Structural/Chemical Characterization and Bonding Effectiveness of a New Self-adhesive Bulk-fill Restorative

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Purpose: The material structure and chemical elemental composition of a new 'self-adhesive composite hybrid' were investigated. The bonding performance when applied onto flat ('FLAT') versus high C-factor class-I cavity-bottom ('CAVITY') dentin and in light-cure ('LC') versus self-cure ('SC') mode was determined.

Materials and Methods: The self-adhesive bulk-fill composite Surefil One ('Su-O') (Dentsply Sirona) was compared with the resin-modified glass-ionomer Fuji II LC Improved ('Fuji2LC') (GC) and the ion-releasing 'alkasite' material Cention N ('CentionN') (Ivoclar Vivadent). The material structure was examined by S/TEM, while the chemical elemental composition was analyzed by EDS. The 'immediate' and 'aged' micro-tensile bond strength (µTBS) of Su-O_LC/SC was compared to that of Fuji2LC, applied without any pre-treatment, and to that of CentionN, applied following bonding with Adhese Universal ('AU') (Ivoclar Vivadent) in self-etch mode ('AU/CentionN'). All restorative materials were bonded onto FLAT and CAVITY dentin. Statistical analysis was performed with the Kruskal Wallis non-parametric test.

Results: EDS analysis revealed Su-O was richer in C and P than the reference restorative materials. Applied to FLAT dentin, the significantly highest immediate and aged µTBS was recorded for AU/CentionN, solely not being significantly different from Su-O_LC. Applied to CAVITY dentin, the significantly highest immediate µTBS was recorded for AU/CentionN, solely not being significantly different from Su-O_SC. Su-O_LC bonded to CAVITY dentin suffered from a high incidence of pre-test failures.

Conclusion: While Su-O_LC bonded effectively and durably to FLAT dentin, Su-O_SC bonded more favorably than Su-O_LC in class-I cavities, most likely related to shrinking stress differently challenging the respective bond.

Keywords: Adhesion, Aging, Composite, Curing, EDS, TEM

Clinical Relevance: Filling Class-I cavities in bulk without adhesive is more favorable when the self-adhesive composite hybrid is allowed to self-cure.

Self-adhesive tooth-colored restorative materials are highly desired to further simplify clinical filling procedures.[14,30,45] Self-adhesive composites do not require a separate adhesive or any kind of surface pretreatment to bond to tooth substrate.[19,38] One of the first commercial self-adhesive composites has been the self-adhesive flowable composite Vertise Flow (Kerr; Orange, CA, USA). Its self-adhesiveness depends on the contained functional monomers phosphoric-acid ester methacrylate and glycerolphosphate dimethacrylate (GPDM).[14] Although Vertise Flow (Kerr) was documented to exhibit less microleakage than conventional fissure sealants,[39] a clinical trial of sealants revealed a disappointing retention rate of only 62.9% after two years of clinical service.[27] In-depth ultra-morphological interfacial characterization showed that the bonding effectiveness of the self-adhesive composite Vertise Flow (Kerr) to aprismatic enamel and smear-covered tooth surface underscored that of contemporary adhesives.[32] In that study, interfaces at flat surfaces were investigated, while in clinical situations less favorable cavity configurations must challenge the self-adhesively obtained interface even much more. The suboptimal interfacial findings correlated with inferior bond-strength and interfacial fracture-toughness data reported in three other studies[9,10,38] Previous *in-vitro*[6] and short-term 6-month clinical[8] research on another self-adhesive flowable composite, namely Fusio Liquid Dentin (Pentron, Orange, CA, USA) when bonded to dentin, revealed both a low bond strength and low (33%) clinical success rate, indicating unsatisfactory self-adhesiveness. Otherwise, a tighter interface at both enamel and dentin was ultra-structurally imaged for the experimental 3M-ESPE (Seefeld, Germany) ‘Exp. 564’ self-adhesive filling material, containing phosphoric acid-6-methacryloxy-hexylesters as self-adhering functional monomers.[19] Unfortunately, actual bonding-effectiveness measurements were not reported, although they are needed to substantiate the findings of the exploratory interfacial characterization study.

