dental materials xxx (2016) xxx–xxx

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Effectiveness and stability of silane coupling agent incorporated in ‘universal’ adhesives

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ARTICLE INFO

Article history:
Received 23 November 2015
Received in revised form
12 May 2016
Accepted 4 July 2016
Available online xxx

Keywords:
Silane
Coupling agent
Universal adhesive
NMR
FTIR
Bond strength

ABSTRACT

Objective. For bonding indirect restorations, some ‘universal’ adhesives incorporate a silane coupling agent to chemically bond to glass-rich ceramics so that a separate ceramic primer is claimed to be no longer needed. With this work, we investigated the effectiveness/stability of the silane coupling function of the silanecontaining experimentally prepared adhesives and Scotchbond Universal (3MESPE).

Methods and materials. Experimental adhesives consisted of Scotchbond Universal and the silane-free Clearfil S3 ND Quick (Kuraray Noritake) mixed with Clearfil Porcelain Bond Activator (Kuraray Noritake) and the two adhesives to which γ-methacryloxypropyltrimethoxysilane (γ-MPTS) was added. Shear bond strength was measured onto silica-glass plates; the adhesive formulations were analyzed using fourier transform infrared spectroscopy (FTIR) and 13C nuclear magnetic resonance (NMR). In addition, shear bond strength onto CAD-CAM composite blocks was measured without and after thermo-cycling ageing.

Results. A significantly higher bond strength was recorded when Clearfil Porcelain Bond Activator was freshly mixed with the adhesive. Likewise, the experimental adhesives, to which

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http://dx.doi.org/10.1016/j.dental.2016.07.002

Please cite this article in press as: Yoshihara K, et al. Effectiveness and stability of silane coupling agent incorporated in ‘universal’ adhesives. Dent Mater (2016), http://dx.doi.org/10.1016/j.dental.2016.07.002

γ-MPTS was added, revealed a significantly higher bond strength, but only when the adhesive was applied immediately after mixing; delayed application resulted in a significantly lower bond strength. FTIR and ^{13}C NMR revealed hydrolysis and dehydration condensation to progress with the time after γ-MPTS was mixed with the two adhesives. After thermocycling, the bond strength onto CAD-CAM composite blocks remained stable only for the two adhesives with which Clearfil Porcelain Bond Activator was mixed.

Significance. Only the silane coupling effect of freshly prepared silanecontaining adhesives was effective. Clinically, the use of a separate silane primer or silane freshly mixed with the adhesive remains recommended to bond glass-rich ceramics.

1. Introduction

In restorative dentistry, ceramics meet best the patient's demand for aesthetics. Glass-rich dental ceramics, such as feldspar ceramics, the diverse kinds of glass-ceramics (including monolithic lithium disilicate ceramics) and some new polymer-infiltrated ceramics, are least invasive to restore teeth, as they can be fully bonded to the remaining sound tooth tissue using composite cements. At the restoration site, the bonding protocol of preference to adhesively lute these 'etchable' ceramics consists of hydrofluoric acid (HF) etching to provide micro-retention to the cement that by silanization also chemically bonds to the ceramic. A silane functional monomer, like the most commonly in dentistry used methacrylate silane monomer (γ-methacryloyloxypropyltrimethoxysilane or γ-MTPS), basically possesses a methacrylate end to co-polymerize with the adhesive and/or composite cement and the actual silane group to covalently bond to the ceramic glass phase. Besides needed for bonding to ceramic, silane coupling agents are also often used as part of a restoration-repair protocol to intra-orally repair both ceramic and composite restorations [1]. Silane primers are mostly water-free solutions [2]; one-bottle and two-bottle silane primers exist. Silane primers that contain non-hydrolyzed silane, are most often dissolved in ethanol in one bottle that needs to be activated and hydrolyzed by mixing it with an aqueous acetic acid solution or an acidic adhesive in the other bottle [2]. Both water and lower pH cause silane to hydrolyse. The latest generation of silane primers contain silane mostly dissolved in a water-free and only mildly acidic solution [2], so that it has a relatively long shelf life. A kind of multi-purpose ceramic/metal primers are also water-free solutions and contain besides a silane functional monomer other functional monomers in order not only to bond 'glass-rich' (requiring silane) and 'glass-poor' ceramics like zirconia (requiring 10-methacryloyloxydecyl dihydrogen phosphate or 10-MDP), but also to bond precious metal alloys (requiring a monomer with one end carrying a thiol (—SH) group). Most recently, so-called 'universal' adhesives enable the dentist not only to opt for an 'etch-and-rinse' or 'self-etch' bonding protocol, but they can also be employed for both direct and indirect indications [3–5]. Among such universal adhesives, some adhesives also incorporate a silane coupling agent, having been claimed to provide the adhesive direct chemical bonding potential to glass-rich ceramics without the need of a separate ceramic primer [6].

