

Effect of the glass surface modification on the strength of methacrylate monolith attachment

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Abstract

The influence of glass surface modification in order to determine strength of the monolith attachment was studied. Modification consists of pre-treatment of the glass with chemicals or boiling in deionized water, silanization and drying has been investigated on different types of glass. Amount of silane groups was determined by measurement of the contact angle between the glass surface and water drop. The highest values were found for soda–lime glass. Strength of the monolith attachment was established by pumping ethanol through the monolithic capillaries and measuring the pressure drop at which monolith was dislodged. Surprisingly, it was found that the critical part of the glass surface modification procedure is glass pre-treatment. Good results were obtained with glass boiled in water for 2.5 h or more.

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1. Introduction

Use of the monoliths as a stationary phase in capillary columns was greatly expanded in the last few years [1]. The reason for that is an easy preparation, possibility of attachment to the glass surface, absence of the packing procedure and excellent performance [2].

The procedure for the capillary column preparation consists normally of three steps [1,3]: glass surface modification, polymerization and washing. The glass surface modification consisting of glass pre-treatment, surface activation, commonly using silane to achieve covalent attachment of the monolith, and drying might be the most labour demanding part of the whole procedure. Although the silanization of the glass surface [4–10] as well as characterisation of monolithic capillary [1,2,11,12] have been studied extensively only few reports describe the influence of the glass surface modification procedure on the binding of the chromatographic monolith to the glass surface [3,13].

A major need for bonding of organic polymers to inorganic phase arose in 1940 when glass fibres were for the first time used as reinforcement material in organic resins like reinforced plastics and electric cables composed of cross linked polyethylene [4]. Normally, vinyl silane or methacrylate silane was used as a coupling agent, because it contains at least one functional group with double bond, which can readily react with organic polymer, and functional groups that react with silanol groups on the glass surface [4]. It acts as a compound that provide at the interface of dissimilar materials in a composite, a stable bond resulting in improved composite properties and preservation of these properties [14]. The molecular mechanism of silane coupling is a complex process and depends on the type of glass and silane, type of pre-treatment, silane solution and also drying conditions [5]. Naviroj et al. indicated that different mineral surfaces have different interactions with the silane coupling agent [15]. In addition, the methods used to apply the silane to the glass surface influence the structure and properties of the silane layer [4].

In this article the modification of the glass surface for methacrylate monolith attachment is investigated. The efficiency of glass surface modification procedure consisting of

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a glass pre-treatment, silanization and drying protocol, using different types of glass, was studied.

2. Experimental

2.1. Instrumentation

A scanning electron microscope (SEM, JEOL, Tokyo, Japan) was used to obtain the scanning electron micrographs. The vacuum desiccator was purchased from Kambič (Semič, Slovenia). A HPLC micro pump was from Knauer (Berlin, Germany) and the balance from Chyo balance, Chyo JL-180 (Tokyo, Japan). The heater was purchased from Tehnica, Rotamix 550 MMH (Železniki, Slovenia). The camera Powershot Pro 90 IS was provided from Canon (Canon, Ireland). Surface roughness measurements were performed with Mitutoyo tester (Kanagawa, Japan).

2.2. Materials

Glycidyl methacrylate (GMA, 99%), ethylene dimethacrylate (EDMA, 98%) and 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, 95%) were purchased from Sigma–Aldrich (Steinheim, Germany). Cyclohexanol (CyOH, 99%), 1-dodecanol (DoOH, 99%), 3-(trimethoxysilyl)propyl methacrylate ($\geq 98\%$) and dried toluene were obtained from Fluka (Buchs, Switzerland). Diethylamine (DEA, 99%), benzoyl peroxide (BPO, with 25% water), hydrochloric acid (37%), acetic acid (100%) and *N,N*-dimethylformamide (DMF, 99.5%) were from Merck (Darmstadt, Germany). Acetone was purchased from Rathburn (Walkerburn, UK) and ethanol was from Pharmachem (Ljubljana, Slovenia). Potassium permanganate was obtained from Applichem (Darmstadt, Germany). Deionised water was obtained by passing water through a water deionizer, from Watek (Ledec nad Sazavou, Czech Republic).

