ORIGINAL ARTICLE

Self-adhesive resin cements: pH-neutralization, hydrophilicity, and hygroscopic expansion stress

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Abstract

Objectives The objective of the study was to investigate the relationship between pH-neutralization, hydrophilicity, and free hygroscopic expansion stress of self-adhesive resin cements (SARCs) after storage in artificial saliva.

Materials and methods The SARCs RelyX Unicem Automix 2 (RX2, 3 M ESPE), iCEM (iCEM, Heraeus) and Maxcem Elite (MCE, Kerr) were under investigation in this study. Cylinders (height × diameter, 6 × 4mm) were prepared from each material and stored in artificial saliva (7d at 37 °C). Cylinder height was measured at baseline and after 7 days. After storage, the compression modulus was measured to calculate the free hygroscopic expansion stress. For pH-neutralization and hydrophilicity assessment, disks (height × diameter, 1 × 1.5 mm) were prepared, covered with electrolyte, and monitored over 24 h at 37 °C. Hydrophilicity was assessed using the static sessile drop technique at baseline and at different time intervals up to 24 h. Data were analyzed using one-way ANOVA and post hoc Student-Newman-Keuls test (S-N-K, $\alpha = 0.05$).

Results After 24 h, RX2 (pH_{24h} 4.68) had a significantly higher ($p < 0.05$) pH-value than MCE (pH_{24h} 4.2) and iCEM (pH_{24h} 3.23). iCEM showed the significantly highest hydrophilicity ($p < 0.05$) after 24 h (θ_{24h} 85.02°), while MCE resulted lower (θ_{24h} 113.01°) in comparison with RX2 (θ_{24h} 108.11°). The resulting hygroscopic expansion stress of iCEM (29.15 MPa) was significantly higher ($p < 0.05$) compared to RX2 (14.5 MPa) and MCE (21.02 MPa).

Conclusions The material with lowest pH-neutralization capacity displayed higher hydrophilicity after 24 h and higher hygroscopic expansion stress after 7 days compared to those with high pH-neutralization.

Clinical significance Remnant hydrophilicity due to low pH-neutralization of SARCs could lead to cement interface stress build-up and long-term failure of silicate ceramic restorations.

Keywords Self-adhesive resin cements · pH · Hydrophilicity · Hygroscopicity · Expansion stress

Introduction

The luting of indirect silicate ceramic restorations such as inlays, onlays, and crowns has been simplified with the introduction of self-adhesive resin cements (SARCs). Restorations can be adhesively placed on the tooth without extra etching, priming and bonding procedures. To achieve bonding to the tooth, SARCs rely on a complex chemistry based on methacrylate monomers modified with carboxylic or phosphoric acid-groups [1]. After mixing, SARCs should have a high hydrophilicity to facilitate the wetting of the tooth surfaces and a low pH capable of etching the tooth substrates [1]. Due to demineralization, the carboxylic and phosphoric acid-groups of the modified methacrylate monomers interact by complex formation between the calcium from the hydroxyapatite of enamel and dentin [2] creating adhesion to the tooth [3]. Once adhesion to the tooth is achieved, an acidic pH and a high hydrophilicity are no longer required. Ideally, pH would increase and the material should turn hydrophobic. This takes place by an acid-base neutralization reaction between acidic groups of functionalized monomers and ions of the acid-soluble glass fillers of the material or the hydroxyapatite of

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the tooth substrates [1]. This process of pH-value increase is called pH-neutralization [4].

SARCs differ significantly in their pH-neutralization behavior [5, 6]. Low pH-neutralization has consequences on the material like inhibition of free-radical chain reaction resulting in reduced degree of conversion [7], insufficient biocompatibility by leached out components [8], low wear resistance [9], loss of mechanical [5] and bond strength [10]. Another implication of low pH-neutralization of SARCs is remnant hydrophilicity [1], which is suspected to lead to hygroscopic expansion [11, 12]. Hygroscopic expansion is of central importance [13–16], as expansion stresses arising from restorative and luting materials were found accountable for crack formation in silicate ceramic restorations in-vitro [17–19]. Further studies with experimental SARCs as core build-ups showed severe damage of lithium-disilicate crowns [19]. However, an assessment and correlation between pH-neutralization, hydrophilicity, and hygroscopic expansion stress of SARCs have not yet been described in the literature. These correlations are of clinical relevance as the hygroscopic expansion stresses could lead to fracture of silicate ceramic restorations.