It is generally well known that water-containing and acidic, single-bottle, pre-hydrolyzed silane coupling agents have a relatively short shelf life [2]. In light of this knowledge and because independent research data are insufficiently available, we hereby investigated the silanization potential of a universal adhesive incorporating a silane coupling agent. Bond strength to glass plates and CAD-CAM composite blocks was measured, as well as the adhesive formulations were chemically characterized using Fourier transform infrared spectrometry (FTIR) and nuclear magnetic resonance (NMR). Besides the commercially available 'universal' and silane-containing adhesive Scotchbond Universal (3M ESPE), we also investigated the commercially available silane-free adhesive Clearfil S3 Bond ND Quick (Kuraray Noritake Dental, Tokyo, Japan), as well as experimental adhesives to which γ-methacryloxypropyltrimethoxysilane (γ-MPTS) was added. The null hypotheses tested were that an adhesive incorporating a silane coupling agent was more effective in terms of bonding effectiveness than an adhesive that does not contain silane (1) and that the addition of silane to the adhesive formulation improved bond strength (2) and remained effective with time (3).

2. Materials and methods

2.1. Shear bond strength onto glass plates

Silica-glass plates (Shin-Etsu Quartz Products, Tokyo, Japan) with a smooth surface and thus low potential for micro-mechanical interlocking were employed to represent glass-rich ceramics; the plates were 10 mm × 10 mm wide and 3 mm thick. Six different adhesive protocols using the universal and silane-containing adhesive Scotchbond Universal (3M ESPE) and the silane-free adhesive Clearfil S3 Bond ND Quick (Kuraray Noritake) were tested as follows: (1) application of the adhesive 'as such'; (2) immediate application of a 1:1 drop mixture of the adhesive with Clearfil Porcelain Bond Activator (Kuraray Noritake); (3) 'immediate' application of the adhesive to which 2 wt% γ-MPTS (Sigma–Aldrich, St. Louis, MO, USA) was added; (4) '1 day' delayed application of the 2 wt% γ-MTPS-containing adhesive; (5) '3 days' delayed application of the 2 wt% γ-MTPS-containing adhesive; (6) '7 days' delayed application of the 2 wt% γ-MTPS-containing adhesive. Clearfil Porcelain Bond Activator (Kuraray Noritake) is a water-free silane coupling agent. We used 2 wt% γ-MTPS as this concentration corresponded to the silane concentration

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most common within commercial silane primers, as they were listed by Lung and Matinlinna [2]. To achieve a homogeneous mixture, the 2 wt% γ-MTPS was added to the adhesives using a magnetic stirrer. The silica-glass plates were treated following the abovementioned experimental protocols, upon which they were air-dried. Zirconia cylinder blocks (Tosoh, Tokyo, Japan) with a 3.6-mm diameter were sandblasted using Shofu High Blaster (Shofu, Kyoto, Japan) with 50-μm alumina particles (Shofu), followed by silanization using Clearfil Ceramic primer (Kuraray Noritake); they were eventually luted onto the glass plates using the composite cement Clearfil Esthetic Cement (Kuraray Noritake). The cement was light-cured for 40 s from two opposing directions (totaling to a 80-s curing time) using G-Light Prima II Plus (light irradiance of 2800 mW/cm^2; GC, Tokyo, Japan); the specimens were next stored in 37 °C water for 24 h prior to being subjected to a shear bond-strength test. Per experimental group, ten specimens were prepared. The specimens were mounted into a testing machine (AG-X, Shimadzu, Kyoto, Japan) and subjected to shear stress at a crosshead speed of 0.5 mm/min. All fractured specimens were analyzed utilizing a light microscope (SMZ-10, Nikon, Tokyo, Japan) at 4× magnification to determine the mode of fracture. For statistical comparisons of the data, the Scheffé's test was applied with $p < 0.05$ considered statistically significant.

2.2. *FTIR chemical analysis of the adhesive formulations*

The commercial adhesives Scotchbond Universal and Clearfil S3 Bond ND Quick, and the experimental adhesive formulations consisting of the commercial adhesives to which 2 wt% γ-MTPS was mixed, were analyzed using a Shimadzu IRAffinity-1 FTIR Spectrophotometer (Shimadzu, Kyoto, Japan) with a KBr plate (Jasco, Tokyo, Japan) in transmission mode. As control, we used a 2 wt% γ-MTPS in 98% ethanol solution and the same solution mixed with a solution of 2 wt% acetic acid (Sigma–Aldrich) in 70 wt% ethanol and 28 wt% water. The FTIR spectra were recorded upon 256 successive scans and a spectral resolution of 4 cm^{-1}. Each sample was measured three times.

