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# Surface hydration and nanoindentation of silicate glasses

Damir R. Tadjiev and Russell J. Hand<sup>1</sup>

*Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building  
Mappin Street, Sheffield S1 3JD, UK*

## Abstract

The near-surface mechanical properties of glasses and differences in mechanical behaviour between high and low durability silicate glasses are investigated. Nanoindentation is used to examine the effect of hydration on the near-surface mechanical properties of silicate glasses with varying degrees of chemical durability. It is shown that hydration has little if any effect on high durability glasses even at long immersion times, whereas in low durable glasses hydration reduces the near-surface mechanical properties significantly and the thickness of hydrated layer may exceed the indentation depth. In addition an attempt is made to measure the thickness and mechanical properties of hydrated layer in low durability glasses where influence of the substrate is negligible.

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**Keywords:** silicate glasses, hydration, nanoindentation, near-surface mechanical properties, hydrated layer

## 1. Introduction

It is well known that surfaces of silicate glasses hydrate when in water containing environments, including normal air.<sup>1-7</sup> Hydration degrades the surface of the glass<sup>7-9</sup> and may affect glass strength due to interaction of hydrated layer with strength controlling defects.<sup>9,10</sup> Although, the phenomenon of glass surface hydration is still not fully understood, most researchers agree that hydration involves several competing processes, the most significant of which are leaching (often referred to as ion exchange) and network dissolution.<sup>11-15</sup> These processes can occur simultaneously, although, depending on environmental conditions (such as pH and temperature) as well as chemical durability of glass, one or other of the processes can be predominant.<sup>8,14-17</sup> On the other hand it has been suggested that depending on durability of glasses, different types of hydrated surface layers can be formed<sup>18</sup> and that the structure of hydrated layer will be different for durable and non-durable glass.<sup>2,15</sup>

The effect of hydration on the surfaces of silicate glasses has been traditionally assessed by measuring alkali/hydrogen concentration profiles in the glass surface.<sup>2-4,9</sup> Although, the use of such approach provides information on the chemical composition of the hydrated region, it is still not clear how, and to what extent, hydration affects the near-surface mechanical properties of glasses. Furthermore, concentration profiles do not give information on the mechanical properties of hydrated layer. Recent results obtained by nanoindentation show that hydration alters the near-surface mechanical properties of silicate glasses and that composition is the main factor that determines resistance of glass to attack by an aqueous solution.<sup>19,20</sup> In this work an attempt is made to examine whether nanoindentation can be used to measure the thickness and mechanical properties of the hydrated layer as well as to confirm previously reported results.

Hence, the ultimate purpose of this work is to access hydration phenomena in silicate glasses by means of shallow depth (<80 nm) nanoindentation. The relationships between the chemical durability of silicate glasses and their composition and mechanical properties have been investigated. For these purposes a series of glasses with varying degrees of chemical durability are examined before and after hydration. Hydration of the surface is achieved by immersion of glasses into water at various periods. Atomic force microscopy (AFM) is used to assess surface deterioration in the course of hydration as well as to ensure that surface roughness of as prepared glasses does not affect the accuracy of nanoindentation measurements.

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<sup>1</sup>Corresponding author. Tel.: +44 (0)114 2225465. Email address: [r.hand@shef.ac.uk](mailto:r.hand@shef.ac.uk) (R.J. Hand).

## 2. Experimental procedure

### 2.1 Materials and sample preparation

Glasses (see Table 1) were prepared by melting powdered mixtures of oxide and carbonate powders in a platinum crucible at 1450°C for 5 h, with 1 h to achieve a batch free melt and 4 h stirring with a platinum stirrer. After melting each melt was poured into a preheated (590°C) steel mould and annealed at this temperature for 1 h. After annealing glass bars were sliced into 10 × 10 × 5 mm samples and the surfaces of the samples were successively ground and polished using 400/800/1200 SiC grits and then 6/3/1/0.25 μm diamond pastes. Then samples were re-annealed at their glass transition temperatures ( $T_g$ ) for 1 h.  $T_g$  of each composition was determined by differential scanning calorimeter (DSC7, Perkin-Elmer), where samples were heated in aluminum pans to 620°C at 10°C min<sup>-1</sup> and the onset of the first endothermic peak was used to estimate  $T_g$  (measurement error ±2°C). Final surface roughness of every sample was assessed by tapping mode atomic force microscopy (AFM, Veeco) on a 10 × 10 μm area and did not exceed 2 nm. Densities were measured by the Archimedes technique with water being used as the immersion medium (measurements error ± 0.005 Mg m<sup>-3</sup>).  $T_g$  values and densities for all glasses are summarized in Table 1. Before nanoindentation testing as prepared samples were rinsed with absolute ethanol to remove any dirt.

