the aggregate surface. Whilst reductions in microhardness for the ITZ relative to the bulk regions are consistent with the hypothesis that the ITZ is a region of higher than average porosity, such observations are not universal. Increases in microhardness within 50 μm of the aggregate surface have been reported [8], and Igurashi et al. [9] suggested four ITZ/bulk region microhardness profiles. For example, in specimens where the microstructure of the ITZ is similar to the bulk region, the close proximity of the aggregate surface can increase microhardness values above those recorded for the bulk region by impeding the displacement of material from the indentation site. In contrast, where the ITZ microstructure is weaker than the bulk region, a depression in the microhardness profile is expected within the zone of influence of the aggregate, the profile at the aggregate surface also being influenced by the strength of the paste–aggregate bond.

The aim of the work to be described was to characterise variations in microhardness as a function of distance from the aggregate for the hydrated Portland cement matrix of model mortars prepared with an aggregate content of 35 vol.%. The

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Table 1
Properties of Portland cement and metakaolin

	Portland cement (mass%)	Metakaolin (mass%)
SiO_2	20.8	55.4
Al_2O_3	5.2	40.9
Fe_2O_3	2.0	0.64
CaO	63.8	0.01
MgO	1.6	0.23
SO_3	2.5	
K_2O	1.1	0.81
Na_2O	0.1	0.01
LOI		0.7
Pozzolanic reactivity (mg $Ca(OH)_2$/g)		1050

Table 2
Mix descriptions

Binder	Portland cement or Portland cement/ metakaolin (90/10 wt/wt)
Water/binder ratio	0.4, 0.5, 0.6
Aggregate content (vol.%)	35

effects of variations in water/binder contents in the range 0.4–0.6 and the effect of metakaolin as a partial substitute (10% by mass) of Portland cement were investigated.

Table 3
Microhardness data—water/binder ratio=0.4

Portland cement binder	Knoop microhardness (*10^{-1} MPa) (at distance from aggregate surface in µm)					
	20	40	60	80	100	120
	38	56	75	51	40	51
	28	26	24	38	43	50
	82*	43	41	50	53	51
	33	33	46	41	54	55
	29	37	42	61	45	42
	28	41	43	33	39	37
Mean <40µm	36					
Mean >40µm			46			
Mean all data	43					

Portland cement/ metakaolin binder	Knoop microhardness (*10^{-1} MPa) (at distance from aggregate surface in µm)					
	20	40	60	80	100	120
	57	46	43	39	63	55
	28	49	47	42	67	37
	30	37	40	49	56	39
	46	30	43	84*	68	37
	34	48	70	51	54	46
	47	46	59	47	50	56
	48	50	44	46	57	46
Mean <40µm	43					
Mean >40µm			50			
Mean all data	47					

* Values excluded from mean values

2. Experimental

Microhardness testing uses small loads to create indentations with typical widths of 10–15 µm. Larger indentations would potentially overlap a number of hardened paste components, e.g. paste, voids, unhydrated grains. As a general note, microhardness tests are very sensitive to the surface smoothness and hence to sample preparation and polishing techniques.

The Portland cement (PC) used was a commercial product (CEM I: 42.5 N) and was sieved at 150 µm to remove any coarser particles or agglomerates prior to use. The metakaolin was also a commercially available product (MetaStar 501 from IMERYS Minerals). Chemical and physical properties of the Portland cement and the metakaolin used are shown in Table 1.

The aggregate used to prepare the model mortars was a silicate glass bead supplied by British Optical with a typical bead size of 1.00–1.25 mm and a specific gravity of 2.57 kg/m^3. The stability of such beads when in contact with the alkaline pore solution of the hydrated paste has previously

Table 4
Microhardness data—water/binder ratio=0.5

Portland cement binder	Knoop microhardness (*10^{-1} MPa) (at distance from aggregate surface in µm)				
	20	40	60	80	100
	30	30	29	44	37
	20	21	24	28	32
	30	23	53	34	28
	32	29	26	27	26
	25	31	35	32	35
	26	30	31	30	27
	28	27	82*	50	36
Mean <40µm	27				
Mean >40µm				33	
Mean all data			31		

