Journal of the European Ceramic Society 22 (2002) 1437–1445

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Measurement of hardness on traditional ceramics

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Received 8 June 2001; received in revised form 31 August 2001; accepted 19 September 2001

Abstract

To reveal quantitatively the hardness of clayware and stoneware, Mohs, Vickers (micro and macro) and superficial Rockwell indentation measurements were applied to roofing tiles with different porosity. This work discusses the comparison of different indentation results, indentation size effect on porous clayware and the effect of microstructure on hardness of tiles. As a result, for Vickers indentation test, the critical indent load was found to 0.5 and 1 kg for soft and hard tiles, respectively, and indentation size/load effect (ISE) appeared clearly in hard tiles. The relationship between load (*P*) and indent size (*d*) on tiles was very close to a modified Myer's law. The PSR (proportional specimen resistance) model gave $P/d = 0.67 + 0.02d$, $P/d = 1.33 + 0.1d$ for soft and hard tiles, respectively. It was found that there were no difference in hardness of tiles mounted with epoxy or copper and as-received sample under superficial Rockwell indentation. These concepts on the harness evaluation of tiles would be applicable to other clayware.

Keywords: Hardness; Indentation; Stoneware; Tiles

1. Introduction

Recently, discovery of old science and technology through traditional ceramics, especially pottery, has been of interest in archaeology and history as well as in modern ceramics due to development of characterization methods and diverse applications.[1,2] Pottery (ceramics) is classified into several groups depending on raw materials and firing temperature, and some of them containing pores, stoneware and clayware, are divided into two categories in terms of hardness. This hardness can be measured with the familiar, simple and convenient test, although water absorption, density, porosity, strength, and fracture toughness tests are also considered for physical and mechanical properties of clayware and stoneware. The hardness measurements of pottery give some reliable information on maximum firing temperature and raw materials, and suggest approximate strengths and wear rates.[3]

Although data from Mohs scratch test, Knoop, Vickers and Rockwell indentation methods for hardness of ceramics is available and the hardness database has increased, the experimental conditions are not constant and ambiguous so that the comparison of data is quite difficult.[4,5] Also, data on clayware and stoneware is still lacking. It is well known that the variation of hardness with load and hence indentation size/load effect (ISE) has been observed in a very wide range of materials, mainly engineering ceramics.[6–9] However the ISE has not been studied in pottery (clayware and stoneware) and is not clear whether it would be applicable for porous ceramics with complicated microstructures like composite materials.

In this work, several hardness measurements, Mohs, Vickers (macro and micro) and superficial Rockwell tests, were made on roofing tiles and the results were compared. The ISE was applied to tiles and the physical meaning of the ISE result on tiles was discussed based on the previous suggestions by others.[6–9] Finally, specimen preparation methods using different materials were compared to hardness results by superficial Rockwell indenter to confirm that a support for tile specimen must be of sufficient rigidity to prevent its permanent deformation during indentation.

2. Experimental methods

Six different roofing tiles (MS, SS, KS, MH, SH, KH), which have different porosity, were used for

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0955-2219/02/$ - see front matter
PII: S0955-2219(01)00457-5

materials for the indentation test. After cutting samples with a dimension of $1.5\times1.5\times1.5$ cm^3, they were mounted with epoxy resin and polished down to 0.5 μm with diamond paste and finally coated with gold in a vacuum to improve reflectivity in order to precisely measure the indention's dimensions under microscopy.

For measurement of hardness, a Mohs scratch tester (HS94-2012, Hansol Edu., Korea), a micro Vickers tester (MVK-E3, Mitutoyo, Japan) loading at 200, 300 and 500 g load and macro Vickers tester (AVK-2, Akashi, Japan) loading at 1, 2 and 5 kg loads for 15 s were used. Also, a superficial Rockwell hardness tester (Indentec, UK) was employed with 1/16 in. steel-ball indenters loading at a minor load of 3 kg and major load of 15, 30 and 45 kg. Three different mounting procedures were used for measuring superficial Rockwell hardness testing: epoxy molding (cold mounting), copper molding (hot mounting) and no mounting (on plane-surface anvil). Ten determinations were performed on each test piece and the results averaged. Porosity and water absorption of tiles followed the method ASTM C20-92 and microstructure images were obtained by scanning electron microscopy (SEM, S-3500N, Hitachi, Japan). Crystal phases of tiles were investigated using an X-ray diffractometer (XRD, XD-D1 Shimadzu, Japan).