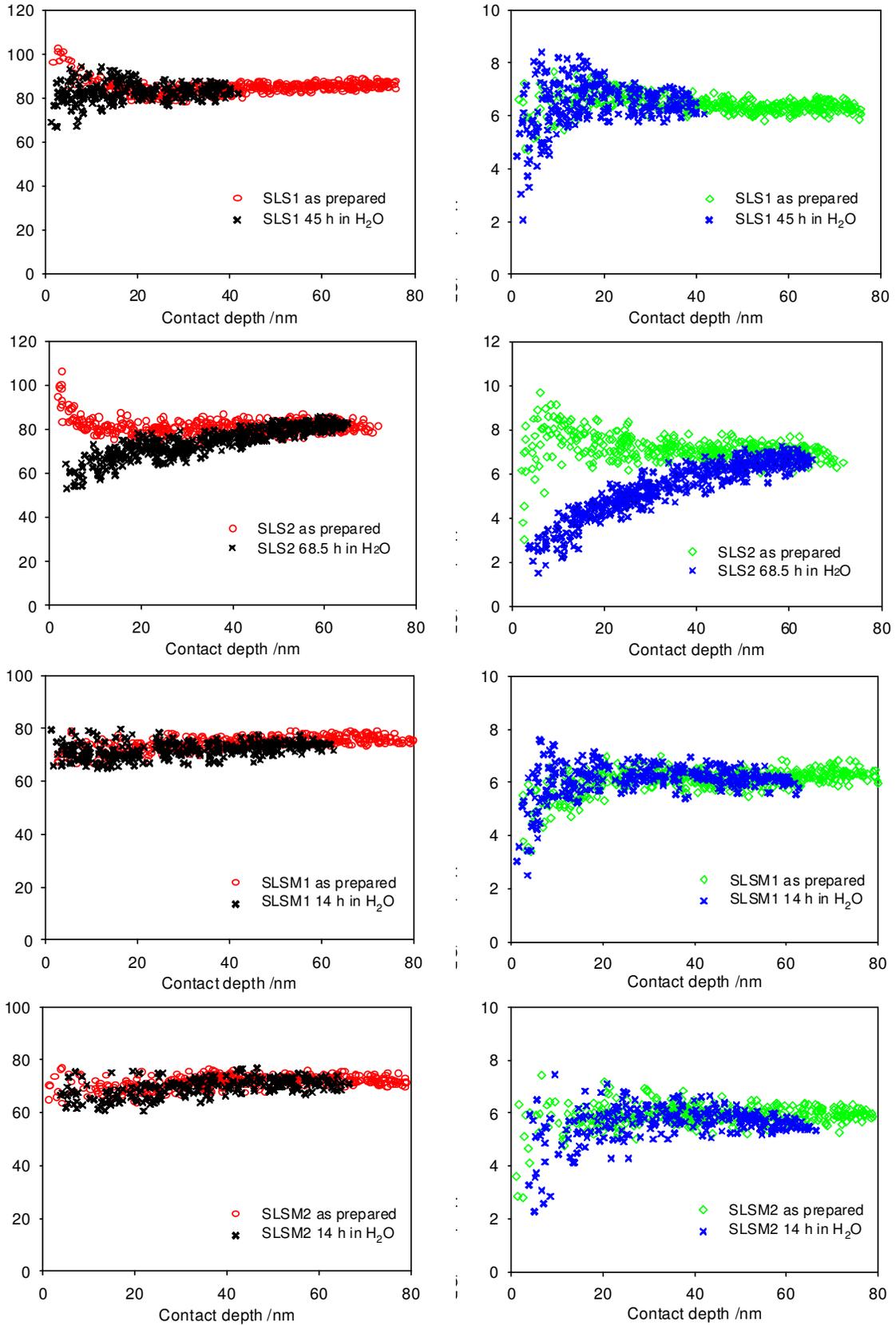
To assess the effect of hydration on the near-surface mechanical properties samples were exposed to distilled water at 22±1°C for various periods of time. Samples were removed from the solution just before nanoindentation testing and gently dried with a warm air blower to minimise any damage of the hydrated layer.