Soda–lime capillaries (50 mm \times 510 μm I.D. \times 750 μm O.D.) were purchased from Euroglass (Ljubljana, Slovenia). Pyrex glass plates (25 mm \times 25 mm) were donated from Ematag (Baden, Switzerland), the soda–lime glass and the borosilicate glass plates (25 mm \times 25 mm) were supplied by Brand (Wertheim/Main, Germany). Fused silica untreated capillaries of 50 mm \times 250 μm I.D. were obtained from Supelco (Bellefonte, PA, USA)

2.3. Glass surface modification

2.3.1. Pre-treatment

The glass plates were extensively washed with ethanol and deionized water to remove any surface impurities, immersed in the solution and treated as follows:

- (i) 2 mol l⁻¹ hydrochloric acid solution, 3 h at b.p.

- (ii) 0.1 mol l⁻¹ sodium hydroxide solution, 30 min in an ultrasonic bath [8];
- (iii) Deionized water [16], 3 h at b.p. [17];
- (iv) 1 mol l⁻¹ sodium hydroxide solution for 2 h at b.p. [3,13,18];
- (v) 0.2 mol l⁻¹ sodium hydroxide for 30 min, washed with water, immersed in 0.2 mol l⁻¹ hydrochloric acid solution and washed with water [19–23];

When pre-treatment was completed, glass was rinsed with ethanol and dried at 110 °C overnight in a vacuum desiccator [4,16].

2.3.2. Silanization

Thereafter, the glass was treated with one of the listed solutions containing 3-(trimethoxysilyl)propyl methacrylate [4,24] in order to provide bonding sites (double bonds) for the polymer onto the glass surface:

- (i) 0.5% solution of silane in water [25] adjusted with 1 mol l⁻¹ acetic acid to pH 4, 1 h [4,7,8,26];
- (ii) 30% solution of silane in acetone, 24 h at 25 °C [19,21];
- (iii) 15% solution of silane in dried toluene, overnight at 35 °C [4];
- (iv) 50% solution of silane in *N,N*-dimethylformamide with 0.01% 2,2-diphenyl-1-picrylhydrazyl hydrate [3,11,13,18], 6 h, 40 °C;

2.3.3. Washing and drying

Finally, the glass was extensively rinsed with a solvent solution without silane with acetone afterwards [27] and dried using two different drying conditions:

- (i) dried at 110 °C for 7 min [24];
- (ii) dried in a vacuum desiccator [8] at room temperature, overnight.

2.4. Contact angle measurements

The amount of the bound silane was also estimated with contact angle measurements [3,6]. Contact angle was determined by drawing a tangent line on a liquid droplet at the contact between a droplet and the solid surface.

The 10 μL droplets of deionized water were applied on the glass surfaces and the pictures were taken with a digital camera. The contact angle measurement was estimated from a picture and calculated as the mean value of 3 separate measurements. The standard deviation of the measurements was $<3^\circ$. Experiments were performed at ambient conditions.

2.5. Monolith polymerization

Polymerization mixture consisted of glycidyl methacrylate, ethylene dimethacrylate and benzoyl peroxide in the presence of porogenic solvents, cyclohexanol and 1-dodecanol (60 vol.% of the reaction mixture). Soda–lime (50 mm long) and fused silica capillaries, where the glass

wall was modified, were filled up completely with the polymeric mixture, closed on both sides and the polymerization was allowed to proceed for 24 h [28]. Once the polymerization was completed, capillary ends were opened and the monoliths were washed with ethanol for 7 days by placing capillaries into ethanol. Ethanol was exchanged in the first two days every 12 h, afterwards every 24 h. Finally, the monolithic capillaries were washed by pumping the ethanol through the monolith for 30 min at the flow rate of 0.05 ml/min.

2.6. Modification of the monolithic capillaries

In order to introduce weak-ion exchange groups on the monolith, the monolithic capillaries polymerized in soda–lime glass were immersed in 50% solution of ethanol and diethylamine, overnight at 35 °C. Thereafter, capillaries were extensively washed with distilled water for several days by changing water every day twice.

2.7. Strength of monolith attachment measurements

The strength of the monolith attachment to the capillary wall was determined by the pumping the ethanol through the capillary at flow rates up to 0.3 ml/min (equal to the linear velocity up to 8816 cm/h). The pressure drop required to remove the monolith from the glass capillary was recorded and normalized on a column length for easier comparison of results.

2.8. Microscopy

Examination of the monolith attachment to capillary wall was performed using a scanning electron microscope, which operated at 15 kV and the applied magnification was 2000. The capillary samples were cut into ca. 2 mm long pieces, dried in a vacuum drier overnight and fixed on a stub using a carbon paste. Afterwards, they were sputter-coated with gold forming 20–30 nm thick layer.