2.3. *NMR chemical analysis of the adhesive formulations*

Half of the samples of Scotchbond Universal and Clearfil S3 Bond ND Quick, to which 4 wt% γ-MTPS was added, were analyzed immediately after mixing, while the others were kept for 1 day before being analyzed. As control, Scotchbond Universal and Clearfil S3 Bond ND Quick were also measured. Before measurement, the same amount of d-ethanol was added to the samples, after which they were poured into NMR test glass tubes with a 5-mm diameter and an 8-inch length (Wilmad, Buena, New Jersey). An NMR spectrometer (UNITY INOVA400NB, Varian Japan, Tokyo, Japan) was employed to acquire ^{13}C NMR spectra at 100.58 MHz in CD_3CD_2OD. ^{13}C NMR spectra were referenced at the internal CD_3 peak ($\delta = 17$ ppm) of D-ethanol. Two samples of each adhesive formulation were analyzed by NMR.

2.4. *Shear bond strength onto CAD-CAM composite blocks*

CAD-CAM composite blocks (shade A3-LT, size 14L; Lava Ultimate, 3M ESPE) were cut to discs with a 1.5-mm thickness. The surface was polished using 15-μm diamond lapping film (Struers, Ballerup Denmark) in order to reduce the potential for mechanical micro-retention; this was followed by either one of the following surface treatments: (1) Scotchbond Universal (incorporating silane) applied 'as such'; (2) Clearfil S3 Bond ND Quick (silane-free) applied 'as such'; (3) 1:1 drop mixture of Scotchbond Universal with Clearfil Porcelain Bond Activator; (4) 1:1 drop mixture of Clearfil S3 Bond ND Quick with Clearfil Porcelain Bond Activator. Zirconia cylinders, prepared in the same manner as for the bond-strength measurements onto glass plates, were luted onto CAD-CAM composite blocks using Clearfil Esthetic Cement and light-cured for 40 s from two opposing directions (totaling to a 80-s curing time) using G-Light Prima II Plus. Per experimental group, 20 specimens were prepared; all specimens were subjected to a shear bond-strength testing protocol, likewise as described above, this for half of the specimens after 24-h storage in water at 37 °C, while the other half were artificially aged through thermo-cycling (60 s of immersion, alternatively, in a 5 and 55 °C water bath) during 15,000 times prior to bond-strength measurement. For statistical comparisons of data, two-way ANOVA followed by Tukey's post-hoc tests ($\alpha < 0.05$) was used with $p < 0.05$ considered statistically significant.

3. Results

3.1. *Shear bond strength onto glass plates (Fig. 1)*

No difference in bond strength onto glass plates was measured for the silane-containing Scotchbond Universal and the silane-free Clearfil S3 Bond ND Quick when applied 'as such'. When both adhesives were beforehand mixed with Clearfil Porcelain Bond Activator, a significantly higher bond strength was recorded, again without significant difference between the two adhesives. A significantly higher bond strength (as compared to that for the application of the adhesives 'as such') was also measured when γ-MTPS was added to the adhesives and the bond strength was measured immediately; delayed application after 1, 3 or 7 days resulted in a significantly lower bond strength; no difference in bond strength was measured between all the delayed applications and between both the two γ-MTPS-added adhesives.

3.2. *FTIR chemical analysis of the adhesive formulations (Fig. 2a–c)*

FTIR revealed a strong peak at 2835 cm^{-1} that should be assigned to the C—H stretch of $-Si-O-CH_3$, thereby representing γ-MTPS (Fig. 2a, b). When acetic acid was added to γ-MTPS, the peak at 2835 cm^{-1} was no longer detected, as well it was not detected for the two adhesives Scotchbond Universal and Clearfil S3 Bond ND Quick with and without γ-MTPS (Fig. 2b). No clear Si—O signals were detected in the 1100–850 cm $^{-1}$ region (Fig. 2c).