The aim of this study was to investigate the influence of pH-neutralization on hydrophilicity and hygroscopic expansion stress of different commercially available SARCs. For the SARCs under investigation, the following research hypotheses were tested:

(1) pH-neutralization behavior does not influence hydrophilicity of SARCs
(2) increased hydrophilicity does not result in increased hygroscopic expansion stress of SARCs.

Materials and methods

Materials under investigation

Three commercially available self-adhesive resin cements were investigated in this study: RelyX Unicem 2 Automix (RX2, 3 M ESPE, Seefeld, Germany), iCEM (iCEM, Heraeus, Hanau, Germany) and Maxcem Elite (MCE, Kerr Hawe, Bioggio, Switzerland). Table 1 describes the chemical composition of the three investigated SARCs, as far as disclosed by the manufacturers.

pH-neutralization

Flat disks ($n = 5$ per material) with 1 mm height and 15 mm in diameter were prepared using a metal mold. The material was filled into the mold, covered with a mylar strip on top and bottom to prevent the formation of an oxygen inhibition layer,

light cured from both sides (20 s, 800 mW/cm^2; Elipar Trilight, 3 M ESPE, Seefeld, Germany) and left to maturate for 10 min at 37 °C in the dark measurement chamber at 100 % humidity (Bühler TH15 Incubator, Edmund Bühler GmbH, Hechingen, Germany). For pH-neutralization measurement, each specimen was covered with 30 μL of 1 mmol/L NaCl solution and a flat pH-electrode (InLab Surface, Mettler Toledo, Germany) was placed on top of the specimen. The measurements started 15 min after specimen preparation and lasted for 24 h. After each measurement, the pH electrode was recalibrated at pH 4 and pH 7 [5].

Hydrophilicity

Flat disks ($n = 5$ per material) with 1 mm height and 15 mm in diameter and were prepared as described above. After maturation, the specimens were stored in distilled water at 37 °C. Before measurement, specimens were gently dried. The hydrophilicity was determined by contact angle measurement using the sessile drop technique (3 μL distilled water, Drop Shape Analyzer DSA30, Krüss, Germany). The measurements started 15 min after specimen preparation and lasted for 24 h.

Free hygroscopic expansion stress

For each material, cylindrical samples ($n = 5$) with 6 mm height and 4 mm in diameter were made using a Teflon mold. The mold was filled incrementally with 2-mm-thick layers to prevent air void formation and to assure a successful light curing (20 s, 800 mW/cm^2; Elipar Trilight, 3MESPE). After 15 min, the specimens were polished up to 4000 grit with SiC paper to achieve a plane parallel surface and eliminate the oxygen inhibition layer. Subsequently, the baseline height (h_0) of each specimen was measured with a digital caliper (accuracy ±0.01 mm, HOLEX digital caliper 150 mm, Hoffmann GmbH, Achim, Germany). After the baseline measurement, the specimens were stored for 7 days in 10 mL artificial saliva at 37 °C [20]. Specimens height after storage (h_7) was measured as described before, and the change in height ($\Delta_h = h_7 - h_0$) was calculated. The compression modulus (C) of the specimens after storage was measured using a universal testing machine (Zwick Z2.5, Zwick Roell, Ulm, Germany) equipped with a 2 kN load cell (KAP-S 2 kN Force Transducer, accuracy ±0.2 % F_{nom} (class 0.5, ISO 7500–1), A.S.T.—Angewandte System Technik, Mess- und Regeltechnik, Dresden, Germany) and an extensometer (Zwick 057092—displacement transducer for compression tests and 3- and 4-point flexure tests, Zwick Roell). The hygroscopic expansion stress (σ) was estimated to be equivalent to the stress needed to compress the specimen back to its baseline height (h_0). Therefore, the hygroscopic expansion stress (σ) was calculated as the product of the compressive

Table 1 Materials under investigation (information as disclosed by the manufacturers)