Recently, a new self-adhesive bulk-fill composite was commercially introduced as Surefil One (‘Su-O’) (Dentsply Sirona; Konstanz, Germany),[11] being subject of the current study. The primary objectives of this study were to characterize ultra-structurally and chemically the filler-matrix configuration of Su-O as well as to measure its dentin-bonding effectiveness and durability to flat and high C-factor cavity-bottom dentin when used in light- and self-cure mode. The self-adhering resin-modified glass-ionomer cement (GIC) Fuji II LC Improved (‘Fuji2LC’) (GC; Tokyo, Japan) and the recently introduced amalgam-replacing ‘alkasite’ restorative material Cention N (‘CentionN’) (Ivoclar Vivadent; Schaan, Liechtenstein) served as reference restorative materials. The null hypotheses tested were (1) that there was no structural/chemical difference in filler-matrix configuration between Su-O and the two reference materials, and (2) that the ‘immediate’ and ‘aged’ bonding effectiveness to flat and high C-factor cavity-bottom dentin did not significantly differ from that obtained by the reference materials.

MATERIAL AND METHODS

Preparation of restorative material disks

Four disks with a 2-mm thickness and 7-mm diameter were prepared from each restorative material. Two Su-O disks were self-cured, by allowing them to set for 6 min in the dark. The two other remaining disks were light-cured for 30 s on each side using the light-emitting diode (LED) light-curing unit Bluephase 20i (Ivoclar Vivadent) with an output of 1200 mW/cm^2, when used in ‘high mode’, as determined and confirmed regularly during the experiment using a Marc Resin Calibrator (BlueLight Analytics; Halifax, Canada). Once prepared, the specimens were kept for 1 hr at 100% humidity, prior to being embedded in epoxy resin using a Teflon mold with an 18-mm thickness and 25-mm diameter. The embedded disks were next polished with silicon carbide papers in a sequence of P320 (Hermes; Hamburg, Germany), P1200 and P4000 (Struers; Ballerup, Denmark), and then subjected to 3- and 1-µm diamond suspensions (Kemet International; Maidestone, UK) on cloth paper, all using a grinding/polishing machine (Beta Grinder-Polisher, Buehler; Lake Bluff, IL, USA).

Structural Scanning Electron Microscopy (SEM) characterization of restorative materials

Two metallo-graphically polished specimens for each light-cured material were coated with gold using a gold-sputter machine (JFC-1300, JEOL; Tokyo, Japan) and imaged using a scanning electron microscope (JSM-6610LV, JEOL) at an accelerating voltage of 5 kV. The SEM photomicrographs were obtained at 5000× original magnification with a working distance of around 10 mm.

SEM Energy Dispersive X-ray spectroscopy (SEM/EDS) elemental analysis of restorative materials

SEM coupled with EDS (FEI-Nova Nanosem 450, FEI; Eindhoven, The Netherlands) was used to evaluate the elemental composition and distribution in two polished disks (n=2) prepared from each material. Disk surfaces of Fuji2LC and CentionN were coated with a thin platinum layer (Q150T S, Quorum, United Kingdom). In order to avoid peak overlapping of the Pt-coating with phosphorus contained in self-cured Su-O, a thin gold coating was instead applied using a gold-sputter machine (JFC-1300, JEOL). On each disk, two areas of 20×20 µm with a representative filler-matrix configuration were mapped for the chemical elements expected, as based on technical compositional data obtained for the three restorative materials investigated. Drift correction was enabled to avoid drifts that might have occurred at nanoscale for non-conductive specimens. Areas of 10×10 µm on Su-O disks were additionally characterized using multi-element EDS mapping.

Ultra-structural Transmission Electron Microscopy (TEM) of restorative materials

To disclose the ultra-structure of the experimental self-adhesive restorative material Su-O as compared to that of the two reference restoratives, TEM specimens were prepared by embedding set material into silicon molds using TEM epoxy resin (Sigma-Aldrich; Steinheim, Germany). Specimens were light-cured for 60 s (30 s per side) using the LED curing light Bluephase 20i (Ivoclar Vivadent) with an output of 1200 mW/cm^2 when used in ‘high mode’. After the specimens were kept for 1 hr at 100% humidity, they were processed for TEM, employing routine TEM-specimen preparation/processing, as described in detailed before by Van Meerbeek *et al.* (1998).[48]