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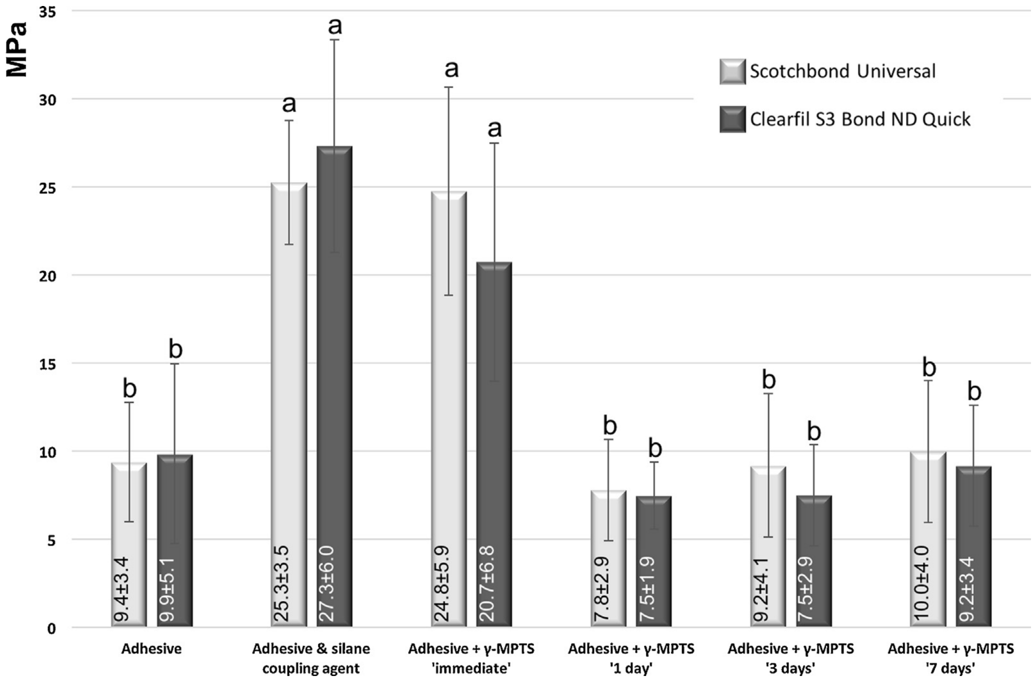

Fig. 1 – Shear bond strength (SBS) onto glass plates of the adhesives Scotchbond Universal (3M ESPE) and Clearfil S3 ND Quick (Kuraray Noritake Dental) applied 'as such' and according to their modified versions. Bars denote the mean bond strength and the whiskers define the standard deviation. Inside the bars, the mean SBS value and the standard deviation are indicated. Means with the same letter are not significantly different.

3.3. ^{13}C NMR chemical analysis of the adhesive formulations (Fig. 3)

^{13}C NMR revealed diverse speaks that should be ascribed to the specific composition of both the adhesives Scotchbond Universal and Clearfil S3 Bond ND Quick. When γ-MTPS was added to either of the adhesives, most characteristic were the strong peaks at 8.6 and 8.8 ppm that should be attributed to silanol [7]. These peaks were detected for both the adhesives when γ-MTPS was added and when the solutions were analyzed immediately; they were however no longer detected when the solutions were '1 day' old.

3.4. Shear bond strength onto CAD-CAM composite blocks (Fig. 4)

No difference in 24-h bond strength was measured for both the adhesives applied 'as such' or for their 1:1 drop mixtures with Clearfil Porcelain Bond Activator. After 15,000 times thermo-cycles, the bond strength of the two adhesives applied 'as such' dropped significantly, while not for their 1:1 drop mixtures with Clearfil Porcelain Bond Activator.

4. Discussion

The main objective of this study was to evaluate the effectiveness and stability of a silane coupling agent incorporated in an universal adhesive. Therefore, the shear bond strength of a silane-containing universal adhesive and a silane-free adhesive was measured onto two material kinds, being smooth glass plates, which represent glass-rich ceramic, and CAD-CAM composite blocks, for which silanization is also indicated as part of the bonding protocol. No difference in bond strength between the silane-containing and silane-free adhesive onto both material kinds was measured, by which hypothesis (1) was rejected. Adding silane to the adhesive formulation improved the bond strength, by which hypothesis (2) was accepted. This increased bonding effectiveness was however lost for the delayed applications, by which hypothesis (3) was rejected.

The reaction mechanism of silanization is detailed in Fig. 5. To activate a silane bifunctional monomer like γ-MTPS, it should react with water, by which it hydrolyses to silanol. As silane hydrolysis is slow in water, acetic acid is commonly used as reaction catalyst, as was also done in this study. This silanol adsorbs and chemically bonds to glass. However, upon hydrolysis silane may undergo dehydration condensation, thereby forming an oligomer that no longer can bond to glass [2,8]. The rate of oligomer formation depends on the structure of the silane coupling agent, its pH, the solvent kind and the environmental temperature [2,9,10].

FTIR revealed a clear peak at 2835 cm^{-1} that should be attributed to Si—O—CH$_3$ of γ-MTPS, which was no longer detected when acetic acid was added. This indicates that silane hydrolyses immediately upon exposure to acetic acid. No peak representing Si—O—CH$_3$ was detected for the two adhesives investigated, this with and without γ-MTPS. These results demonstrate that any non-hydrolysed γ-MTPS was present in both the commercial and the experimental γ-MTPS-added adhesive formulations. Hooshmand et al. [11] found using FTIR that hydrolysis of silane takes 24 h. The