Material	Manufacturer and batch no.	Shade	Content	Fillers
RelyX Unicem 2 Automix	3 M ESPE 510927	A2	Base paste: • Mono-, Di-, and Triglycerindimthacrylateester of phosphoric acid 20–30 wt% • 2,2′-Ethylenedioxydiethylmethacrylate 10–20 wt% Catalyst paste: • Bisphenol A bis3- (methacryloxypropyl) ether substituted dimethacrylate 20–30 wt% Barbituric acid <5 wt% • 1,12-Dodecandiylbismethacrylate <5 wt% • Sodiumtoluol-4-sulfinate <5 wt% • Calciumhydroxide <2 wt% • Methacrylated aliphatic amin <1 wt%	Base: • Inorganic fillers 43 vol% • Glaspowder 45–55 wt% • Silanized SiO_2 1–10 wt% • Grain size (D 90 %) 12.5 μm Catalyst: • Glaspowder 45–55 wt% • TiO_2 < 0.5 wt%
iCEM	Heraeus 385129	Uni	• Di-, Tri-, and multifunctional acrylate monomers	• 41 vol%
Maxcem Elite	Kerr Hawe 4819701	Clear	• 2–5 % Hydroxyethylmethacrylayte (HEMA) • 4-Methoxyphenol (MEHQ) >1 % • Cumolhydroxperoxid (CHPO) >1 %	• 69 wt%

strain ($\varepsilon = \frac{\Delta_h}{h_0}$) and the compression modulus (C) of each specimen (Eq. 1):

$$\sigma = \varepsilon \cdot C \qquad (1)$$

Statistical analysis

Data were analyzed using one-way analysis of variance (ANOVA), and homogenous subsets were determined by post hoc Student-Newman-Keuls test (S-N-K). All tests were performed at a significance level of $\alpha = 0.05$, with a statistical software (SPSS Version 21.0, IBM Corporation, Armonk, USA).

Results

The results of the pH-neutralization, hydrophilicity, and free hygroscopic expansion stress experiments are shown in Table 2.

pH-neutralization

Significant differences in pH-neutralization behavior among the materials under investigation could be observed (Fig. 1). In contrast to RX2, which shows a continuous increase in pH-value over time, iCEM and MCE display an initial decrease in pH-value. iCEM reached the significantly lowest ($p > 0.05$) pH-value (pH_{min} 2.89) followed by RX2 (pH_{min} 3.77) and MCE (pH_{min} 3.98). After 4 h, RX2 had a significant increase in pH-value (pH_{4h} 4.46) whereas iCEM (pH_{4h} 2.97) and MCE (pH_{4h} 4.02) displayed no significant change in acidity. After

24 h, RX2 (pH_{24h} 4.68) reached the significant highest pH-value ($p > 0.05$) followed by MCE (pH_{24h} 4.20) and iCEM (pH_{24h} 3.23) had the significant lowest ($p > 0.05$) pH-value.

Hydrophilicity

Significant differences in contact angle development of the materials under investigation could be observed (Fig. 2). After 15 min, MCE (θ_{15min} 85.06°) had a significant higher ($p > 0.05$) contact angle than RX2 (θ_{15min} 69.85°) and iCEM (θ_{15min} 67.60°). After 24 h, the contact angles of all materials increased significantly compared to the previous time point (15 min). MCE (θ_{24h} 113.01°) and RX2 (θ_{24h} 108.11°) showed significant higher ($p > 0.05$) contact angles compared to iCEM (θ_{24h} 85.02°) after 24 h.

Free hygroscopic expansion stress

After storage, iCEM showed a mean increase in height of 0.062 mm (±0.010 mm), RX2 0.016 mm (±0.002 mm) and MCE 0.034 mm (±0.005 mm). iCEM presented a compression modulus of 2.7 ± 0.3 GPa, RX2 5.3 ± 0.6 GPa and MCE 3.5 ± 0.5 GPa. The resulting hygroscopic expansion stress of iCEM (29.15 MPa) was significant higher ($p > 0.05$) than the one of RX2 (14.50 MPa) and MCE (21.02 MPa).