### 2.2 Nanoindentation and data analysis

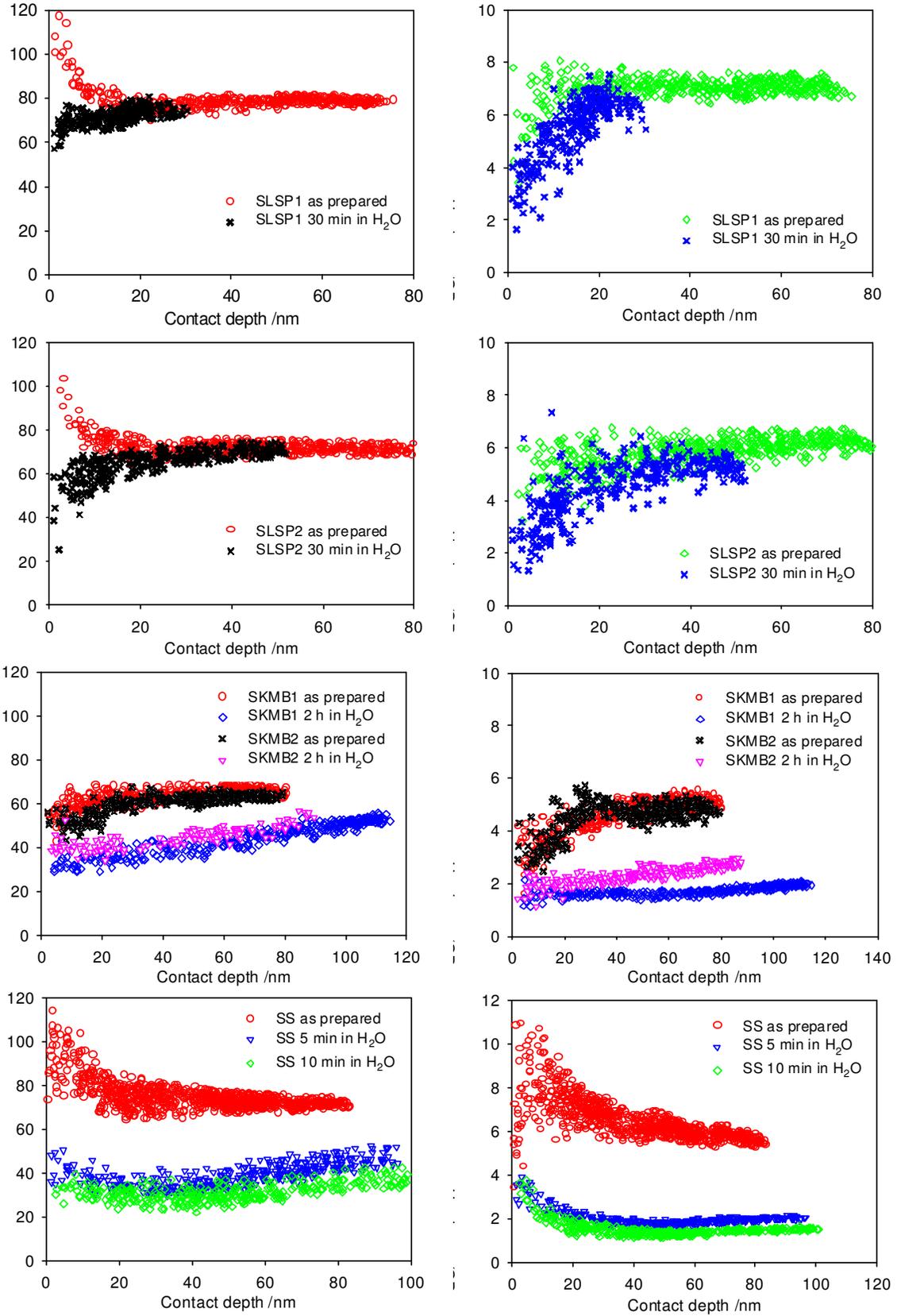
For nanoindentation samples were mounted on a stainless steel stage by means of vacuum. Measurements were carried out using Triboscope (Hysitron Inc.) nanoindenter mounted on a Dimension 3100 (Veeco) nanoscope with Berkovich indenter (70.3°). Measurements were taken at room temperature (24±1°C) and 60-80% relative humidity. Prior to testing the machine compliance and the indenter area function were calibrated on a fused silica slide with  $R_a = 0.540$  nm at depths up to 90 nm. Data were collected using automated 8 x 8 arrays with 60 s between each indent. All measurements were done with drift correction on. Drift was measured by running 0.1μN test with a 20 s hold at peak load and measuring displacement drift during this hold. Data analysis was carried out using the procedure proposed by Oliver and Pharr.<sup>21</sup>