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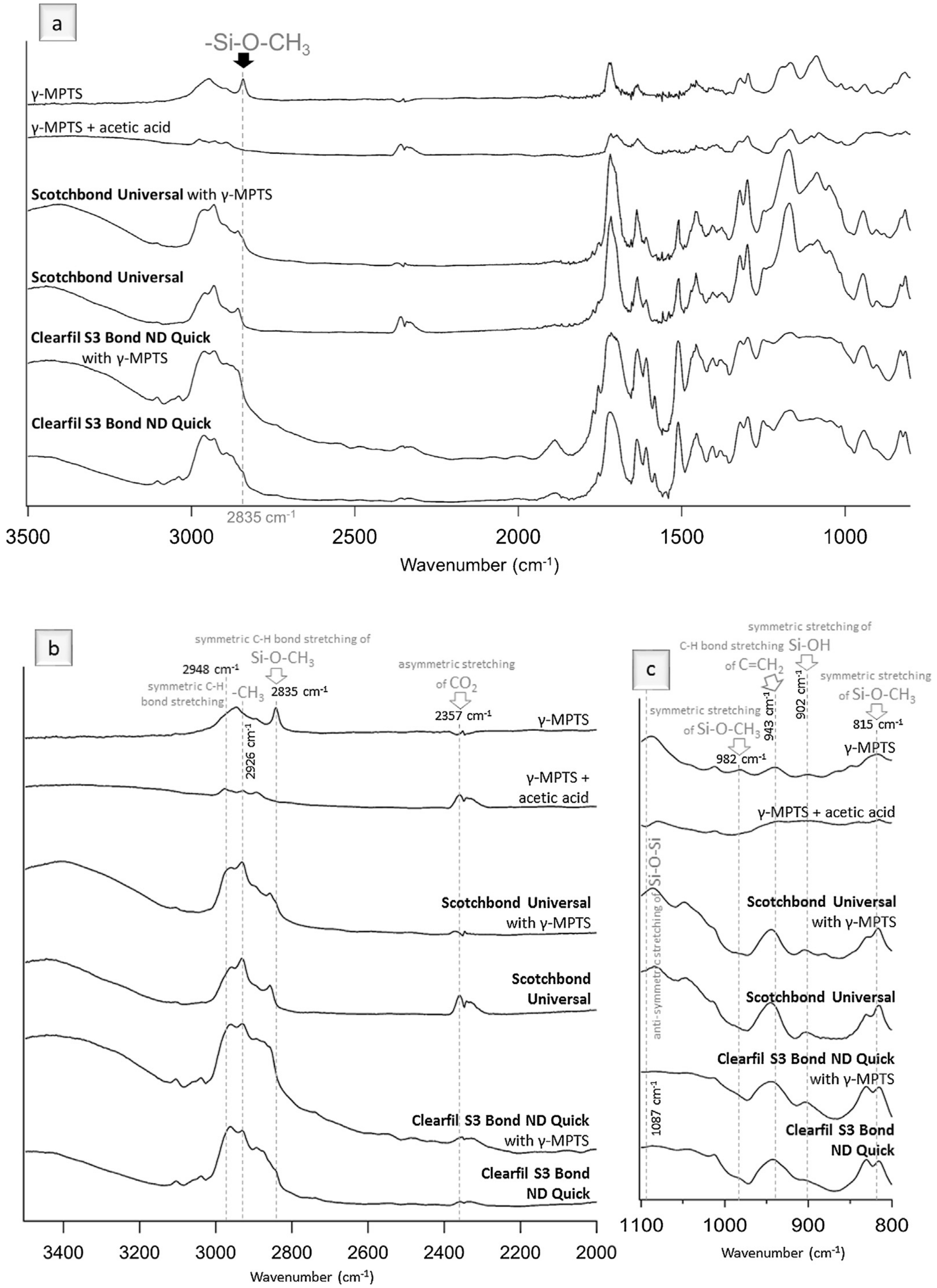

Fig. 2 – FTIR spectra of the adhesives Scotchbond Universal (3M ESPE) and Clearfil S3 ND Quick (Kuraray Noritake) with and without γ-MTPS added. As control, we used a 2 wt% γ-MTPS in 98% ethanol solution and the same solution mixed with a solution of 2 wt% acetic acid (Sigma–Aldrich) in 70 wt% ethanol and 28 wt% water. (a) FTIR full 3500–800 cm^{-1} spectrum; (b) FTIR 3500–2000 cm^{-1} spectrum; (c) FTIR 1100–800 cm^{-1} spectrum.

composition of the silane solution tested in their study was 2.5% γ-MTPS and 2.5% acetic acid in 95% ethanol (no water).