Portland cement/ Metakaolin binder	Knoop microhardness (*10^{-1} MPa) (at distance from aggregate surface in µm)				
	20	40	60	80	100
	31	33	57	33	32
	20	28	33	32	44
	33	31	32	43	76*
	47	27	26	26	31
	25	27	33	33	30
	32	36	36	34	45
	43	38	34	37	46
	53	35	41	38	33
Mean <40µm	34				
Mean >40µm				36	
Mean all data			35		

* Values excluded from mean values

Table 5
Microhardness data—water/binder ratio=0.6

Portland cement binder	Knoop microhardness ($*10^{-1}$ MPa) (at distance from aggregate surface in μm)				
	20	40	60	80	100
	24	21	18	22	22
	19	24	42*	24	22
	46*	40*	32	25	29
	30	33	29	25	23
	26	26	27	25	24
	24	22	18	24	23
	24	23	21	23	26
	23	23	21	24	23
Mean <40μm	24				
Mean >40μm				24	
Mean all data			24		
Portland cement/ Metakaolin binder	**Knoop microhardness ($*10^{-1}$ MPa) (at distance from aggregate surface in μm)**				
	20	40	60	80	100
	50	41	38	34	48
	64	33	26	30	29
	38	32	33	37	34
	31	27	32	28	25
	37	42	58	42	35
Mean <40μm	40				
Mean >40μm				35	
Mean all data			37		

* Values excluded from mean values

been reported [1,10]. The compositions of mortars are given in Table 2.

A planetary mixer was used to prepare all samples, the cement and metakaolin being preblended. The components were mixed and cast into cylindrical moulds (60 mm diameter, 90 mm depth), which were rotated slowly end-over-end for 24 h (at 8–10 rpm) to inhibit segregation. The samples were then demoulded and immersed in 0.032 M NaOH at 20 °C for 60 days. At the end of this period, the top (cast face) 12 mm of the sample cylinder was removed using a diamond saw. A further slice approximately 15 mm thick was then removed for subsequent microhardness measurements. These sections were immersed in isopropanol in an ultrasonic bath to displace moisture from the samples, thus stopping further hydration and stabilising the samples. They were stored in a desiccator over silica gel and carbosorb.

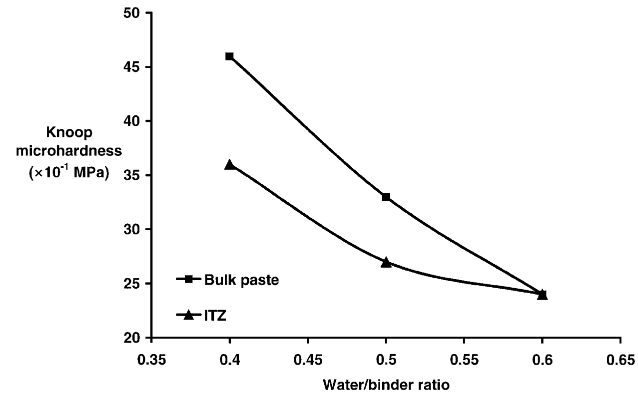

Fig. 1. Variation in microhardness of bulk paste and ITZ with water/binder ratio (Portland cement binder).

Samples were polished on fixed diamond abrasive pads using polishing oil lubricant, no water being used. Successively finer grades of abrasive were used to obtain the necessary surface finish. Care was taken with coarser grinding papers not to damage the surface by "pulling out" aggregate beads. After polishing, the sample surfaces were sprayed with bromo-cresol green indicator solution. The resulting coloration of the surface increased contrast between indentations and their surrounding areas, which thus facilitated the observation of indentations when making measurements. Samples were mounted on glass plates ensuring that the plate base and measurement surface were parallel.