**Table 1** Batched composition (in mol %), physical properties and surface roughness of examined glasses.

Glass code	Batched composition (mol %)						$T_g$ °C	$\rho$ Mg m <sup>-3</sup>	$R_a$ nm
	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	BaO			
SLS1	75	10	15	-	-	-	557	2.48	1.142
SLS2	65	15	20	-	-	-	556	2.58	0.866
SLSM1	75	7.5	15	-	2.5	-	538	2.45	1.389
SLSM2	75	2.5	15	-	7.5	-	526	2.43	1.094
SLSP1	65	15	8	12	-	-	557	2.56	1.164
SLSP2	65	15	-	20	-	-	539	2.54	1.346
SKMB1	70	-	-	20	-	10	525	2.77	1.985
SKMB2	70	-	-	20	6.25	3.75	538	2.55	1.980
SS	66.7	-	33.3	-	-	-	480	2.49	1.500



**Fig. 1.** The near-surface mechanical properties of high durability glasses: hydration has little if any effect on the near-surface mechanical properties.



**Fig. 2.** The near-surface mechanical properties of low durability glasses: curves obtained for as prepared and hydrated samples do not overlap indicating on the presence of hydrated surface layer.

### 3. Results

Fig. 1 presents results obtained for high durability glasses. It can be seen from the graphs that the near-surface mechanical properties of as prepared glasses show limited variation with depth. The approximately linear increase of hardness values in the depth range of 0-20 nm is due to purely elastic contact associated with indenter bluntness,<sup>22</sup> which becomes more marked at shallow depths. Hydration causes little if any effect on SLS1, SLSM1 and SLSM2 samples where the curves obtained on as prepared and hydrated samples overlap. Data obtained on the hydrated SLS2 sample indicates the presence of a hydrated layer, but composition is still durable because it takes almost three days to produce hydrated layer with a thickness less than 40 nm. The lower durability of this composition in relation to other compositions studied is due to the relatively low percentage of silica and high percentage of soda in this glass (see Table 1). In all cases, slightly increased noise in the data for hydrated samples at lower end is due to increased surface roughness associated with surface deterioration<sup>7-9</sup> as discussed in the next section. Overestimation of reduced modulus values at <10 nm depth for SLS1 and SLS2 samples is presumably due to their higher moduli than silica (see Table 2) when compared to that of pure silica used for calibrating the indenter area function (69.9 GPa). Peak in hardness curve, which can be easily seen on SLS1, SLS2 and SLSM1 samples, is attributed to the combined effect of the indenter bluntness and the contact stiffness of the material compared to the pure silica used for calibration as is shown elsewhere<sup>23</sup> and discussed further in the next section.