3. Result

Mohs hardness of tiles is given in Table 1 and is classified into two groups by the scale. There is not a clear boundary between soft and hard tiles, but the soft type has a value of 2–3 and the hard type has a value of 5–6.[10]

The Vickers hardness of tiles under different loads is shown in Fig. 1. In the soft group (MS, SS, KS), at a load of 0.2–1 kg, MS has 450–740 MPa, but it decreased to 150 MPa under a 5 kg load. For SS and KS, the hardness showed very little difference and a similar trend with increasing load to the MS sample. For hard tiles (MH, SH, KH), the hardness decreased with increasing load as observed in the soft ones Hardness values were in the range 1.7–3.5 GPa until a load of 2 kg for MH (Fig. 1b). Above a 2 kg load, however, the hardness suddenly dropped and became very low under a 5 kg load. For soft tile, with up to a 1 kg load, the hardness was 500–600 MPa with a standard deviation of 60–140 MPa. Up to 2 kg for hard tiles, the hardness was determined to 2.5–3.0 GPa. The standard deviation of the hardness of tiles from Fig. 1 is compared in Table 2 with indent size (Fig. 2). It can be seen that the scatter has a tendency to decrease as the load increased, while the indent size showed an inverse trend with increasing loads. The result suggests that at lower loads, the deviation is large because of the non-uniform microstructure of tiles.

With a superficial Rockwell tester, hardness of tiles with different mounting methods was compared: without mounting, with mounting of copper metal and with epoxy resin. Table 3 shows the result of only hard tile because the soft one is not hard not enough to use the superficial Rockwell tester measure because of the heavy loads (15–45 kg) required. Rockwell indentation can be observed on only hard tiles (Fig. 3). The hardness decreased as load increased irrespective of mounting methods and there was no difference between three hard tiles under 45T (highest load in this test). It seems that samples without mounting had a higher hardness num-

Table 1
Mohs scale of roofing tiles

Samples	MS	SS	KS	MH	SH	KH
Mohs	3	3–3.5	3	5	6.5	5.5
Types		Soft			Hard	

Table 2
Standard deviation of hardness (Hv) and indent size of soft and hard tiles as a function of indent loads

Samples	Load (kg)	Standard deviation (MPa)	Mean indent size (μm)
MS	0.2	137.1	78.2
	0.3	65.1	95.3
	0.5	63.9	134
	1	95.6	185
	2	86.6	331
	5	13.5	883
SS	0.2	120.0	81.5
	0.3	60.9	94.9
	0.5	91.4	137
	1	56.9	191
	2	70.6	356
	5	6.1	943
KS	0.2	97.3	84.2
	0.3	75.1	94.1
	0.5	81.4	135
	1	49.5	196
	2	52.2	369
	5	0.5	986
MH	0.2	736	37
	0.5	410	63.2
	1	451	98.1
	2	506	128
	5	138	458
SH	0.2	756	38.4
	0.5	598	65.8
	1	502	99.6
	2	468	139
	5	128	407
KH	0.2	599	36.9
	0.5	600	62.8
	1	417	95.2
	2	352	130
	5	121	430