Discussion

Compared to RX2 and MCE, iCEM showed the significantly lowest pH-neutralization (pH_{24h} 3.23) as well as the lowest increase in contact angle (25 %) and was the most hydrophilic

Table 2 Results of the pH-value measurement, hydrophilicity, the free hygroscopic expansion stress test, and standard deviation ()

Material	pH-Value ( )			pH-increase (%)	Hydrophilicity contact angle θ (°)		Contact angle increase (%)	Free expansion Stress (MPa)
	Minimal	4 h	24 h		15 min	24 h		
RelyX Unicem Automix 2	3.77 E (0.12)	4.46 B (0.09)	4.68 A (0.03)	24.13	69.85 C (5.46)	108.11 A (3.03)	54.77	14.50 (7.19) A
iCEM	2.89 G (0.10)	2.97 G (0.11)	3.23 F (0.09)	11.76	67.60 C (9.060)	85.02 B (8.74)	25.76	29.15 (4.79) B
Maxcem Elite	3.98 D (0.13)	4.02 D (0.14)	4.20 C (0.14)	5.52	85.06 B (11.54)	113.01 A (3.12)	32.85	21.02 (3.17) A

Homogenous subsets, within the same kind of measurement, are indicated by same letters (SNK-Test, $p = 0.05$)

material (θ_{24h} 85.02°) after 24 h. Under this aspect, the first research hypothesis has to be rejected, as the pH-neutralization has an influence on the hydrophilicity of the SARCs under investigation.

A study by Madruga et al. [4] investigated the effect of different calcium hydroxide ($Ca[OH]_2$) concentrations on the pH-neutralization of experimental SARCs. In that study, the incorporation of 2–4 % $Ca(OH)_2$ to the experimental SARCs led to higher pH-neutralization after 24 h, with a similar neutralization behavior as RX2 in similar studies [5, 21]. Madruga et al. attributed this finding to the interaction of the Ca^{2+} ions, or with the free valences of the calcium on solid $Ca(OH)_2$ particles with unbound phosphate monomers, resulting in time-dependent neutralization. RX2, as far as disclosed by the manufacturer (Table 1), contains <2%wt $Ca(OH)_2$ in the catalyst paste which might contribute to the superior pH-neutralization. Marghalani et al. [22] concluded that the low sorption and solubility of RX2 after storage in lactic acid, compared to other SARCs, was due to the more effective neutralization of the acidic phosphate component by ions released from its fillers. Unfortunately, the manufacturers do not disclose detailed information about the components and chemistry of their products, hindering a deeper understanding of these materials. Differences in the pH-curves over measurement time can be observed among the investigated materials as well (Fig. 1). While RX2 shows a continuous increase in pH-value over the first 4 h, the pH-values of MCE and iCEM initially dropped within the first hour before increasing slowly. This leads to the presumption that manufacturers have different strategies to manage the acid-base reaction, resulting in more or less successful pH-neutralization. Small changes in pH-value result in remarkable differences in the acid concentration: change of 1 pH-value describes a 10-fold difference in acid concentration. The acid concentration is supposed to be the main factor on polarity of SARCs resulting in hydrophilicity. Those materials with the highest pH-value after 24 h displayed the significantly lowest contact angles. A correlation between contact-angle and pH-value was found for RX2 (Pearson's $r = 0.87$) and iCEM (Pearson's $r = 0.85$). However, the general principles of the acid-base neutralization reaction between acidic groups of functionalized monomers and ions of the acid-soluble glass fillers of the material or the hydroxyapatite of

the tooth substrates [1] are too general and not sufficient to explain the differences in the resulting pH-neutralization of the materials under investigation.

After storage, iCEM had significantly superior hydrophilicity (θ_{24h} 85.02°) and significantly highest expansive stress (29.15 MPa), compared to MCE (θ_{24h} 113.01°, 21.02 MPa) and RX2 (θ_{24h} 108.11°, 14.50 MPa). Therefore, the second research hypothesis has to be rejected, since increased hydrophilicity resulted in increased hygroscopic expansion stress of SARCs under investigation. High hydrophilicity, in order to enable wetting of the tooth substrates for etching, is a desired initial property for SARCs [1]. This is possible due to the acidic monomers whose phosphate, hydroxyl, or carboxylate groups are excellent hydrogen bonding sites [23]. These sites facilitate the uptake of "bound water" into the polymer network. Yiu et al. described this as "interaction theory" [24] and made this process responsible for the significant higher moisture absorption in polymers containing hydrophilic and ionic comonomers with functional hydroxyl, carboxylate, and phosphate groups. Among the materials under investigation, RX2 (θ_{15min} 69.85°, pH_{min} 3.77) and iCEM (θ_{15min} 67.60°, pH_{min} 2.89) were initially hydrophilic and acidic. However, the potential of the materials to eliminate the hydrophilicity, resulting from the hydrogen bonding sites of the acidic monomers, differed significantly. In the case of iCEM, the remnant hydrophilicity led to water sorption and significant higher hygroscopic expansion stress. Probably the formulation of the acidic monomers, the balance of their concentration, and the composition of the soluble fillers or additives might be the clue to explain the remnant hydrophilicity and subsequent hygroscopic expansion stress.