Micro-tensile bond strength (μTBS) of restorative materials to dentin

A total of 64 non-carious human third molars were collected (following informed consent approved by the Commission for Medical Ethics of KU Leuven under the file number S57622), stored in 0.5% chloramine T/water and used within 1 month after extraction. All teeth were randomly subdivided into 8 experimental groups. For the four 'FLAT' groups, the crown was cut 4 mm below the cusp tips, ending with a flat surface in mid-coronal dentin. For the four 'CAVITY' groups, the cusp tips were first flattened, upon which a standard box-type class-I cavity (3.5×3.5×4 mm) was prepared with the cavity bottom again ending in mid-coronal dentin. All preparations were made using the MicroSpecimen Former (University of Iowa; Iowa, IA, USA), equipped with a high-speed medium-grit (107 μm) diamond bur (882, Komet; Lemgo, Germany). A 3.5×3.5×4 mm buildup in one of the restorative materials investigated was made in bulk on the flat dentin surfaces using an addition-silicone mould (Aquasil medium body, Dentsply Sirona), while the cavities were likewise bulk-filled with one of the restorative materials as well. The restorative material was applied strictly following the respective manufacturer's instructions (Table 1). Besides application of the experimental self-adhesive bulk-fill restorative material Su-O, the resin-modified GIC Fuji2LC was applied without beforehand poly-alkenoic acid conditioning, while the alkasite restorative material CentionN was applied to dentin beforehand self-etched using AdheSE Universal ('AU') (Ivoclar Vivadent). All specimens of the three FLAT and three CAVITY experimental groups were light-cured using the LED light-curing unit Bluephase 20i (Ivoclar Vivadent) with an output of 1200 mW/cm^2. Specimens of two additional experimental groups involved application of Su-O to FLAT and CAVITY dentin that was allowed to self-cure for 6 min.

Subsequently, the bonded specimens were kept for 1 hr at 100% humidity prior to being immersed and stored for 1 week in distilled water at 37°C. Upon 1-week water storage, all specimens were sectioned perpendicular to the interface using a water-cooled diamond saw (Accutom-50, Struers; Ballerup, Denmark) to obtain rectangular sticks (4 micro(μ)-specimens per tooth: 1×1 mm wide). For each group, 16 μ-specimens (2 μ-specimens per tooth) were immediately tested and another 16 µ-specimens were aged for 50k thermocycles between two water baths at 5°C and 55°C using a THE-1200 thermocycler (SD Mechatronik; Munich, Germany) prior to testing. For the µTBS test, the specimens were fixed to a BIOMAT jig with cyanoacrylate-based glue (Model Repair II Blue, Dentsply Sirona Sankin; Tochigiken, Japan) and stressed at a crosshead speed of 1 mm/min until failure in a LRX testing device (LRX, Lloyd; Hampshire, UK) using a load cell of 100N. When specimens failed before actual testing, they were recorded as pre-test failures (ptf's) with each ptf included as 0 MPa.[1] Statistical differences were examined using Kruskal Wallis non-parametric statistical analysis with the statistical significance set at α=0.05.

Fractographic analysis of µTBS specimens

The fractured specimens were evaluated using stereomicroscopy (Stemi 2000-CS, Zeiss; Oberkochen, Germany) at 50x magnification to classify the failure mode in either 'cohesive failure in dentin', 'cohesive failure in composite', 'adhesive (interfacial) failure', or 'mixed failure'. Representative fractured surfaces, exhibiting the most frequently occurred failure mode and originating from specimens with a µTBS reported close to the mean or from ptf specimens, were selected for SEM observation (JSM-6610LV, Jeol). After fixation using 2.5% glutaraldehyde, the SEM specimens were gradually dehydrated in ethanol and dried with hexamethyldisilazane (Acros Organics, Thermo Fisher Scientific; Geel, Belgium). Afterwards, specimens were coated with gold using the gold-sputter device (JFC-1300, Jeol). The SEM photomicrographs were originally captured at 85-90×, 2000×, and 9000× magnification with a working distance of around 10 mm.

RESULTS

Structural SEM characterization of restorative materials (Fig. 1)

The three restorative materials contained filler particles that differed in shape and size (Fig 1$a_{1\text{-}3}$). The self-adhesive bulk-fill composite Su-O visually presented the most homogeneous filler-matrix configuration with particles that overall are smaller in size (Fig 1a_1) as compared with those within Fuji2LC (Fig 1a_2) and CentionN (Fig 1a_3). At high magnification (Fig 1$c_{1\text{-}3}$), the maximum filler size within Su-O was estimated to be around 5 µm (Fig 1c_1), while the filler size within Fuji2LC widely ranged between 1 and 10 µm (Fig 1c_2) and CentionN contained larger filler particles up to 15 µm (Fig 1c_3). Filler particles were more rounded in Su-O (Fig 1a/c_1), while Fuji2LC's filler particles appeared sharper (Fig 1a/c_2), somewhat typical of GICs, and CentionN's particles varied most in shape and size (Fig 1a/c_3). Morphologically, the filler loading appeared to decrease in the order of Fuji2LC > Su-O > CentionN, while according to technical information provided by the manufacturer the filler loading of the three restoratives does not differ much (Table 1).