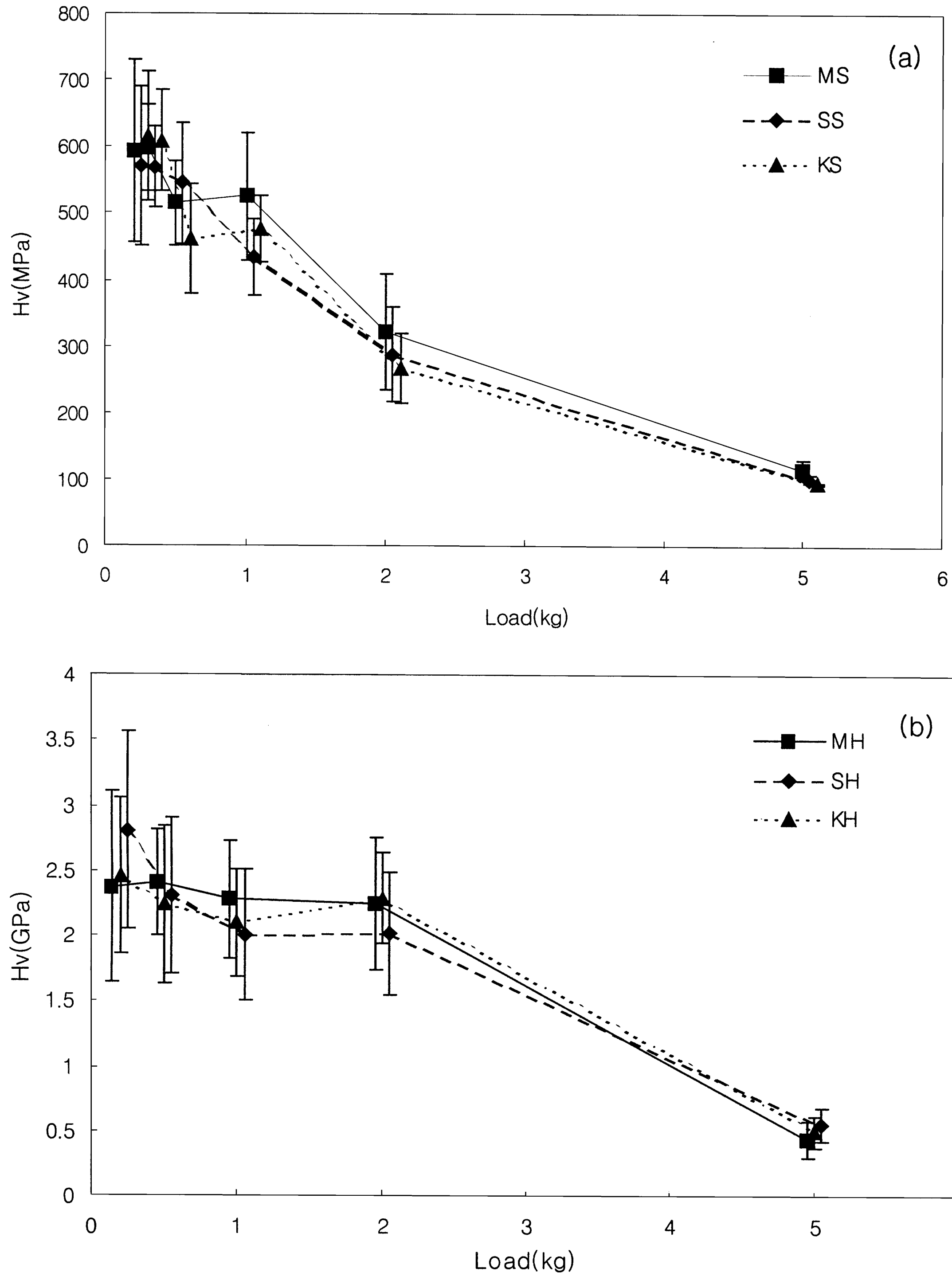


Fig. 1. Vickers hardness of soft (a) and hard (b) tiles as a function of indent loads.

ber (0.5–6.0) than samples with mounting (copper and epoxy). However, a careful observation of data in Table 3 shows that there is not a statistically significant difference in these values so that the hardness tested under the same load showed nearly same value. When hardness of tiles with copper mounting was compared to those of epoxy mounting, there were no difference between the two different mounting methods.

In Table 4, porosity, water absorption and the crystal phase data of the tiles are given. Tiles with porous structure has a wide range of porosity depending on green density and firing temperature, so that the hard

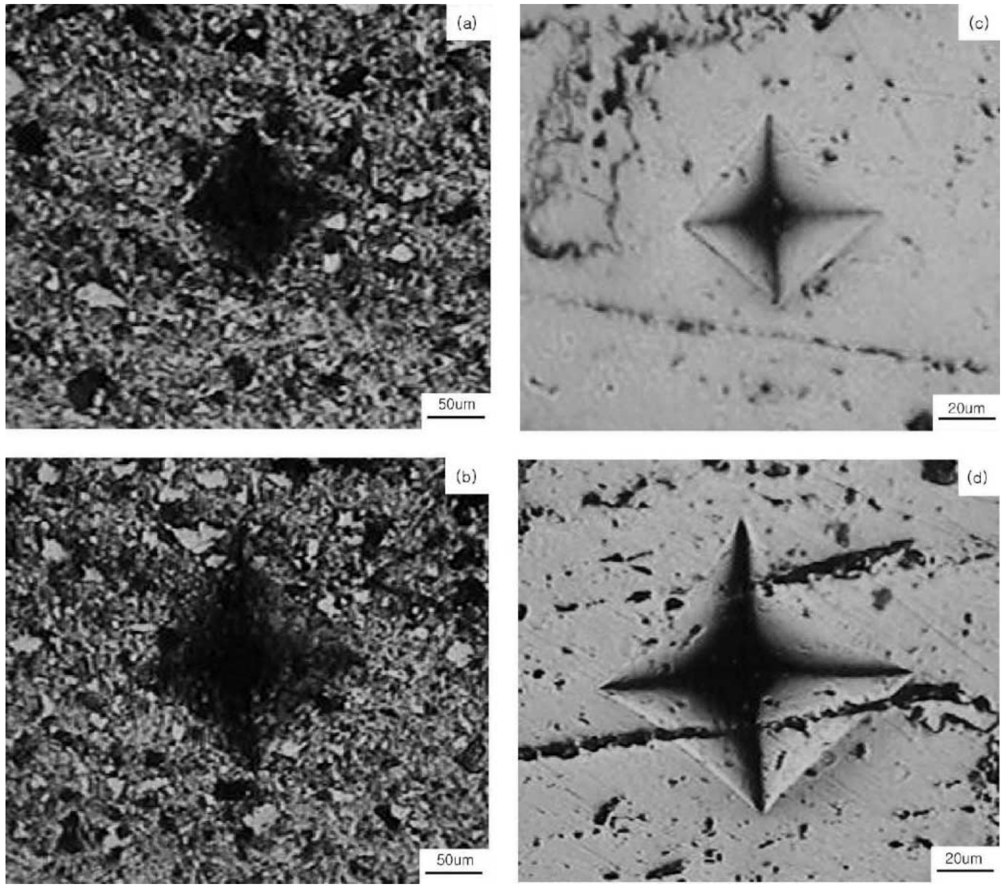


Fig. 2. Vickers indentation at different forces: (a) 0.5 kg and (b) 1 kg on soft tiles, and (c) 0.5 kg and (d) 1 kg on hard tiles.