2.9. Surface roughness measurements

Surface roughness measurements were performed on the glass surface of the untreated and pre-treated glass boiled for 2.5 h in deionized water and afterwards dried at 110 °C overnight in a vacuum desiccator. Roughness of the surface was measured by moving the metal tip of the instrument over the surface and measure vertical amplitude.

3. Results and discussion

Several wall modification procedures, all applying silanes, are described in the literature [1–4,7,8,11,13,18,19,21,25,26]:

- (i) 15% solution of silane in dried toluene [4];
- (ii) 50% solution of silane in *N,N*-dimethylformamide (DMF) with 0.01% 2,2-diphenyl-1-picrylhydrazyl (DPPH) [3,11,13,18];
- (iii) up to 2% solution of silane in water adjusted with 1 mol l⁻¹ acetic acid to pH 4 [4,7,8,25,26];
- (iv) 30% solution of silane in acetone [19,21].

Typically, 3-(trimethoxysilyl)propyl methacrylate is used as a silane coupling agent [1–4,11–13,18–23,25,26]. In some cases, the inhibitor DPPH was added to the silane solution in order to slow down the reaction between the silane double bonds [13]. Such columns exhibited excellent mechanical stability and were not destroyed even when high pressure was applied [3]. It was observed that without addition of the DPPH, there might appear voids between the monolith and the inner wall of the capillary, whereas in the presence of DPPH, the monolith was attached to the capillary inner wall [13].

The structure, properties and amount of the bound silane on the glass surface depend not only on the type of silane and silanization method but also on the type of glass, pre-treatment procedure and drying conditions [5]. In order to increase a density of the silanol groups, the glass surface is firstly pre-treated by washing with acid [19,20] or strong basic solution [3,13,18] and drying afterwards, usually overnight [8]. After pre-treatment and silanization, the glass surface is first washed with suitable organic or aqueous solution to remove unreacted chemicals and dried afterwards to make the silane bonds available for reaction with the monolith [2]. Drying is rather critical step due to a sensitivity of the methacrylate groups present on the silane. It was found that most of the methacrylate double bonds are lost during one hour drying at temperatures above 100 °C in air [4]. However, several polyester laminates silanized with the methacrylate silane and dried briefly at 110 °C gave much better performance than the ones dried at room temperature [4]. On the other hand, the binding capability was rather poor when drying was performed at 160 °C [4]. From the reported data it is obvious that some optimum in terms of a temperature and duration of drying has to be determined for a particular system.

Published data about the effect of various glass surface modifications were used as a frame for design of our experiments. Due to many different reported procedures, we closely investigated influence of each step. Different types of glasses in plate format, like soda–lime, Pyrex and borosilicate glass were tested. Each type of glass was pre-treated with chemicals such as water, sodium hydroxide or hydrochloric acid, immersed in aqueous or organic solution of silane and dried, according to procedures described in details in the Section 2.3. All together over 80 experiments were performed. Detail list of tested parameters and applied combinations is given in Table 1.

To evaluate efficiency of the glass surface treatment procedures, the quantity of silane groups was determinate. The contact angle measurement between the glass surface and

Table 1
Detailed list of performed treating experiment on the glass

Treatment step	Condition ^a	Soda–lime glass	Pyrex glass	Borosilicate glass
Pre-treatment	2 mol l ⁻¹ HCl	✓	✓	✓
	0.1 mol l ⁻¹ NaOH	✓	✓	✓
	Deionized water	✓	✓	✓
	1 mol l ⁻¹ NaOH	✓	✓	✓
	0.2 mol l ⁻¹ NaOH, 0.2 mol l ⁻¹ HCl	✓	✓	✓
Silanization	0.5% Silane in water, pH 4	✓		✓
	30% Silane in acetone	✓		✓
	15% Silane in dried toluene	✓	✓	✓
	50% Silane in <i>N,N</i> -DMF + 0.01% DPPH	✓	✓	✓
Drying	110 °C	✓		✓
	Vacuum desiccator, room temperature	✓	✓	✓

^a For condition detail see Section 2, glass modification.

water droplet [6,14] and chemical test using permanganate solution [14,29] were used. The latter method was turned out to be not sensitive enough for this particular system due to low silanized surface area and consequently lower silane amount in comparison to a fibrous sample, for each the method was originally introduced [14]. Therefore, no conclusion about the quantity of bound silane could be made with permanganate method and alternative method, by measuring the contact angle, was applied. This method is particularly suitable for smooth surfaces. It is based on an increase of hydrophobicity after silane binding as a result of hydrophobic double bonds present on vinyl silane. Higher the contact angle, higher the hydrophobicity, higher the amount of the present double bonds and consequently higher strength of attachment is expected. Therefore, the quality of surface treatment was checked by the difference in contact angle of water on silanized and unsilanized glass surface. The unsilanized glass was used as a reference, to eliminate the effects of treatment

procedure. It was prepared in exactly the same manner, using equal type of glass, same type of a pre-treatment and silanization procedure but without addition of silane as well the same washing and drying protocol. Results of the contact angle difference measurements between silanized and unsilanized glasses are shown in Table 2.