In order to confirm the status of silane coupling agents, FTIR is most commonly used [11–13]. FTIR did not suit for our study, since peaks representing silanol or dehydration condensation could not be (clearly) detected because of the multitude of overlapping peaks that should be associated with the complex composition of the two adhesives investigated and also due to presence of water and silane-treated filler in the adhesives. Although Si—O signals should appear in the

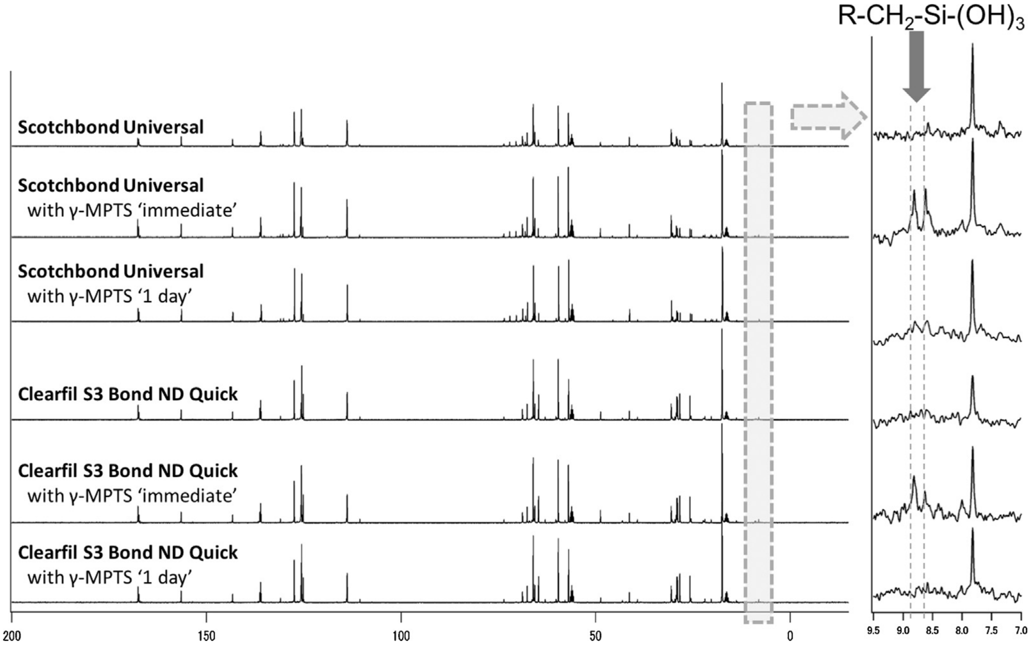

Fig. 3 – ^{13}C NMR spectra of the adhesives Scotchbond Universal (3M ESPE) and Clearfil S3 ND Quick (Kuraray Noritake Dental) with and without γ-MPTS added and analysed 'immediately' or '1 day' after mixing.

1100–850 cm^{-1} region after hydrolysis and siloxane-network formation, they could however not be detected because of overlapping peaks representing silane-treated filler.

NMR has also been used to analyze silane coupling agents [7,10]. In this study, ^{13}C NMR spectra revealed that dehydration condensation progressed with the time after γ-MTPS was mixed with the two adhesives. A multitude of significant peaks were disclosed by ^{13}C NMR spectra that again should be attributed to the complex composition of the adhesive formulations [14]. Nevertheless, two characteristics