Table 3
Comparison of the average hardness and the standard deviation of superficial Rockwell hardness number (HR) for different sample preparation methods

Samples	Mounting method (materials)	Number of HR (15, 30, 45)T		
		HR15T	HR30T	HR45T
MH	No[a]	74.5±5.27	61.7±5.59	42.5±5.17
	Copper	80.6±5.54	61.2±5.03	44.5±5.74
	Epoxy	80.8±3.58	61.5±5.59	45.2±4.13
SH	No	75.7±4.85	63.5±5.65	41.5±5.95
	Copper	77.2±4.79	65.4±5.78	42.7±5.50
	Epoxy	76.5±3.88	66.2±4.23	43.6±4.78
KH	No	72.2±5.43	58.6±8.45	41.8±4.04
	Copper	75.2±5.43	60.8±6.19	39.1±4.60
	Epoxy	75.7±5.54	62.1±8.44	42.2±5.20

[a] Indentation test was carried out on a steel anvil without mounting samples.

and soft tiles in Table 4 have different porosities of 11–18 and 26–44%, respectively. Crystal phases found in the tiles are clearly classified into groups (in Table 4): the soft type has feldspar and the hard type has mullite. The feldspar appeared in the tile matrix comes from unreacted one which was remained after a reaction at high temperature, at least 1100 °C to produce a glass phase or react with quartz. At higher temperature, a mullite phase is found in the matrix. Thus, the presence of mullite indicates that the tile was fired at high temperature, above 1100 °C. Therefore, the hard type was formed at high firing temperature which produced mullite and glass in the matrix, which works to reduce pores and make a dense structure (Fig. 4).

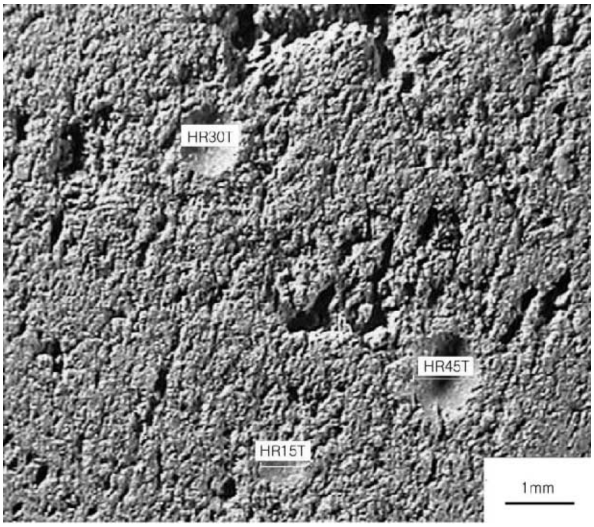


Fig. 3. Superficial Rockwell indentation at different forces (15, 30 and 45 kg) on hard tiles.

4. Discussion

Hard and soft tiles had a high standard deviation of hardness when a Vickers indenter was used because traditional ceramics like roofing tiles have non-uniform microstructure consisting of pores and many mineral phases in the matrix (Fig. 4). Regarding the Vickers test, it has a disadvantage in the experimental process because determining the diagonal length of indents has a certain degree of error which is dependent on the load level. These factors might increase the standard deviation of hardness with the Vickers indenter. However, one of the other indentation methods, the superficial Rockwell test, has an advantage compared to the Vickers method in terms of analysis and experiment: because of the wide contacting area, which covers non-uniform microstructure, and the measurement of spherical indents' volume dimension (depth) rather than diagonal indents (length) on the surface, the hardness error is reduced.