From the Table 2, it can be seen that Pyrex glass for all performed experiments gave the lowest value of the angle difference. Because of that, only few experiments were performed with this type of glass. In contrary, the soda–lime glass demonstrated the highest values for almost all tested conditions and it was therefore used for further experiments. Among all tested silanization procedures, the one using the 15% silane in dried toluene solution gave the highest values in most of the cases. This finding is in agreement with the literature data, where the suggested procedure for methacrylate functional silane binding is dried toluene solution [4]. Since all results for soda–lime glass silanized with dried toluene

Table 2
Contact angle measurement for soda–lime, Pyrex and borosilicate glass (drying conditions: vacuum desiccator, room temperature, overnight)

Pre-treatment condition	Type of glass	Silanization			
		15% Silane in dried toluene, overnight, 35 °C	50% Silane in <i>N,N</i> -DMF + 0.01% DPPH, 6 h, 40 °C	30% Silane in acetone, 24 h, 25 °C	0.5% Silane in water, adjusted with acetic acid to pH 4
2 mol l ⁻¹ HCl, 3 h, b.p.	Soda–lime glass	19°	19°	11°	/
	Pyrex glass	/	0°	/	/
	Borosilicate glass	/	6°	/	/
0.1 mol l ⁻¹ NaOH, 30 min, ultrasonic bath	Soda–lime glass	19°	14°	18°	17°
	Pyrex glass	2°	/	/	/
	Borosilicate glass	4°	/	16°	6°
Deionized water, 3 h, b.p.	Soda–lime glass	20°	10°	18°	10°
	Pyrex glass	0°	/	/	/
	Borosilicate glass	7°	/	4°	2°
1 mol l ⁻¹ NaOH, 2 h, b.p.	Soda–lime glass	/	3°	8°	9°
	Pyrex glass	/	/	/	/
	Borosilicate glass	/	/	4°	0°
0.2 mol l ⁻¹ NaOH, 30 min, 0.2 mol l ⁻¹ HCl, 30 min	Soda–lime glass	/	6°	13°	12°
	Pyrex glass	/	/	/	/
	Borosilicate glass	/	/	1°	1°

solution gave comparable values, for further experiments pre-treatment with boiled deionized water was applied. The only treatment giving comparable value was the one using hydrochloric acid pre-treatment and silanization with *N,N*-dimethylformamide with DPPH, which was also selected for further experiments.

To completely define glass surface modification procedure, effect of drying was investigated on the two selected procedures. We found that in both cases drying under vacuum at room temperature overnight gave higher contact value differences (20° and 19°, respectively) then drying for 7 min at 110 °C (18° and 8°, respectively). Therefore, former drying procedure was chosen for glass treatment after silanization. The two selected procedures can be summarized as follows:

- (i) Glass was washed with ethanol and deionized water and placed in a beaker with 2 mol l⁻¹ hydrochloric acid solution for 3 h at b.p. Afterwards, it was rinsed with ethanol, dried at 110 °C overnight in a vacuum desiccator and immersed in 50% solution of the 3-(trimethoxysilyl)propyl methacrylate in DMF with 0.01% DPPH for 6 h at 40 °C. After the reaction, it was rinsed with DMF and acetone and dried overnight in the vacuum desiccator.
- (ii) Glass was washed with ethanol and deionized water. Afterwards it was placed for 3 h in the deionised water at the b.p., dried at 110 °C overnight in a vacuum desiccator and immersed in 15% solutions of 3-(trimethoxysilyl)propyl methacrylate in dried toluene overnight at 35 °C. After the reaction, it was rinsed with toluene and acetone and dried overnight in the vacuum desiccator.

For all the experiments performed so far, small glass plates were used enabling measurement of contact angle. To evaluate the strength of the monolith attachment, instead of plates, capillaries of the same type of glass (soda–lime) were used. Capillary walls were treated according to two selected procedures and monolith was polymerized within as described in Section 2. Ethanol was pumped through the monolith in the capillary to determine the strength of attachment.