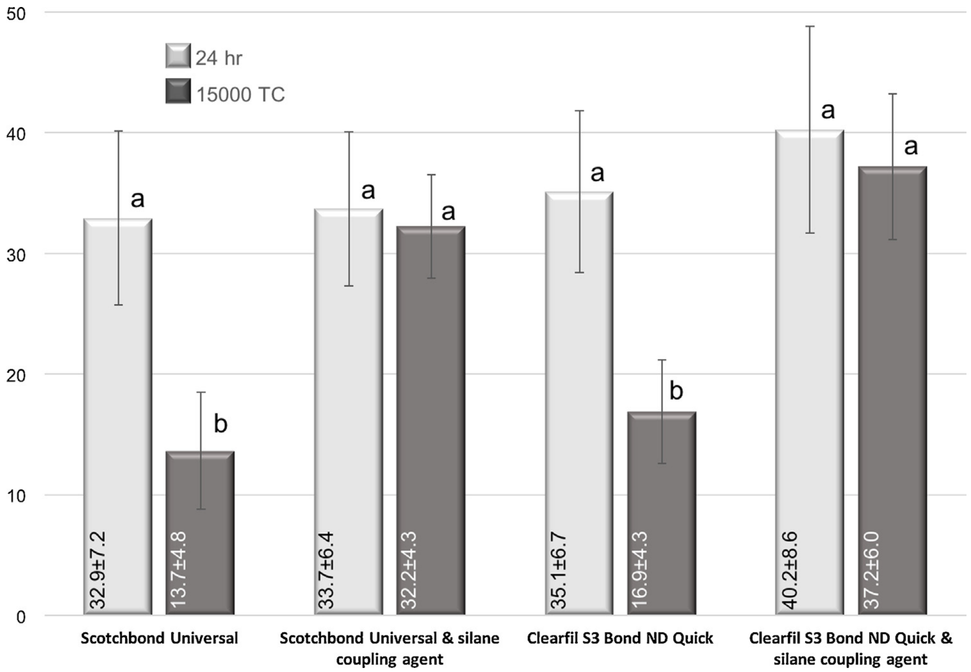

Fig. 4 – Shear bond strength onto CAD-CAM composite blocks at 24 h and after 15,000 thermo-cycles of the adhesives Scotchbond Universal (3M ESPE) and Clearfil S3 ND Quick (Kuraray Noritake Dental), when they were applied 'as such', and of their 1:1 drop mixtures with Clearfil Porcelain Bond Activator (Kuraray Noritake Dental). Bars denote the mean bond strength and the whiskers define the standard deviation. Inside the bars, the mean SBS value and the standard deviation are indicated. Means with the same letter are not significantly different.

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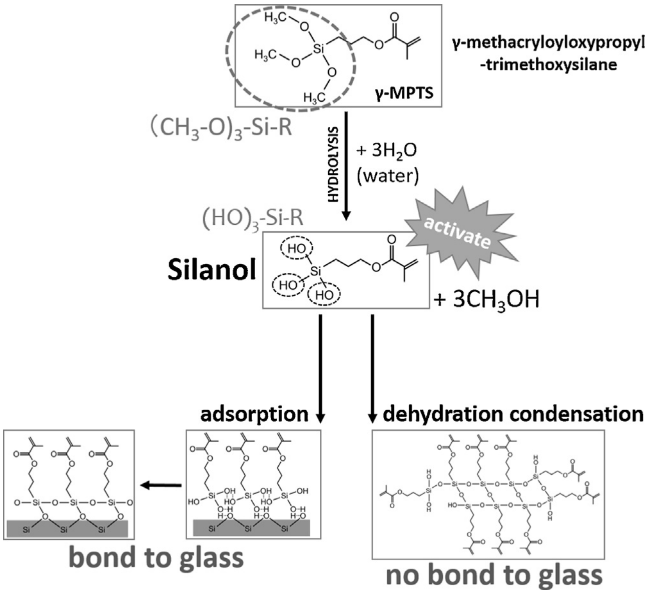

Fig. 5 – Schematic diagram of the chemical interaction of γ-MTPS with glass-rich materials, involving hydrolysis to silanol upon exposure to water and leading to either adsorption and bonding to glass or to dehydration condensation, by which it can no longer bond to glass.

peaks at around 8.5–9.0 ppm should be ascribed to silanol and were detected when the solutions were analyzed immediately after γ-MTPS was added; the '1-day' delayed analysis did not reveal the two silanol peaks. NMR has a concentration-dependent sensitivity. Therefore, we additionally analysed Scotchbond Universal to which 10 wt% γ-MPTS was added (Fig. 6). Silanol-characteristic peaks were only detected by NMR for the freshly prepared, 'immediately' measured adhesive, while these peaks were no longer detectable 3 days later.

Using NMR, Nishiyama et al. [7] could detect peaks that should be attributed to dehydration condensation of γ-MTPS; we, however, could not detect any peaks characteristic for dehydration condensation, this using not only ^{13}C NMR but also ^{1}H NMR (data not shown). This must most likely be attributed to a varying status of self-condensation, to the fact that the concentration of γ-MTPS was not high and to other components of the adhesives that masked condensation-specific peaks. Although Scotchbond Universal is claimed to incorporate silane [15], ^{13}C NMR however could not disclose peaks representing silanol.

Our FTIR and NMR data fully confirmed the bond strength data onto glass plates. Only adhesive solutions applied immediately after γ-MTPS addition promoted bonding. This confirms that γ-MTPS was immediately activated (Fig. 5) and contributed to the 'immediate' bond strength by chemical interaction. The dropped bond strength upon delayed application demonstrated that silanol was not stable in the adhesive solution and was inactivated already after 1 day. 3M ESPE's US Patent 4673354A [15] explained that silanol can be stable in some water/alcohol concentrations at a pH around 4.6. The pH of Scotchbond Universal was documented to be 2.7 [6]. This low pH may thus have promoted hydrolysis and dehydration condensation.