Microhardness measurements were made using a Buehler Micromet Hardness Tester fitted with a Knoop indenter. Measurements were obtained using a 25-g load. The first indentation was made 20 μm from the aggregate surface

Table 6
Statistical analysis and significance levels

Pairs of means (mean value in bold type) 1	2	t	No. of degrees of freedom	Significance level
36 Portland cement, water/binder 0.4, ITZ	**46** Portland cement, water/binder 0.4, bulk	2.94	33	1%
27 Portland cement, water/binder 0.5, ITZ	**33** Portland cement, water/binder 0.5, bulk	2.6	32	2%
24 Portland cement, water/binder 0.6, ITZ	**24** Portland cement, water/binder 0.6, bulk	0.45	35	Not significant at 5%
43 Metakaolin mix, water/binder 0.4, ITZ	**50** Metakaolin mix, water/binder 0.4, bulk	2.42	39	2%
34 Metakaolin mix, water/binder 0.5, ITZ	**36** Metakaolin mix, water/binder 0.5, bulk	0.94	37	Not significant at 5%
40 Metakaolin mix, water/binder 0.6, ITZ	**35** Metakaolin mix, water/binder 0.6, bulk	1.08	23	Not significant at 5%
46 Portland cement, water/binder 0.4, bulk	**50** Metakaolin mix, water/binder 0.4, bulk	1.45	49	Not significant at 5%
33 Portland cement, water/binder 0.5, bulk	**36** Metakaolin mix, water/binder 0.5, bulk	1.24	41	Not significant at 5%
24 Portland cement, water/binder 0.6, bulk	**35** Metakaolin mix, water/binder 0.6, bulk	5.69	36	<0.1%
36 Portland cement, water/binder 0.4, ITZ	**43** Metakaolin mix, water/binder 0.4, ITZ	1.93	23	Not significant at 5%
27 Portland cement, water/binder 0.5, ITZ	**34** Metakaolin mix, water/binder 0.5, ITZ	2.62	28	2%
24 Portland cement, water/binder 0.6, ITZ	**40** Metakaolin mix, water/binder 0.6, ITZ	4.89	22	<0.1%

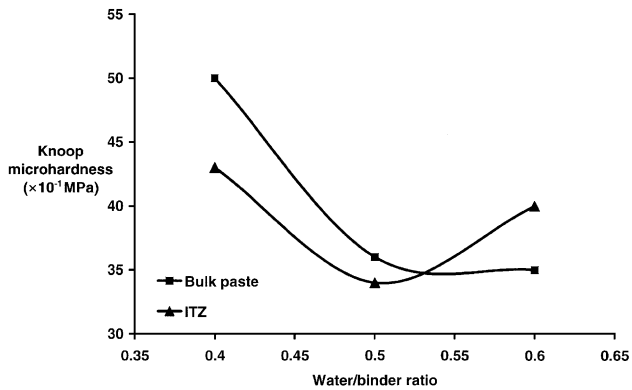

Fig. 2. Variation in microhardness of bulk paste and ITZ with water/binder ratio (Portland cement/metakaolin binder).

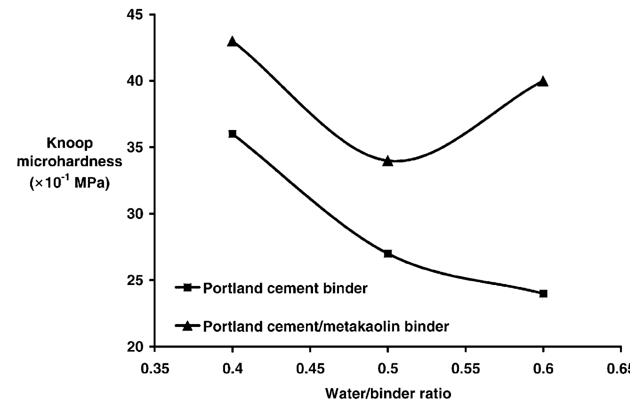

Fig. 4. Variation in microhardness of ITZ with water/binder ratio and binder composition.

with the long axis of the Knoop indentation parallel to the aggregate surface. Care was taken to avoid the presence of voids, other aggregates and sample edges. Subsequent indentations were made approximately 20 μm apart moving away from the aggregate surface and were centred on a line perpendicular to the aggregate surface. Samples prepared at a water/binder ratio of 0.6 were indented up to 120 μm from the aggregate surface. Mean values at the 100- and 120-μm distances showed only small differences, and, therefore, samples at lower water/binder ratios were indented up to 100 μm from the aggregate surface.