Two types of monoliths were used for testing: epoxy and DEAE. To evaluate if there is a by pass between the wall and the monolith, a pressure drop at a flow rate 0.1 ml/min was determined. Similar pressure drop values were obtained for all capillaries regardless the glass surface modification procedure, even for unsilanized glass (see Fig. 1). Since the pressure drop for all capillaries was substantial, it indicates that in all cases the monolith was probably attached to the glass wall. The only significant difference was found between epoxy and DEAE monolith. Pressure drop for DEAE monolith was higher, what might be explained by the irreversible swelling of monolith during modification and consecutively decrease in the pore size. Since the pressure after modification increased, it seems that even a treatment with highly alkaline solution like 50% DEA in ethanol, did not cause detachment of the monolith from the glass surface and it could withstand pressure of at least up to 25 MPa. Especially surprising was the finding that unsilanized capillaries behave similarly to the

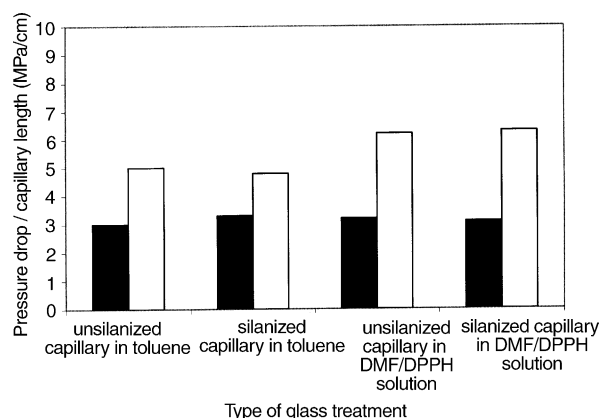


Fig. 1. Effect of the glass surface treatment on the pressure drops per length of the monolithic capillaries. Conditions: monolithic capillaries with epoxy groups (■) and DEAE modified capillaries (□).

silanized ones. These results differ from most of the published data. Gusev et al. observed that the monolith polymerized in unsilanized capillaries did not adhere to the capillary wall at all. The monolith was easily removed by rinsing the column with a 0.1 M solution of sodium hydroxide at a pressure drop of about 0.2 MPa [13]. Similar behaviour was observed even for some silanization procedures. Buszewski et al. compared three methods of glass surface modification to evaluate silanization process [3]. It was discovered that if the polymer was not bound to the capillary wall, the behaviour of the column was unpredictable and in some cases the entire monolith or its part was removed from the capillary during the mobile phase flow [3].

To verify our conclusions based on pressure drop data, scanning electron microscope was used to inspect the monolith attachment to the capillary wall. Scanning electron micrographs of monolithic capillaries are shown in Figs. 2 and 3. There is no visible difference in attachment of the DEAE monolith between the silanized and unsilanized glass surface (Fig. 2). The monolith was of uniform structure and no voids within the structure can be observed. On the other hand, the epoxy monolith in the capillary clearly shows failure as presented by scanning electron micrographs A in B in Fig. 3. This cracks probably occurred during drying of the capillaries, required for scanning electron micrographs, causing shrinkage of the monolith. Nevertheless, the failure did not occur between the wall and the monolith but rather in the outer part of the monolith itself. It seems that the strength of attachment was higher than the connection between the monolith globules. This phenomenon was not observed for DEAE monoliths probably because modification caused swelling of the structure that compensated shrinkage of the monolith during drying.

From the obtained data it seems that the critical part of the glass surface modification procedure is not the silanization, but rather surface pre-treatment. Because of that, duration of the glass pre-treatment with boiled distilled water was studied in details to establish the effect on the attachment strength.