Fig.2 presents results obtained for low durability glasses. As in case of high durability glasses, the near-surface mechanical properties of as prepared glasses show limited variation with depth and the approximately linear increase of hardness values in the range of 0-20 nm depths is again believed to be due to purely elastic contact associated with indenter bluntness. Curves obtained for as prepared and hydrated samples do not overlap indicating the presence of a hydrated surface layer on the latter samples. Mechanical properties of the hydrated layer are clearly lower than those of the bulk and the thickness of the layer increases with immersion time. Based on the depth at which the original bulk properties are seen, the thickness of hydrated layer in SLSP1 sample is  $\leq 20$  nm and in SPSP2 sample is  $\leq 40$  nm, whereas in SKMB1, SKMB2 and SS samples the thickness of hydrated layer probably exceeds indentation depth. Elastic moduli of as prepared SLSP1 and SLSP2 samples are overestimated at indentation depths of <10 nm due to their high elastic moduli compared to silica as was mentioned above for high durability glasses. It can be noted that overestimation of elastic modulus values is not observed on hydrated samples. This is because hydrated layer is softer and plastic deformation of the surface occurs sooner. For the same reason peak in hardness curves is significantly smaller than in case of high durability glasses.<sup>23</sup> The amount of noise in the data (especially on hardness curves) for hydrated samples (see SLSP1 and SLSP2) is greater than in the case of high durability glasses because the surface of low durability glasses deteriorates more quickly and to a greater extent, as is shown in the next section. Curves for low durability SKMB1, SKMB2 samples are non-linear from the very beginning of indentation. It is believed that this is because these glasses react with the water in the atmosphere during the test. Similar results were previously found on the binary, very low durability potassia-silica glass.<sup>19</sup> In spite of having high elastic modulus and hardness values, SS glass has the lowest chemical durability and immersion for even 5 min causes dramatic changes in the near-surface mechanical properties. The thickness of hydrated layer in this glass after first 5 min of hydration exceeds 100 nm, however it can be seen that the rate of hydration decreases over time (the curves obtained after 5 min and 10 min hydration times are close to each other).

**Table 2** Summary of mechanical properties extracted for the bulk and hydrated layer of examined glasses.

Glass code	No. of indents for as prepared/hydrated sample	Mechanical properties measured for the bulk and hydrated layer (GPa)			
		$E_r$	$H$	$E_r$	$H$
SLS1	400/245	84.3 ± 2.1	7.1 ± 0.2	-	-
SLS2	381/412	80.6 ± 2.6	7.0 ± 0.3	-	-
SLSM1	400/300	74.1 ± 2.6	6.2 ± 0.3	72.0 ± 2.9	6.2 ± 0.3
SLSM2	360/235	71.4 ± 2.4	6.0 ± 0.3	69.6 ± 3.3	5.8 ± 0.4
SLSP1	415/252	78.5 ± 2.0	7.1 ± 0.3	-	-
SLSP2	505/301	71.5 ± 2.1	6.0 ± 0.3	-	-
SKMB1	465/330	65.7 ± 1.5	5.1 ± 0.2	39.5 ± 4.5	1.6 ± 0.2
SKMB2	321/290	62.3 ± 1.8	4.8 ± 0.2	50.5 ± 3.7	2.5 ± 0.2
SS (5 min)	830/66/88	73.2 ± 3.0	6.2 ± 0.5	34.5 ± 4.8	1.9 ± 0.2
SS (10 min)				29.3 ± 3.4	1.5 ± 0.2

Measured mechanical properties for all examined glasses are summarized in Table 2. Mechanical properties of the hydrated layer were measured only for SKMB1, SKMB2 (0-30 nm) and SS (20-40 nm) low durability compositions where thickness of the hydrated layer was suitably thick to minimise the contribution of substrate effect.<sup>24-27</sup> Mechanical properties for hydrated SLS1, SLSM1 and SLSM2 high durability glasses are given to show that hydration has little effect on their near-surface mechanical properties. For SS sample mechanical properties of hydrated layer are given for samples hydrated for 5 and 10 min respectively.