SEM/EDS elemental analysis of restorative materials

Representative SEM/EDS spectra revealed different chemical compositions of the three restorative materials (Fig 1b). Further details per element in weight percentage (mean and standard deviation of four measurements) are presented in Table 2 for each restorative material. The main elements C, O and Si were detected in all materials, with Su-O being richer in C and poorer in O than the reference restoratives. Elements detected in Su-O but not detected in the reference restoratives are P (substantial amount), N and Na (scarce amount). All three restoratives contain F, decreasing in the order of Fuji2LC > CentionN > Su-O. Both Su-O and Fuji2LC contain Sr. Typical of CentionN is the relatively high Ca and Ba amount. Semi-quantitative element EDS mapping confirmed the relatively high concentrations of C, O, SI, Sr and P in Su-O (Fig 2).

Ultra-structural TEM of restorative materials

TEM of Su-O disclosed the presence of three kinds of filler particles (Fig 3 and Table 1). The Al-P-Sr-Na-F-Si glass exhibited an irregular polyhedral shape (Fig 3b,c: open arrows). YbF particles were irregular and strongly electron-dense with a size of around 200 nm (Fig 3d: handpointers). Highly dispersed SiO_2 could be found between the larger filler particles (Fig 3e: asterisks).

Typical GIC filler could be detected in Fuji2LC with the filler size ranging between 0.5 and 2 µm (Fig 4a). At high magnification, electron-lucent globules were disclosed within the relatively large glass filler (Fig 4a: open arrows). High quantities of YbF (Fig 4b: handpointers) were interspersed between larger (0.1-1 µm), irregular and rounded filler particles, representing Ca-F-Si and Ca-Ba-Al-F-Si glass as disclosed by the manufacturer (Fig 4b).

µTBS of restorative materials to dentin

The immediate and aged bonding effectiveness to flat and class-I cavity-bottom dentin is graphically presented in Fig 5a.

When bonded to flat dentin, the highest immediate µTBS was recorded for AU/CentionN, being only not significantly different from light-cured Su-O. Fuji2LC presented with the lowest immediate µTBS, mainly due to a high ptf number. Fuji2LC's immediate µTBS did not significantly differ from the immediate µTBS recorded for self-cured Su-O. No significant difference in µTBS was found between light- and self-cured Su-O. Upon aging, the µTBS did not significantly decrease for any of the experimental groups. Overall, the order/pattern of aged µTBSs replicated that of immediate µTBSs.

When bonded onto class-I cavity-bottom dentin, in general lower immediate and aged µTBS, along with higher ptf numbers, were recorded as compared when the restoratives were bonded to flat dentin. The highest immediate µTBS was still recorded for AU/Cention N, solely not being significantly different from self-cured Su-O. Again, no significant difference in µTBS was found between light- and self-cured Su-O. Again, no significant difference between immediate and aged µTBS was measured for any of the experimental groups.

Fractographic analysis of µTBS specimens

When the restoratives were bonded to flat or class-I cavity-bottom dentin, the µ-specimens predominantly failed adhesively at the interface (Fig 5b). Representative SEM photomicrographs of fractured µ-specimens (dentin side) from the different experimental groups, when the restoratives were bonded to flat dentin upon 1w water storage ('immediate') and 50k TC ('aged'), are shown in Fig 6. Low magnification photomicrographs (85-90× original magnification) showed that many voids were located at the interface (Fig 6a_1, $a_{3\text{-}4}$: arrows). Furthermore, fractured light- and self-cured Su-O surfaces often revealed a particle-filled substance that remained attached to dentin along with cohesively fractured dentin with clear collagen-fibril exposure (Fig 6a_1-d_2). AU/CentionN presented often with interfacial failures, as evidenced by the bur scratches clearly observable especially at low magnification (Fig 6e_1-f_2).