The change of hardness with load as shown in Fig. 5 is affected by the indent's size and the relationship between indent size and load (ISE) has been studied since Myer's suggestion.[6] The classic theory to explain ISE is based on Eq. (1):

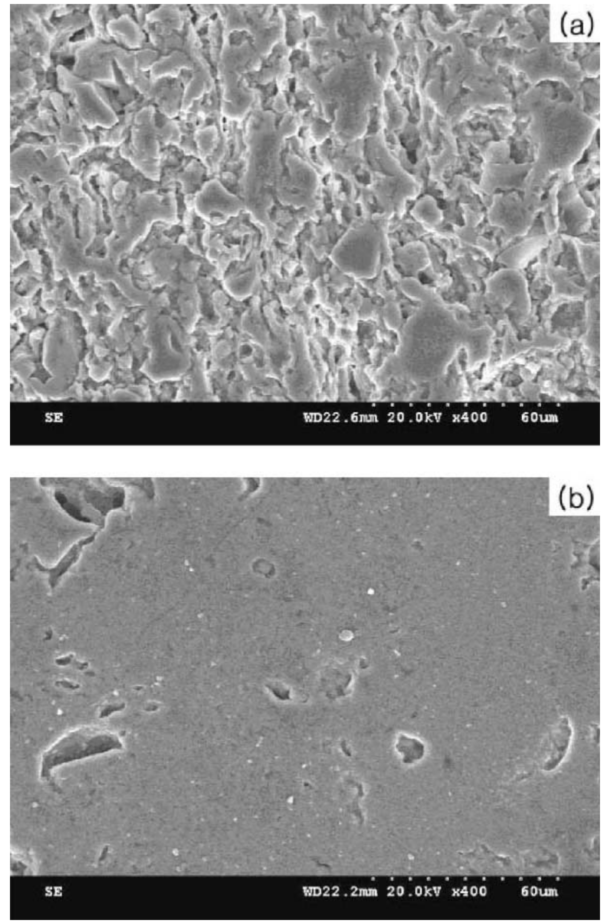


Fig. 4. Microstructures of roofing tiles using SEM. (a) Soft tiles, MS shows porous microstructure with clay agglomerates, while (b) hard one MH dense microstructure with linking of clay particles and closure of channels with spherical-shaped pores in the matrix.

$$P = Ad^n \quad (1)$$

where P and d mean load and indent size, respectively, and A and n are constants to follow Myer's law. Later, Li and Bradt suggested a modified Myer's law, known as proportional specimen resistance (PSR)[6,7] given by Eq. (2):

Table 4
Porosity, water absorption, pore size, crystal phases and mineral phases contents (wt.%) in roofing tiles

Samples		MS	SS	KS	MH	SH	KH
Apparent porosity (%)		44.4	25.7	38.3	18.7	16.6	11.7
Water absorption (%)		25.1	20.1	21.2	17.6	8.2	5.1
Crystal phases		Quartz, feldspar	Quartz, feldspar	Quartz, feldspar	Quartz, mullite	Quartz, mullite, glass	Quartz, mullite, glass, crystoballite
Mineral phases content (wt.%)[a]	Quartz	9.87	29.4	24.5	35.7	22.9	38.0
	Feldspar	12.1	11.9	13.1	14.9	16.7	14.6
	Kaolin	78.9	58.7	62.4	49.3	60.3	47.4

[a] Calculated by XRF analysis.

$$P/d = a_1 + a_2 d \quad (2)$$

where, a_1 and a_2 are experimental constants in the PSR model. The ISE boundary (hardness independent on loads) appears clearly in hard tiles but not in soft ones in Fig. 1. For hard tiles, the ISE boundary was found at around 1 kg load which is a critical indent load. However, in the soft tiles, the critical indent load, which appeared in only MS and KS samples, was 0.5 kg. In general, polycrystalline ceramics (oxides and mono oxides) have values of 0.2–0.6 and 1.4–1.8 for A and n in Eq. (1), respectively. The parameters A and n of MH, SH, and KH determined from Fig. 6 are presented in Table 5 and are close to those of polycrystalline mullite ($A = 0.28$, $n = 1.70$).[6] Considering a dense ceramic, alumina (99.5%), which has $A = 0.46$, $n = 1.74$, tiles with negative