## 4. Discussion

### 4.1 Effect of hydration on near surface mechanical properties.

Results obtained for high durability glasses (Fig. 1) and some of the low durability glasses (SLSP1 and SLSP2, Fig. 2) indicate that the near-surface mechanical properties of silicate glasses do not vary with depth as long as the surface is not affected by hydration which is consistent with previous results.<sup>19,20</sup> Comparatively long immersion of SLS2 glass resulted in formation of a hydrated layer with a thickness of less than 40 nm. Although SLS1, SLSM1 and SLSM2 samples do not show any sign of hydration, this does not necessarily indicate on the absence of the hydrated layer. It has previously been reported<sup>28</sup> that the thickness of the hydrated layer in durable glasses may be of the order of 5 nm which is too small to be detected by nanoindentation due to indenter bluntness.<sup>20,23</sup> However, near-surface mechanical properties of high durability glasses can still be extracted. Furthermore, when analysing low durability glasses, nanoindentation gives insight into changes in the near-surface mechanical properties due to surface hydration and even approximate mechanical properties and the thickness of hydrated layer as discussed below.

Data obtained for low durability glasses show that hydration of these glasses results in formation of hydrated layer with reduced mechanical properties. Based on the results obtained for high durability compositions it can be concluded that the drop in both elastic moduli and hardness values observed on as prepared low durability compositions (SKMB1, SKMB2, SLSP2) at depths <20 nm is due to hydration of the surface in the atmospheric environment during nanoindentation test. The thickness of hydrated layer in SLSP glasses does not exceed 20 nm, while in SKMB and SS glasses it extends beyond the indentation depth (80 nm).

It is interesting to note that the mechanical behaviour of hydrated layer observed on low durability glasses is different from that on the high durability glasses. Thus, in SLSP compositions elastic modulus and hardness values increase from zero contact depth to the point when curves for hydrated samples intercept with the curves for the as prepared samples (as in case of durable SLS2 composition). In less durable SKMB compositions elastic modulus and hardness values remain nearly constant to a certain depth (~30nm) and then start to increase due to the substrate effect. Based on the results obtained for SLSP glasses, it is expected that curves obtained for hydrated samples will, at a certain depth, meet the curves obtained for as prepared samples. Mechanical behaviour of hydrated layer of SS glass indicates the possible densification of the hydrated layer on its top, which agrees with observations of other researchers.<sup>29,30</sup>

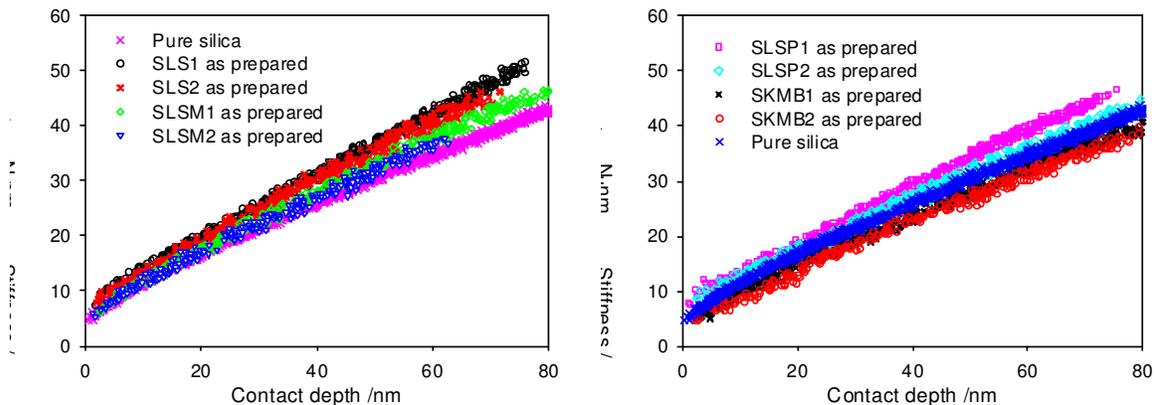


Fig. 3. Stiffness of the high durability and low durability compositions compared to stiffness of pure silica: maximum stiffness is observed for SLS1 and SLS2 (high durability compositions) and SLSP1 and SLSP2 (low durability compositions) glasses.

It was proposed in previous work<sup>23</sup> that the overestimation of stiffness (SLS1 and SLS2, Fig. 1) and (SLSP1 and SLSP2, Fig. 2) is due to high contact stiffness of the material compared to the pure silica used for calibration. Fig. 3 shows that glasses where elastic modulus was overestimated at shallow depth have the maximum contact stiffness of all the glasses examined here.