As silane has also been claimed to promote bonding to CAD-CAM composite blocks, bond strength to Lava Ultimate was also measured. A significant drop in bond strength was measured for both adhesives tested after artificial ageing, but only when silane was not added. This finding confirms the need for 'fresh' silanization as well as the insufficient effectiveness of silane incorporated in the universal adhesive. The indication 'crown' using Lava Ultimate is no longer recommended by 3M ESPE, because crowns were documented to

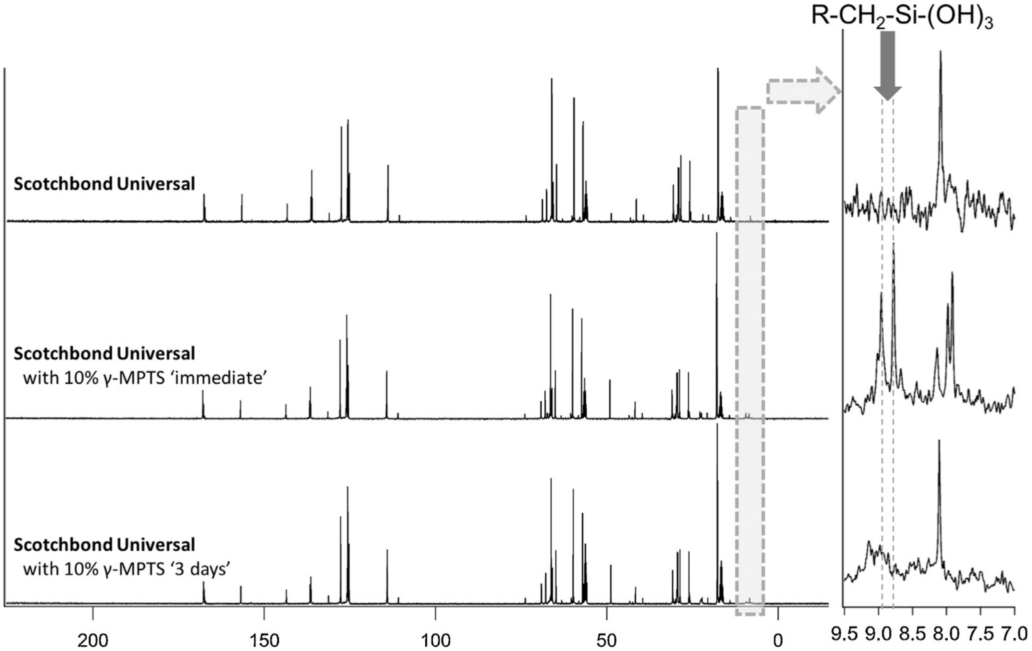

Fig. 6 – ^{13}C NMR spectra of Scotchbond Universal (3M ESPE) without and with 10 wt% γ-MTPS added; the latter NMR spectra were acquired 'immediately' and '3 days' after γ-MTPS was added to the adhesive.

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de-bond at a higher than originally anticipated rate. As Lava Ultimate composite blocks are recommended to be luted using the composite cement RelyX Ultimate (3M ESPE) in combination with Scotchbond Universal, the in this study found insufficient effectiveness of silane incorporated in Scotchbond Universal may have contributed to the higher incidence of crown de-bonding.

Similar *in vitro* data that a silane-containing universal adhesive was less effective and/or stable, have already been reported for composite [16] and lithium disilicate ceramics [17–19]. In order to bond to glass-rich ceramics, HF etching followed by silanization is the standard bonding protocol [8,20]. A universal adhesive like Scotchbond Universal must be beneficial as surface wetting agent and must, thanks to its low viscosity, be able to flow effectively into the micro-etch pits at the etched ceramic surface. Although a higher initial bond strength may be obtained, the bond strength may decrease on the long term because stable chemical bonding is lacking.

In this study, a shear bond-strength test was applied to measure the bond strength to the silica-glass plates and CAD-CAM composite blocks. We opted for the simplest bond-strength test mainly because of the high brittleness of the silica-glass plates, which otherwise would more easily have fractured within the plate rather than at the interface when for instance a micro-tensile bond strength approach would have been used. The latter could have been more suited to measure the bonding effectiveness to the CAD-CAM composite blocks, but we also opted for the shear bond-strength test in order to be consistent for test methodology. Although the discriminative power of a shear bond-strength test is lower than that of a micro-tensile bond-strength test [21], the data provided and the significant differences found were of that order that definitive conclusions could be drawn.

5. Conclusion

It is concluded that the silane-coupling effect in the tested silane-containing universal adhesive did not appear very effective and stable, most likely because the acidic solution promoted dehydration condensation. Clinically, the use of a separate silane primer (or silane freshly mixed with the adhesive) remains recommended to achieve enough silane-coupling effect on etchable ceramics.

Acknowledgements

The current research was supported by a JSPS KAKENHI Grant Numbers JP 26893156, 16K2045508. The authors declare no potential conflicts of interest with respect to the authorship and/or publication of this article.

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Please cite this article in press as: Yoshihara K, et al. Effectiveness and stability of silane coupling agent incorporated in 'universal' adhesives. Dent Mater (2016), http://dx.doi.org/10.1016/j.dental.2016.07.002