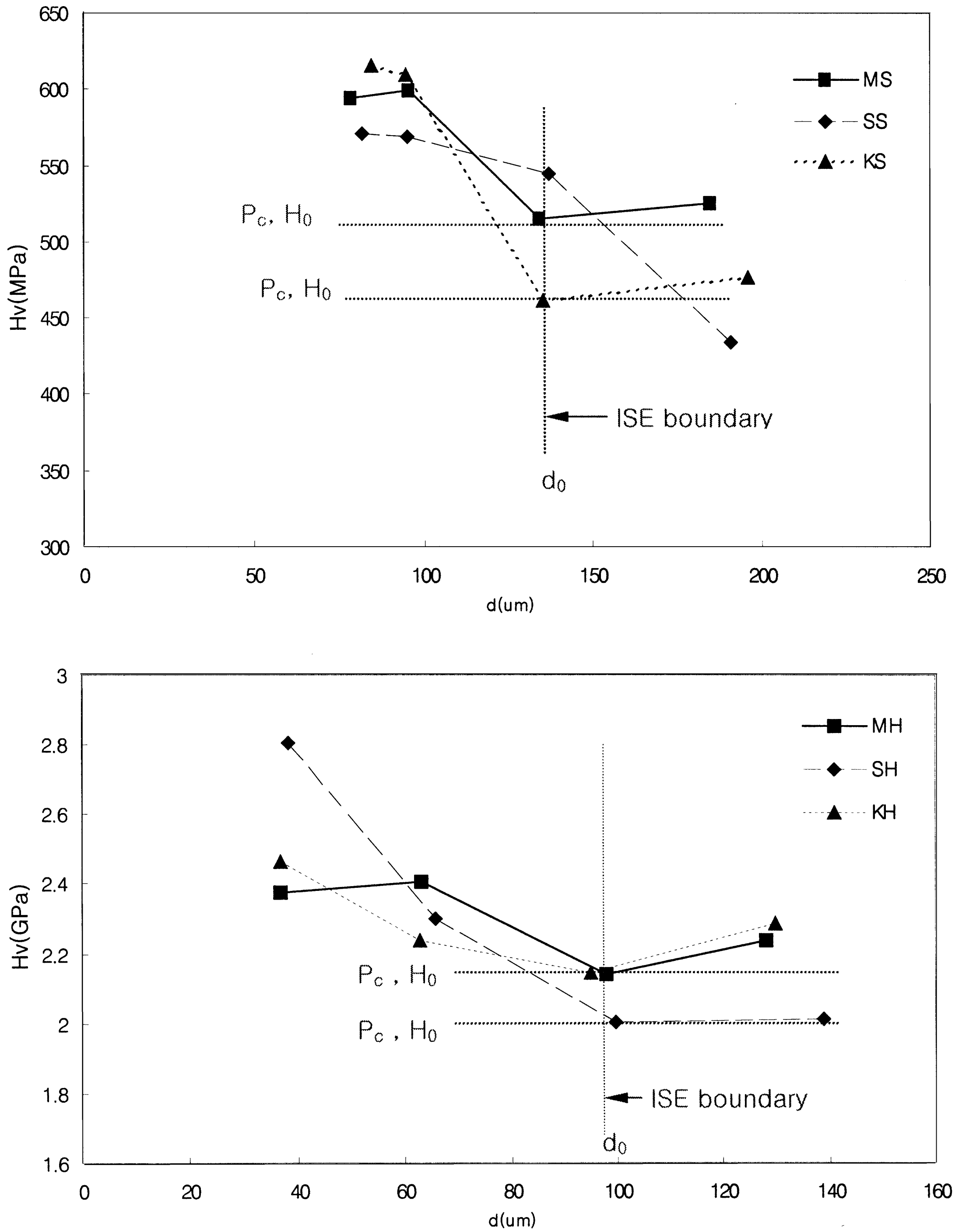
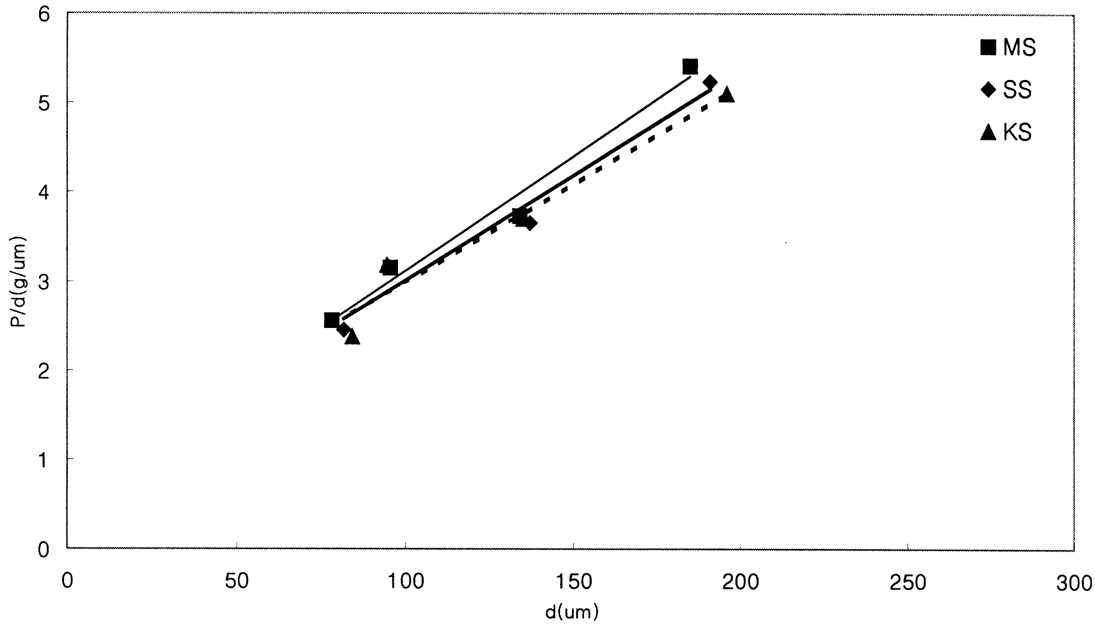


Fig. 5. Hardness of soft (a) and hard (b) tiles against indent size (d) showing ISE boundaries where, Ho is a load-independent true hardness and Pc is a critical indentation test load, and do is a characteristic indentation size.