Representative SEM photomicrographs of fractured µ-specimens (dentin side) from the different experimental groups, when the restoratives were bonded to class-I cavity-bottom dentin upon 1w water storage and 50k TC, are shown in Fig 7. Fractured light- and self-cured Su-O surfaces often revealed smear-layer parts that were potentially mixed with Su-O fragments and together remained attached to dentin (Fig 7$a_{1\text{-}2}$, $d_{1\text{-}2}$). AU/CentionN often presented with large parts having fractured at the actual interface, as based upon observation of circular bur scratches at low magnification, and with exposed dentin tubules obstructed by smear plugs, as was observed at high magnification (Fig 7e_1-f_2).

High-magnification SEM photomicrographs of the fractured restorative materials investigated revealed the different shapes and sizes of the restoratives' filler particles, hereby confirming the filler-particle details characterized by SEM, EDS and TEM. More specifically, the overall filler-particle size of Su-O, containing particles below 2 µm along with nanofiller, was smaller than that of Fuji2LC and CentionN (Fig 8).

DISCUSSION

Thanks to their aesthetic potential, composites are the main plastic filling materials currently used in daily dental practice.[40] As a new generation, self-adhesive composites are being developed in a further step to simplify their clinical application, often also claiming to have been developed as true amalgam-replacing restorative materials.[3,18,38] In this study, the recently introduced so-called 'self-adhesive composite hybrid' Surefil One (Su-O) (Dentsply Sirona), allegedly combining the simplicity of GICs with the stability of resin-based composites,[11] was investigated. As first of two reference restorative materials, the resin-modified GIC Fuji2LC was selected, since conventional and resin-modified GICs also auto-adhere to tooth tissue, an adhesion mechanism based on shallow hybridization combined with ionic interaction of polyalkenoic acid with its multiple carboxyl groups binding to Ca in hydroxyapatite.[37,47] Second, the recently introduced 'alkasite' amalgam-replacing restorative material CentionN was tested when combined with the universal adhesive AU applied in self-etch mode.

Representing a new generation of self-adhesive restorative materials, the filler-matrix configuration was structurally and chemically characterized, correlatively using SEM, TEM and SEM/EDS. Another primary property that was investigated in this study, concerned its bonding effectiveness and bond durability upon artificial and accelerated aging. The self-adhesive composite is hypothetically expected to interact with tooth substrate through its acidic functional mono/polymer ingredients, potentially not only to provide micro-retention by etching the substrate surface, but also to ionically bind with Ca in hydroxyapatite. In-depth ultra-structural TEM along with chemical interfacial analysis is needed to fully elucidate the self-adhesiveness of Su-O. A clinically relevant research question to be answered in this study was whether Su-O's self-adhesiveness was sufficiently efficient to bond to bur-cut and thus smear-layer covered dentin. As an amalgam alternative to bulk-fill posterior cavities, bond strength to flat dentin in the most ideal condition was compared with bonding in high C-factor class-I cavities in light of a 'worst-case scenario', when shrinkage stress was high and severely challenged the bond to cavity-bottom dentin.[42,43] As Su-O self-cures but also can be light-cured, both the dual-cure as the solely chemical curing mode was comparatively investigated. Self-curing composites are known to produce lower polymerization-contraction stress in high C-factor cavities and thus may challenge less the bond to cavity-bottom dentin than the dual-cure polymerization mode.[22,26]

The SEM/TEM structural and EDS chemical element characterizations revealed that the three restorative materials, while according to technical manufacturer's data possessing nearly similar filler loading, widely vary in filler-particle nature, size and shape. Hence, the first null hypothesis that there was no structural/chemical difference in filler-matrix configuration between Su-O and the two reference materials, failed to be accepted.

Previous studies reported that filler size and shape greatly influence diverse properties, among which also mechanical strength and aesthetics.[20,25] Moreover, filler size and especially filler loading, obviously in addition to composite matrix parameters, such as monomer kinds, their molecular weight and concentration, will altogether have an effect on polymerization efficiency and the resultant polymerization shrinkage.[5,28] Thus, the current structural/chemical characterization has put some light on the filler-matrix configuration of the three restorative materials investigated in this study. SEM revealed that Su-O contained relatively large filler particles with a maximum size of around 5 µm, while high-resolution TEM disclosed plenty of small filler particles ranging between 50 nm and 1 µm. This finding is confirmed by technical information provided by Su-O's manufacturer (unpublished communication), revealing that the d50 filler size is 2 µm with addition of nanofiller. In contrast, Fuji2LC and CentionN showed to consist generally of larger filler, often exceeding 10 µm, while also containing nano-filler of about 100 nm. These filler characterization data confirmed the trend that the particle-filler distribution of dental composite has continuously evolved from initially macrofiller-based composites towards nano-hybrid compositions.[14,20] In general, small filler sizes can result in enhanced filler/matrix surface interactions,[4] hereby also resulting in more light scattering. On the other hand, Fujita *et al.* (2011) demonstrated that a decrease in particle size of silica filler can lead to increased transmission of visible light.[15] Following the latter finding, the smaller filler size of Su-O might have improved light-penetration depth, also favorable to reach a sufficiently high degree of conversion.