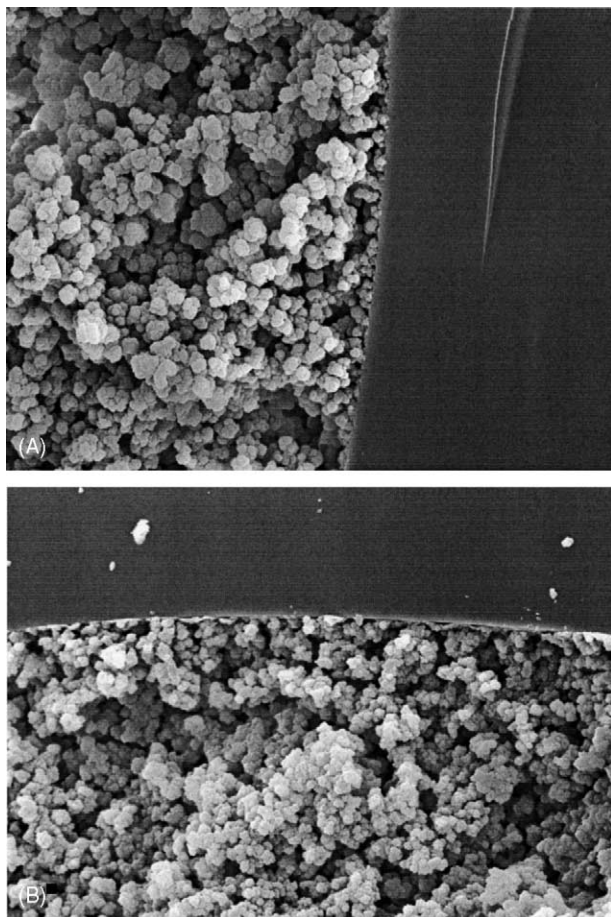


Fig. 2. Scanning electron micrograph of the inner wall of DEAE modified monolithic capillaries. The capillary's inner wall was pre-treated with hydrochloric acid and silanized in 50% solution of DMF with DPPH (A) and just pre-treated with hydrochloric acid, without silanization (B).

The soda–lime capillaries were boiled in deionized water for 0.5, 1, 2, 2.5 or 3 h and the monolith was polymerized in capillaries afterwards. The monolithic capillaries were further modified into DEAE groups to exhibit even higher-pressure drop, and tested to the attachment strength afterwards.

Effect of the flow velocity on the pressure drop normalized on capillary length is shown in Fig. 4. A linear relation is observed, confirming good attachment of the monolith and no by pass between the monolith and the capillary wall. Such linear relation is typical for methacrylate monolithic columns at proper functioning [30,31]. To determine the strength at which the monolith is detached from the wall even higher flow rates were applied. Fig. 5 shows the lowest strength at which the monolith is detached from the capillaries. As we can see, there is a good agreement between time of pre-treatment and strength of attachment. This finding confirms speculation that the pre-treatment is crucial part of the entire glass treatment procedure. After 2.5 h of boiling, we were no more able to detach the monolith from the wall (the same is true also for longer boiling times) although the pressure on the capillary was above 25 MPa, approaching the upper limit of the chromatographic pumps. Similar

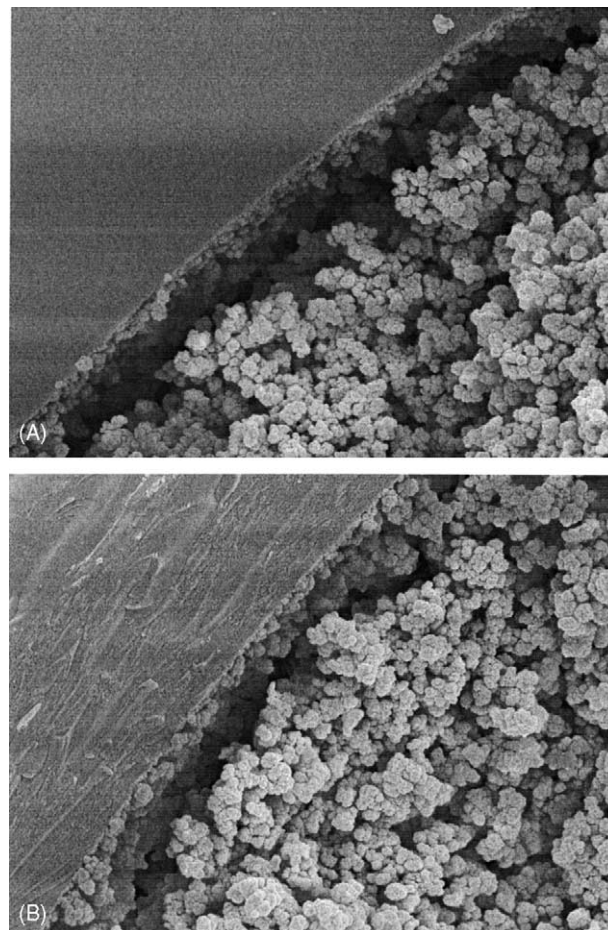


Fig. 3. Scanning electron micrograph of monolith in soda–lime capillaries with the inner wall of capillaries pre-treated with water and silanized with 3-(trimethoxysilyl)propyl methacrylate in dried toluene (A) and the capillary's inner wall pre-treated just with water, without additional silanization (B).

experiments were performed also with fused silica capillaries. In this case, three-fold stronger attachment was obtained indicating that this type of capillaries is even more stable.