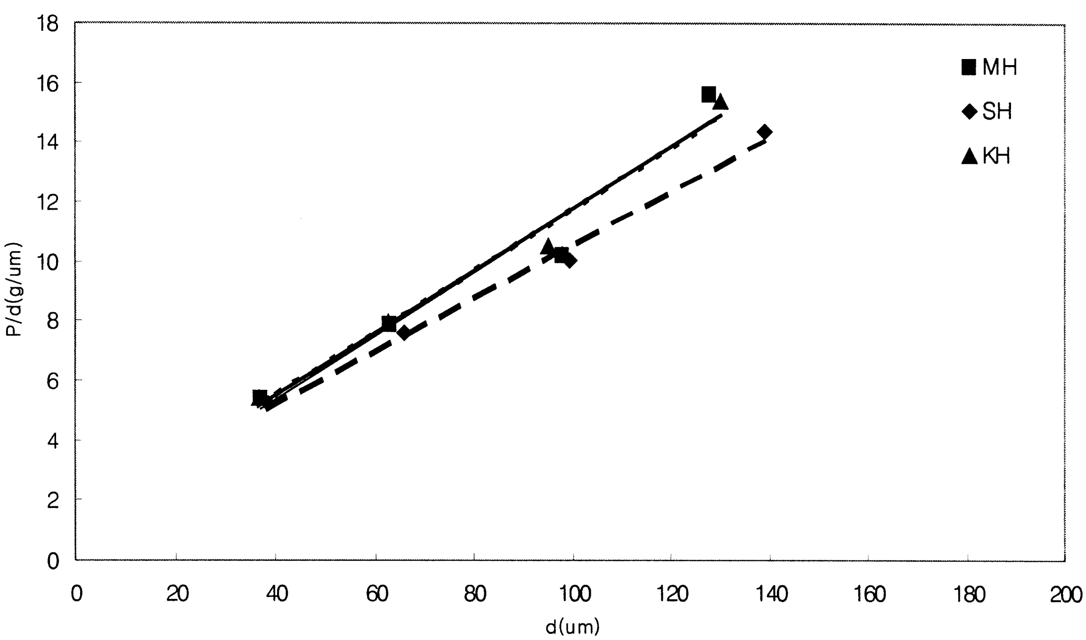


Fig. 6. Relationship between P/d and d for (a) soft tiles and (b) hard tiles.

Table 5
Several parameters in the relationship between load and indent size

Materials	P_c (g)	d_o (um)	Myer's law		PSR Model				
			A (g/μm^n)	n	a_1 (g/μm)	Average a_1 (g/μm)	a_2 (g/μm^2)	Average a_2 (g/μm^2)	Pc/do^2 (g/μm^2)
MS	500	140	−1.15	1.83	0.56	0.67	0.026	0.024	0.026
KS	500	145	−1.09	1.84	0.76		0.022		0.024
SS	500	135	−1.18	1.78	0.68		0.024		0.027
MH	1000	97	−0.54	1.80	1.07	1.33	0.107	0.100	0.106
SH	1000	100	−0.51	1.77	1.61		0.089		0.100
KH	1000	94	−0.53	1.80	1.32		0.105		0.113

where P_c = critical indentation test load and d_o = indentation size at the onset of the load-independent hardness (Ho).

values of A are supposed to result from porous and not well-sintered microstructure. The results of Table 5 suggest that, apparently, large negative A values related more to soft microstructure. In fact, the parameters in Eq. (1) do not give any physical meaning because the units of A and n are peculiar.

However, for the PSR coefficients from Eq. (2), the harder materials, with higher Young's moduli, generally have higher a_1 values.[6] Based on the PSR model which is very close to experimental result,[6] a_1 values of SH, KH, MH, KS, SS, and MS show a decreasing order in Table 5. Thus suggesting a classification of two groups, soft and hard types having average a_1 values of 0.67 and 1.33, respectively. The relative a_1 rank of tiles determined from the PSR model is related to the rank from other indentation methods, Mohs and superficial Rockwell tests in Table 6. Li and Bradt showed that a linear relationship of a_1 versus E on several ceramics is evident, where the regression coefficient is equal to 0.99.[6] The following equation is an empirical equation based on Li and Bradt's result, which can be used for predicting the elastic constant of tiles.

$$E = 124.5\ a_1 + 85.7 \quad (3)$$

where a_1 is the PSR model parameter and E the Young's modulus. The elastic constants of tiles were predicted to be around 170 GPa for the soft type and 265 GPa for the hard one, which do not match with the previous experimental data, 9.3 GPa and 22–27 GPa for soft and hard tiles[11] and are out of the range of around 25–50 GPa of Young's modulus for 0.5–2 GPa of Vickers hardness from another source.[12] Thus, the deviation of Young's modulus using Eq. (3) when compared to experimental data is quite large, so that the problem of solving the relationship between a_1 and E continues.