Semi-quantitative EDS disclosed that the three restorative materials contained C in the highest amount, with Su-O containing about 28 wt% C, which is substantially higher than the nearly 19 wt% C present in the two reference restorative materials. Since C is part of the organic resin network,[17] the high C concentration within Su-O appeared to suggest that Su-O has a lower filler content than the two other materials. This did however not appear from the manufacturer's provided filler-loading data, as presented in Table 1; the filler loading of the three restorative materials was indeed quite similar. The fact that Si was found in relatively high amounts in the three restorative materials, was expected as silica filler and/or silicon-based glass filler are very common fillers of many dental restorative materials. Striking is the significantly lower O content within Su-O. This finding is not in concordance with those of other authors, who observed 20-40 wt% O within commonly used composites.[36,41] Specific for Su-O is its relatively high P content, which should be attributed for a large extent to P-containing glass filler but could also be related to the by-the-manufacturer mentioned 'bifunctional acrylate', potentially referring to a phosphate-based functional monomer added to render Su-O self-adhesiveness. The N presence in Su-O may point to the addition of some acrylamide monomers, known for their better hydrolytic resistance. Other elements like Al, P, Sr, Na, F and Si are part of the Su-O's 'aluminum-phoshor-strontium-sodium-fluoro-silicate' glass filler, and regarding Si also part of the silica filler, as the presence of both filler kinds was released by the manufacturer. To achieve radiopacity, Yb was added to Su-O. A selected area of Su-O, containing both resin matrix and filler, was additionally subjected to EDS multi-elemental mapping (Fig 2); area differences for signals representing filler and surrounding resin were quite low, indicating a homogeneous filler-matrix configuration.

Fuji2LC self-evidently contains as resin-modified GIC F, Al and Sr as part of GC's classical GIC filler. From all three restorative materials investigated, Fuji2LC contains F in the highest concentration, so to be released and render Fuji2LC anti-cariogenic potential.[29] Peculiar for the 'alkasite' restorative material, CentionN contains a relatively large Ca amount, most likely for the claimed remineralization potential. When the oral environment's pH is low (acidic), the released Ca ions are claimed to aid reduction of tooth demineralization.[23,24] Because of their high atomic number, Ba and Yb were added to CentionN to achieve adequate radiopacity.[17,25,31]

An essential test for a self-adhering restorative material is assessing its immediate and aged bonding effectiveness to dentin. More specifically, the optimum bonding potential was assessed when the restorative materials were bonded to flat dentin and thus when the bond was hardly challenged by polymerization shrinkage of the material in this low C-factor model. Previous research calculated a C-factor as low as 0.18, when employing a similar study set-up.[43] While the separate application of a self-etch adhesive resulted in a better bonding performance for CentionN, the relatively high variance recorded for the latter material caused its bonding effectiveness not to be significantly better than that recorded for light-cured Su-O. Both their immediate and aged μTBSs were however significantly higher than that of self-cured Su-O and Fuji2LC, the latter applied without previous polyalkenoic-acid conditioning, which is known to promote its bonding effectiveness.[7,12] The better optimum self-adhesiveness of light- than self-cured Su-O may be due to the lower mechanical properties reached by self-curing. A μTBS test should be regarded as a strength test of the whole μ-specimen assembly, including also the restorative material in this particular case. This hypothetical explanation should obviously be confirmed by additional mechanical strength testing. Worth mentioning is that all restorative materials resisted accelerated aging, since no drop in optimum bonding effectiveness was recorded upon 50k thermocycles, which lasted about 6 weeks and thus should be considered as a rather severe aging regime.