#### 4.2 Mechanical properties of hydrated layer

Mechanical properties of the hydrated layers cannot be measured accurately due to contribution of the substrate which is often observed when examining soft and hard coatings on substrates.<sup>24-27</sup> To exclude contribution of the substrate empirical or semi-empirical models have been proposed.<sup>31,32</sup> When considering comparatively thick films, the Bückle rule is often employed which states that substrate effect can be negligible if the indentation depth is less than 10% of film thickness.<sup>33</sup> This rule can be used as first approximation for most general cases of a film on substrate system, however, it has been found that in case of soft films on hard substrates or hard films on soft substrates it tends to be inaccurate.<sup>24</sup> Presumably, the hydrated layer on glass can be treated as a soft film on a hard substrate. In addition, models used to extract intrinsic properties of films on substrates are not straightforward and often require complex calculations as well as knowledge of properties of both the bulk and the film, which in the current case is impracticable. Furthermore, it is possible to extract approximate values of mechanical properties of hydrated layer, when it is suitably thick. Thus, in SKMB1 and SKMB2 glasses the thickness of hydrated layer exceeds 120 nm and approximate mechanical properties can be extracted in the depth range of 0-30 nm, while in SS glass the thickness of hydrated layer is well beyond the indentation depth and approximate mechanical properties of the layer can be extracted in the depth range of 20-60 nm (above 20 nm due to densification). Mechanical properties of hydrated layers for SKMB and SS glasses are given in Table 2.

#### 4.3 Effect of composition on chemical durability of glasses

It is interesting to note that good initial mechanical properties (SLSP1 and SLSP2) do not necessarily mean good chemical durability (see Table 2 and Fig. 2). SLS2 composition is less durable than SLS1 due to smaller content of silica and higher content of soda. SLSM glasses are typical soda-lime-silica glasses with a small amount of magnesia and the high silica and lime contents make them durable. The initially good mechanical properties of SLSP compositions are presumably due to high silica and lime contents of these glasses, however the presence of potassium makes them non-durable, and durability decreases with increasing potassia content. SKMB glasses are not durable due to the absence of lime and their high potassia and barium contents. The greater durability of SKMB2 compared to SKMB1 is attributed to the higher magnesia and lower barium contents.

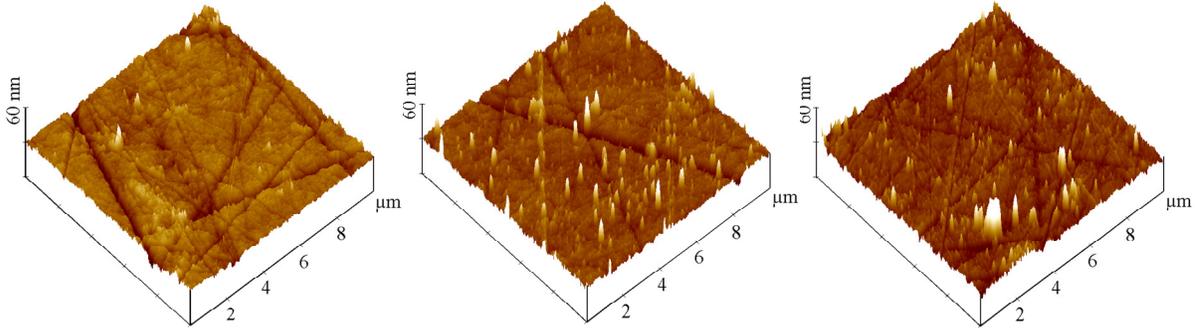
It is known that composition is the main factor which defines both mechanical properties and chemical durability of silicate glasses. However, as our results show, there is no simple relationship between the near-surface mechanical properties and chemical durability of glasses. Overall it can be concluded that hydration affects the near-surface mechanical properties of glasses by forming the surface layer with poorer mechanical properties than that of the bulk. Thickness of this layer depends on both composition of glass and immersion time. Furthermore, the results obtained suggest that hydration in high durability and low durability glasses occurs in a different fashion which might be consistent with the hypothesis of Doremus,<sup>2,15</sup> who suggested that in durable glasses the structure of hydration layer is similar to that of the bulk, while in low durability glasses a transformed layer is formed on the surface with structure different from that of the bulk.