Besides hydrophilicity due to low pH-neutralization, other factors can also lead to hygroscopic expansion. Water sorption, because of porosities in the material, was reported for similar materials [25]. Regarding SARCs, this was found for encapsulated materials, but not for automix-syringe products [5, 22]. An aspect, which has an influence on water uptake is the rate of conversion, which affects the physical and mechanical properties of the material [26]. In several studies, a correlation between acidic monomers and a low degree of
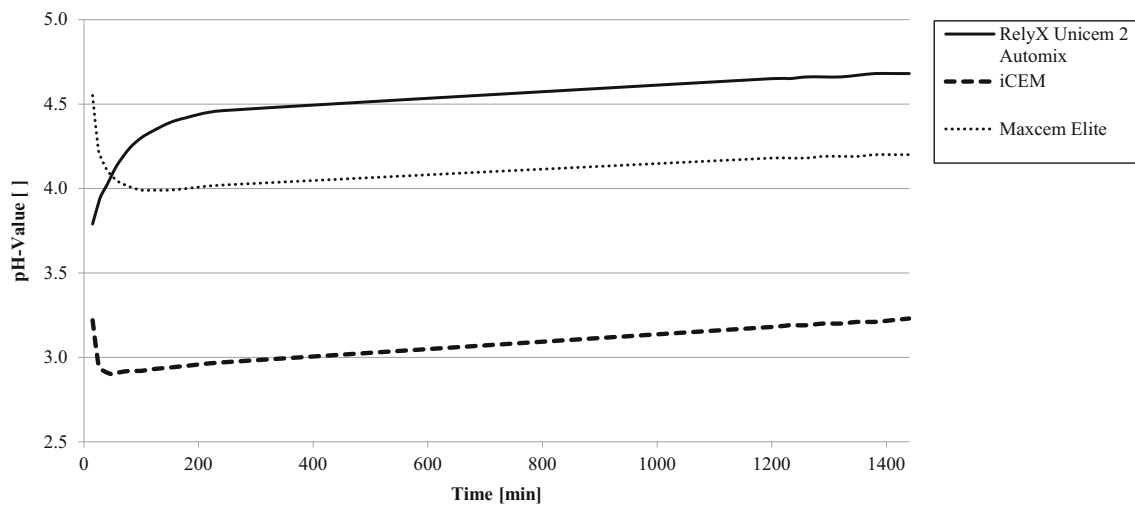
Fig. 1 pH-neutralization behavior over time of RelyX Unicem 2 Automix, iCEM and Maxcem Elite

conversion was reported [9, 27]. The reason for this is believed to be, that acidic monomers presumably interact with the amine initiator of the camphorochinone-amine initiator system, contained in dual-cured resins [8]. Hence, the phosphonated groups represent more stable radicals than the radicals formed by conventional BisGMA monomers. The reduced ability to undergo polymerization results in a lower molar mass of the matrix molecules and more areas of free volume within the sample, in which water can accumulate and rise the water content of the resins [28].

The recorded hygroscopic expansion stresses were measured on material cylinders with 6-mm height and 4 mm in diameter so that the present set-up resembles the size of a core build-up or partial build-up, similar to those in a recent study of Sterzenbach et al. [19]. Supposedly, the investigated volume of material will result in greater hygroscopic expansion stress than those

present in a cementation gap below or around a restoration. In the present set-up, the material is not constrained by a cavity and can expand freely. If the material under investigation would be constrained, a restriction of the hygroscopic expansion could take place, leading to elastic compressive stresses in the material, not making clear on how far hygroscopic expansion stresses are differing among the different formulations. Alternative to the measurement method in the present study, hygroscopic expansion can also be measured with non-contact methods as employed by Wei [29] and Alrahlah et al. [30] with a custom-built laser micrometer, or by optical scanning as performed by Versluis et al. [15]. Archimedes' principle has also been applied to assess hygroscopic expansion [31].