3. Results and discussion

Knoop microhardness data are shown in Tables 3–5. Results marked with an asterisk have not been included in the tabulated mean values. Asterisked values were excluded as they were more than 1.96 standard deviations from the mean for all data values obtained for a specific set. The area within 40 μm of the surface is taken to represent the aggregate area of influence, i.e. the ITZ. The region more than 40 μm from the aggregate surface is taken to represent the bulk paste not affected by the aggregate.

Statistical analysis, using *t* tests, was performed on mean values of sets of data in order to determine whether the means were significantly different from one another. The *t* values and their significance levels are shown in Table 6. Important trends in the mean values are shown in Figs. 1–4.

From Fig. 1, it appears that in Portland cement specimens, the ITZ is softer (more porous) than the bulk matrix at lower water/binder ratios. The microhardness of the ITZ is 22% lower than the bulk matrix at a water/binder ratio of 0.4 and is 18% lower at a water/binder ratio of 0.5. Statistical analysis (Table 6) confirms that this effect is significant at more than the 95% confidence level for specimens of water/binder ratios of 0.4 and 0.5 but not for those of a water/binder ratio of 0.6.

From Fig. 2, it appears that in the specimens prepared with Portland cement and 10% metakaolin as binder (metakaolin samples), the microhardness of the ITZ is similar to that of the bulk matrix. Statistical analysis (Table 6) confirms that only for the specimens of a water/binder ratio of 0.4 was there any significant lowering (at more than the 95% confidence level) of the microhardness of the ITZ compared with that of the bulk matrix.

From Figs. 3 and 4, it appears that the microhardness of the bulk matrix and, to a greater degree, the ITZ is increased when metakaolin is used as a partial replacement for Portland cement. Statistical analysis (Table 6), however, indicates that the effect is significant at more than the 95% confidence level only at a water/binder ratio of 0.6 for the bulk and water/binder ratios of 0.5 and 0.6 for the ITZ.

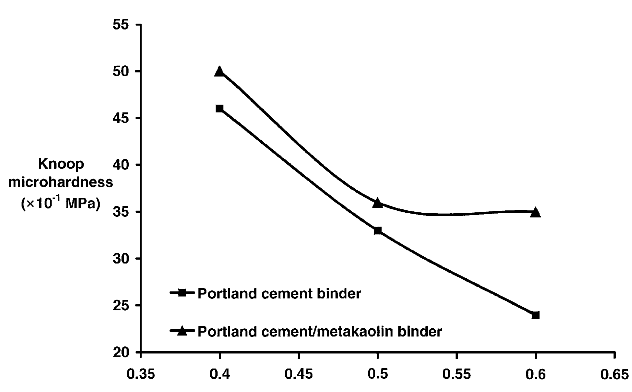

Fig. 3. Variation in microhardness of bulk paste with water/binder ratio and binder composition.

4. Conclusions

The ITZ (within 40 μm of the aggregate surface) was softer than the bulk region for control samples prepared with Portland cement at water/binder ratios of 0.4 and 0.5. The difference between the mean microhardnesses of the ITZ and bulk regions was not significantly different at a water/binder ratio of 0.6. This suggests that the influence of the ITZ will be more marked at lower water/binder ratios, e.g. 0.4, which are typically used in concretes for demanding applications.

For metakaolin samples, the difference between the mean microhardness of the ITZ and bulk regions at a water/binder ratio of 0.4 was less significant than for the control samples. At the higher water/binder ratios of 0.5 and 0.6, the differences between ITZ and bulk regions were not significant, suggesting that metakaolin has a greater effect on the microstructural strength of the ITZ. This, in turn, suggests that metakaolin is contributing to a more homogeneous microstructure in the HCP.

Metakaolin increased microhardness relative to the control samples particularly at water/binder ratios of 0.5 and 0.6, consistent with the hypothesis that metakaolin densifies and strengthens the microstructure of the hydrated cement matrix.

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