Different effects of hydration on low durability and high durability glasses are presumably associated with their chemical composition which could result in different hydration mechanisms. Thus, thick hydrated layers in low durability glasses may indicate that hydration in such glasses occurs by combination of leaching and network dissolution, whereas in high durable glasses a protective layer may be formed during leaching which prevents further hydration of the surface.<sup>18</sup>

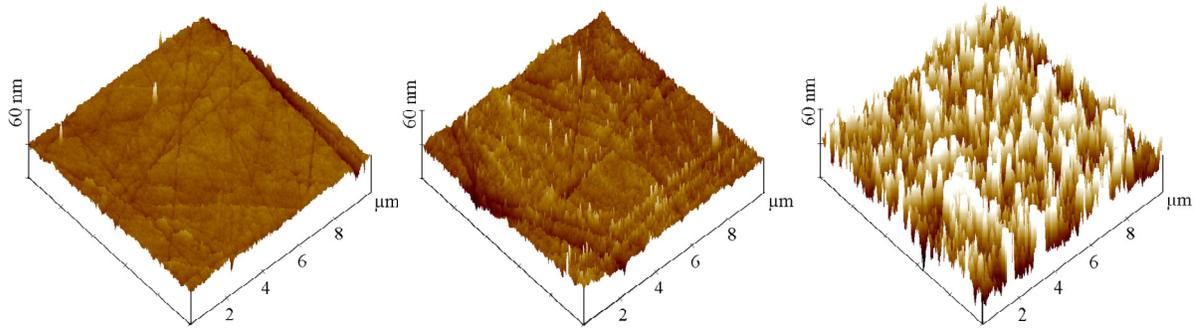
#### 4.4 Surface deterioration. Effect of surface roughness on accuracy of measurements

It has been acknowledged that surface roughness has a significant influence on both the nanohardness and elastic modulus as measured in nanoindentation.<sup>34,35</sup> From Fig. 2 it can be seen that curves for hydrated glasses show increased noise, especially at low indentation depths. This noise is attributed to the increased surface roughness associated with the surface deterioration caused by hydration.<sup>7-9</sup> Factors that affect the deterioration rate of the glass surface are composition, the state of the surface and environment.<sup>8</sup> In present work surface roughness is kept to a minimum and water is being used as an environment, thus deterioration rate is mainly affected by the glass composition. Clearly,

surface deterioration is less for durable and greater for non-durable glasses as shown on Fig. 4 and Fig. 5. In Fig. 2 the data obtained for hydrated SS samples seem to have less noise but this is an optical illusion due to the scale of the graph.



**Fig. 4.** Surface deterioration in high durability (SLSM1) glass: as prepared ( $R_a=1.389$  nm), 30 min in water ( $R_a=1.417$  nm) and 2.5 h in water ( $R_a=1.515$  nm).



**Fig. 5.** Surface deterioration in low durability (SS) glass: as prepared ( $R_a=1.500$  nm), 5 min in water ( $R_a=1.770$  nm) and 40 min in water ( $R_a=7.610$  nm).

## Conclusions

Nanoindentation at shallow depths has been used to assess how hydration affects the near-surface mechanical properties of silicate glasses. It is shown that hydration of the surface results in formation of a hydrated layer with reduced mechanical properties. In high durability glasses there is only a very thin, if any, hydrated layer even after long immersion times, while in low durability glasses thickness of hydration layer may exceed the indentation depth. It is also shown that noise in the data for hydrated samples is caused by surface deterioration which is more pronounced in low durability glasses. Chemical durability as well as the rate and degree of deterioration are determined by both glass composition and immersion times. Nanoindentation can therefore be used to estimate the effect of hydration on the near-surface mechanical properties of silicate glasses. However, due to limitations associated with indenter bluntness and the high initial stiffness of the glasses, the mechanical properties and the thickness of hydrated layer can be measured accurately only for low durability glasses where hydrated layer is suitably thick.

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