The a_2 coefficient of Eq. (2) is directly related to the test specimen's load-independent hardness and also is equal to the quantity (P_c/d_o^2) from the PSR model.[6,7] In Table 5, a_2 values of tiles obtained from the regression analysis from Fig. 6 are very close to calculated values of P_c/d_o^2 using the data from Fig. 5. It is suggested that while a_1 is related to the elastic properties of the material, a_2 is related to the plastic properties of the material. In Table 5, a_2 of hard tiles (0.100) is 4 times greater than that of soft ones (0.024). P_c/d_o^2 in Table 5 and the true hardness in Table 6 also have a similar relationship between soft and hard tiles.

Very recently, Gong et al.[8,9] suggested a modified PSR model designed based on the consideration of the effect of a machining-induced, residually stressed surface on the hardness measurements, giving

$$P = P_o + a_1 d + a_2 d^2 \quad (4)$$

where P_o, a_1 and a_2 are constants. When our data were applied to the model, a_2 had negative values for all materials, suggesting a_2 has no physical meaning although a_2 value is related to the true hardness of material according to Gong.[9] The model is available only in the very low load range where no cracking due to indention occurs. Thus, from our examination of the model, it can be concluded that, within the ISB boundary, using the PSR model to classify samples into the two groups in terms of purely the relationship between load and indent size is appropriate for low hardness materials like tiles. Physical and mechanical properties of traditional ceramics like roofing tiles, unlike single crystals, are strongly dependent on microstructure: tiles are composites which can consist of quartz, feldspar and mullite crystal phases in matrixes with varying pore size and shape, porosity, and interface states between clay (agglomerates) and quartz or feldspar. Roofing tiles consist of spinel, mullite, crystoballite, glass and remained quartz, feldspar and clay. Two factors determine the composition of roofing tiles; the raw materials used, which are mainly clay, quartz and feldspar and the firing temperature (Fig. 4, Table 3).[10] Therefore, the indents of tiles (Figs. 2 and 3) were formed by plastic deformation of a mixture of clay agglomerates, pores and quartz. As shown in Table 4, the soft type fired at low temperature has low hardness because of less dense microstructure of clay and remained feldspar, while the hard one has high hardness resulting from the dense structure of mullite formed at above 1100 °C and of glass appearing at 1100–1200 °C. These connect the clay, quartz and other minerals to increase the hard strength of tiles (Fig. 4).

Hardness values of tiles prepared by three mounting methods (without mounting, with mounting on copper metal (Hv = 443 MPa at 0.2 kg load) and with epoxy

Table 6
Comparison of hardness roofing tiles by different indentation methods

Samples	MS	SS	KS	MH	SH	KH
Mohs	3	3–3.5	3	5	6.5	5.5
Superficial Rockwell (HR15T) no mounting	–	–	–	74.5±5.27	75.7±4.85	72.2±5.43
True hardness[a] (Vickers)	520 MPa	Not constant	470MPa	2.15 GPa	2.0 GPa	2.15 Gpa

[a] Ho: obtained from Fig. 5.

resin (Hv = 246 MPa, at 0.2 kg load) showed no significant difference when tested using a superficial Rockwell indenter. The standard deviation of the results are nearly the same as shown in Table 3, which results from high load indentation on non-uniform microstructures. Those factors do not much affect the hardness of tiles because of high load indentation under the superficial Rockwell indenter, which produced indent sizes of 550, 760 and 820 μm for 15T, 30T and 45T of load, respectively, on the MH sample (with epoxy mounting). It was confirmed that the mounting method did not affect hardness values when tiles were tested using the superficial Rockwell indentation method.

5. Conclusions

The hardness of tiles was dependent on the microstructure consisting of pores with complex matrix. Tiles were classified to two groups in terms of hardness. Under Vickers indenter, soft and hard tiles showed different critical indent loads, 0.5 and 1 kg, respectively. The trend of decreasing hardness with increasing load appeared clearly in the lower range of load, and the ISE (indentation size/load effect) boundary was distinct in hard tiles. Regarding the ISE, the indentation load and the resulting indention size from the hardness of roofing tiles was close to a modified Myer's model. Superficial Rockwell indention data is only available for hard-type tiles, not soft types and does not suggest that there is a difference between hardness values when tiles were mounted using copper or epoxy, or when tested as-received (without mounting).

Acknowledgements

This paper was funded by Research Foundation of Engineering College, Sunchon National University, South Korea. The authors wish to thank Professor D.K. Kim's (KAIST) discussion on this paper.

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