From the results should not be concluded that silanization does not contribute to the strength of attachment since

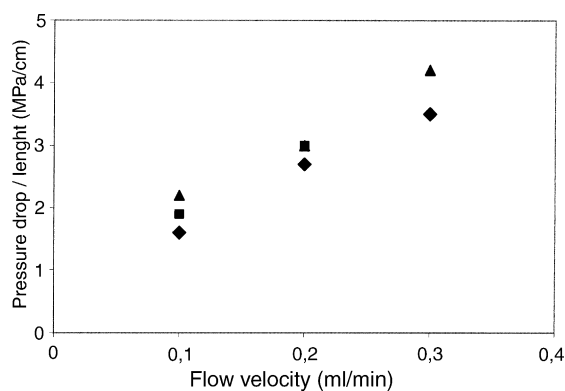


Fig. 4. Effect of the flow velocity on the pressure drop per length of the monolithic capillaries. The glass surfaces were pre-treated for 2 h (◆), 2.5 h (▲) and 3 h (●) in boiling water.

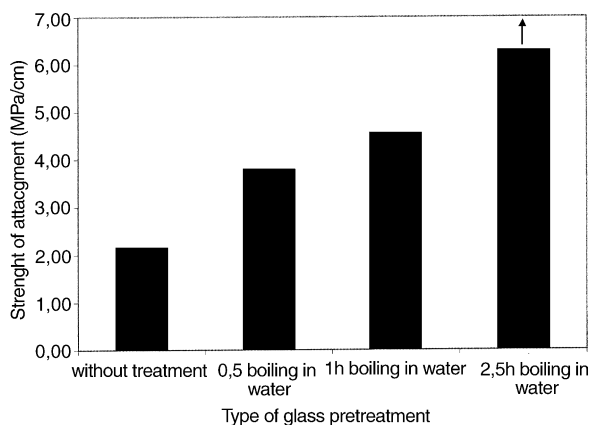


Fig. 5. Effect of the glass surface pre-treatment on the strength of monolith's attachment to the glass surface.

silanized capillaries exhibit high attachment strength too. However, even without silanization sufficiently high attachment strength was obtained. This is somehow similar to the finding of Svec et al. describing that the fused-silica tubing may be used directly without performing any chemical modification of its internal surface. However, the silane can help to increase the adhesion of the monolith to the wall and contributes to better reproducibility [1].

To explain strong attachment of the monolith to the un-silanized glass we closely investigated glass surface. Pre-treatment procedure might increase its roughness and in this way increase also strength of the monolith attachment. To verify this hypothesis the glass surface roughness of the untreated and pre-treated glass boiled for 2.5 h in deionized water was measured. In both cases, the roughness of the glass surface was determined to be $0.01 \mu\text{m}$ what is actually lower limit of the instrument range and therefore no differences between the two samples could be found. We can therefore conclude that the roughness of the glass surface pre-treated in water was not the reason for attachment of the monolith to the capillary wall. An alternative reason might be that boiling results in formation of a thin layer on glass surface, having different chemical composition [32]. This is especially true for soda–lime glass, which is only medium resistant on hydrolytic treatment [32], containing about 30% of alkaline earths (Na_2O , CaO , MgO) and Al_2O_3 [32]. Because of a partial hydrolysis of the layer, its reactivity might be higher, due to formation various hydroxides [Si-OH , Ca(OH)_2 , $\text{Al}_2(\text{OH})_3$, etc.] [33]. An explanation might also be the reaction of epoxy groups with silanol groups of silica for which it was shown to take place in the presence of the catalyst [34]. However, no indication of such reaction without catalyst was observed, therefore such reaction is not very probable explanation. Besides chemical reaction, stronger attachment can be explained by the corrosion caused by boiling water that removes part of alkali from the glass surface and creates a silica porous surface [35].

4. Conclusions

The comparison of different types of glass surface modification surprisingly shows that for attachment of the methacrylate monoliths critical part of the process is the glass pre-treatment, rather than silanization itself. Therefore, for the preparation of soda–lime methacrylate monolithic capillaries, glass surface modification consisting only of boiling in deionized water appears to be sufficient to achieve strong monolith attachment.