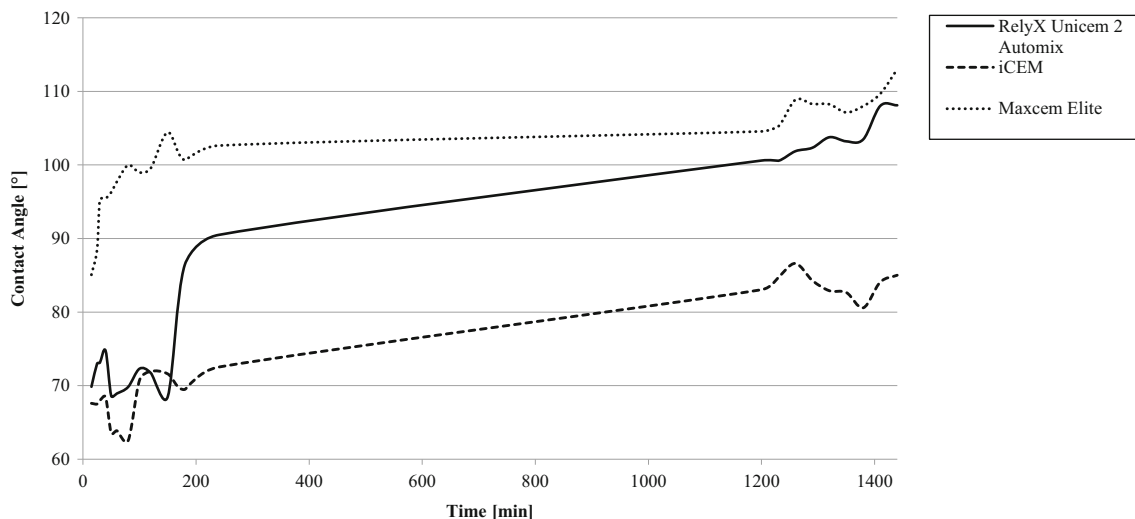As storage medium has an impact on hygroscopic expansion [32], artificial saliva was used for specimen

Fig. 2 Contact angle behavior over time RelyX Unicem 2 Automix, iCEM and Maxcem Elite

storage [20]. The use of distilled water does not take into account the osmotic gradient between the storage solution and the material under investigation. Water sorption following ISO 4049:2009 norm was not performed as this standard does "not cover those polymer-based luting materials that have an adhesive component within the structure of the material" [33]. In this norm, specimens are initially placed in a desiccator, but this could be unfavorable if water is needed for the material's setting reaction [34], leading to damage of the specimens affecting their water sorption behavior [35].

The present study shows, that both hydrophilicity and pH-neutralization behavior have a considerable impact on resulting hygroscopic expansion stress during water storage. However, the effects on tooth structure or restoration cannot be predicted directly from the findings of this study. The expansion stress of a material always acts on the whole restoration–cement–tooth unit and is limited by its restraining forces. In porous materials water uptake can happen with hardly noticeable change in volume [14], as this "unbound water" simply diffuses into the material's voids. It is possible, that when the cement is constrained in a cavity and cannot expand freely, unlike in the present experiment, it could get a higher density by compressing the pores. The resulting hygroscopic expansion stress would be compensated. This could have less effect on tooth structure or restoration than expected by the results of the hygroscopic expansion stress experiment. The results of the present study show significant differences among the investigated materials, but the effect on the restoration should be assessed by experimental set-ups similar to those of Sterzenbach [19] or Sindel et al. [18].

Conclusions

Within the limits of this study, it can be concluded that for the SARCs under investigation, the pH-neutralization behavior has a significant influence on hydrophilicity and on the hygroscopic expansion stress, which arises during and after the setting reaction. The resulting hygroscopic expansion stress varies significantly among the tested formulations. Even though the findings of this study cannot certainly predict the absolute effect in-vivo, it is strongly recommended to use SARCs with low initial pH and strong neutralization reaction and resulting low hygroscopic expansion stress. This holds particularly true for applications such as partial build-up and/or cementation of thin silicate ceramic restorations.

Compliance with ethical standards

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