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References

- [1] F. Svec, E.C. Peters, D. Sýkora, J.M.J. Fréchet, *J. Chromatogr. A* 887 (2000) 3.
- [2] H. Zou, X. Huang, M. Ye, Q. Luo, *J. Chromatogr. A* 954 (2002) 5.
- [3] B. Buszewski, M. Szumski, S. Sus, *LC GC Eur.* 15 (2002) 792.
- [4] E.P. Plueddemann, *Silane Coupling Agents*, Plenum Press, New York, 1982.
- [5] C.G. Pantano, L.A. Carman, S. Warner, *J. Adhesion Sci. Technol.* 6 (1992) 49.
- [6] Y.C. Araujo, P.G. Toledo, V. Leon, H.Y. Gonzales, *J. Colloid Interface Sci.* 176 (1995) 485.
- [7] S.P. Wesson, J.S. Jen, G.M. Nishioka, *J. Adhesion Sci. Technol.* 6 (1992) 151.
- [8] A. Norström, H. Watson, B. Engström, J. Rosenholm, *Colloids Surf., A: Physicochem. Eng. Aspects* 194 (2001) 143.
- [9] A.E.E. Norström, H.M. Fagerholm, J.B. Rosenholm, *J. Adhesion Sci. Technol.* 15 (2001) 665.
- [10] P. Zinck, M.F. Pays, R. Rezakhanlou, J.F. Gerard, *J. Mater. Sci.* 34 (1999) 2121.
- [11] X. Huang, S. Zhang, G.A. Schultz, J. Henion, *Anal. Chem.* 74 (2002) 2336.
- [12] C. Yu, F. Svec, J.M.J. Fréchet, *Electrophoresis* 21 (2000) 120.
- [13] I. Gusev, X. Huang, C. Horváth, *J. Chromatogr. A* 855 (1999) 273.
- [14] N.B. Madsen, Ph.D. Thesis, Risø National Laboratory, Denmark, 1999 (available at: <http://www.risoe.dk/rispubl/fys/ris-r-1113.htm>).
- [15] S. Naviroj, S.R. Culler, J.L. Koenig, H. Ishida, *J. Colloid Interface Sci.* 97 (1984) 308.
- [16] V. Nguyen, W. Yoshida, Y. Cohen, *J. Appl. Polym. Sci.* 87 (2003) 300.
- [17] A.S. D'Souza, C.G. Pantano, *J. Am. Ceram. Soc.* 82 (1999) 1289.
- [18] X. Huang, C. Horváth, *J. Chromatogr. A* 788 (1997) 155.
- [19] C. Yu, S. Mutlu, P. Selvaganapathy, C.H. Mastrangelo, F. Švec, J.M.J. Fréchet, *Anal. Chem.* 75 (2003) 1958.
- [20] D.S. Peterson, T. Rohr, F. Svec, J.M.J. Fréchet, *Anal. Chem.* 75 (2003) 5328.
- [21] C. Yu, M.H. Davey, F. Svec, J.M.J. Fréchet, *Anal. Chem.* 73 (2001) 5088.
- [22] C. Ericson, J.L. Liao, K. Nakazato, S. Hjerten, *J. Chromatogr. A* 767 (1997) 33.
- [23] D.S. Peterson, T. Rohr, F. Svec, J.M.J. Fréchet, *Anal. Chem.* 74 (2002) 4081.
- [24] V.A. Liu, S.N. Bhatia, *Biomed. Microdevices* 4 (2002) 257.

- [25] H. Ishida, S. Naviroj, S.K. Tripathy, J.J. Fitzgerald, J.L. Koenig, J. Polym. Sci., Part B: Polym. Phys. 20 (1982) 701.
- [26] S. Hjertén, J. Chromatogr. 347 (1985) 191.
- [27] H. Watson, P.J. Mikkola, J.G. Matison, J.B. Rosenholm, Colloids Surf., A 161 (2000) 183.
- [28] T.B. Tennikova, B.G. Belenkii, F. Švec, J. Liq. Chromatogr. 13 (1990) 63.
- [29] G. Wiedemann, B. Wustmann, H. Frenzel, S. Keusch, Faserforsch. Textiltech. 29 (1978) 681.
- [30] A. Štrancar, M. Barut, A. Podgornik, P. Koselj, D. Josic, A. Buchacher, LC GC Int. 11 (1998) 660.
- [31] F. Svec, J.M.J. Fréchet, Anal. Chem. 54 (1992) 820.
- [32] Schott Technical Glasses, Physical and Technical Properties, Research and Technology Development, Schott Glass, Mainz, Germany, 2000.
- [33] H. Watson, M. Kaunisto, J. Gustafsson, J. Päävarinta, J. Colloid Interface Sci. 241 (2001) 32.
- [34] Y.-L. Liu, C.-Y. Hsu, M.-L. Wang, H.-S. Chen, Nanotechnology 14 (2003) 813.
- [35] <http://www.corrosion-doctors.org/Household/Glass.htm>.