As Su-O is indicated by the manufacturer to be used as bulk-fill restorative material, its immediate and aged bonding effectiveness onto class-I cavity-bottom dentin with a high C-factor related polymerization-shrinkage challenge, was additionally determined in this study. The additional polymerization shrinkage clearly challenged the bond to cavity-bottom dentin,[33,43,44] since significantly lower μTBSs along with high ptf numbers were recorded for the different restorative materials. The highest μTBS and lowest ptf number was recorded for AU/CentionN, suggesting that a separately applied adhesive appeared to resist better the polymerization-shrinkage challenge. In contrast to when bonded to flat dentin, self-cured Su-O outperformed light-cured Su-O, which most likely should be attributed to the slower polymerization and the lower shrinkage stress developed during polymerization. Previous studies indeed demonstrated that light-cured composites produced more contraction stress in high C-factor class-I cavities, having resulted in a greater tendency to separate from the cavity wall than their self-cured counterparts.[16,22] In fact, light-initiated polymerization is fast, by which restorative (and luting) composites undergo a short gel stage, not allowing the materials to flow fluently and the resin molecules to easily dissipate the tension generated by polymerization contraction.[5,26] The reason why the self-cured composites produce a lower polymerization-contraction stress, should principally be attributed to a lower polymerization rate.[13,26] Therefore, when Su-O bonded to flat dentin and shrank nearly unrestrictedly, the light-cure mode resulted in a better bonding efficiency than the self-cure mode, while an opposite effect was recorded when Su-O was bonded into a high C-factor class-I cavity. Furthermore, self-curing Su-O requires more time to reach maximum polymerization, by which dentists would need to wait longer, thus somewhat contradicting with the concept of restorative 'simplification'. Nevertheless, it should finally be mentioned that with the exception of the bulk-fill flowable composite SDR (Dentsply Sirona), many commercially marketed bulk-fill composites tested in previous research failed in the same class-I cavity μTBS test model,[43,44] indicating that this test indeed involves a worst-case scenario.

Striking is also that Fuji2LC performed worst when bonded to both flat as cavity-bottom dentin, with following the latter condition even all μ-specimens having failed upon aging prior to testing (100% ptfs). When dentin would have been pretreated with a polyalkenoic-acid conditioner, the unfavorable Fuji2LC data recorded in this study could have been better, since the relatively thick/compact bur smear layer would have interfered less and enabled the GIC to have interacted more intimately with underlying dentin surface.[7,47]

Nevertheless, it is not that surprising that a good bonding performance was recorded for AU/CentionN. Three main factors may have contributed to this better bonding effectiveness. First, the universal adhesive AU must have better wetted the dentin surface, having enabled the incorporated acidic functional monomer 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP) to chemically interact with Ca in hydroxyapatite.[49,50] In addition, SEM fracture analysis disclosed the formation of a hybrid layer along with resin tags, indicating AU partially demineralized the dentin surface and interdiffused into partially exposed collagen fibrils. Second, previous studies found that a relatively thick adhesive with shock-absorbing/elastic potential[34,46] was less affected by the C-factor when bonded to class-I cavity-bottom dentin.[42] The adhesive acted as an intermediary stress reliever to compensate in part for the shrinkage stress induced.[2] While universal adhesives like AU generally have a rather thin film thickness, their separate application and polymerization may have contributed to withstand better the high polymerization shrinkage induced in a class-I cavity. Such a stress-absorbing role of adhesives cannot be taken over by the self-adhesive material. A third reason that may explain the better bonding effectiveness of AU/CentionN, might be the special photo-initiator 'Ivocerin' within Cention N, which is a dibenzoyl germanium derivative according to manufacturer's technical data.[23] Previous research pointed out that the germanium-based photo-initiator has a higher photocuring reactivity than camphorquinone with a higher light-absorption potential in the 400-450 nm wavelength region.[21,35]

Altogether, the second null hypothesis that the 'immediate' and 'aged' bonding effectiveness to flat and high C-factor cavity-bottom dentin did not significantly differ from that obtained by the reference materials, partially failed to be accepted, in particular as compared to AU/CentionN.

CONCLUSION

Ultrastructural/chemical characterization revealed that the 'self-adhesive composite hybrid' Su-O mainly consisted of small-sized filler particles, which were rich in Al, P, Sr and Si. A favorable bonding performance of Su-O was achieved when applied in light-cure mode onto flat dentin. Nevertheless, Su-O applied in light-cure mode presented with a less favorable bonding effectiveness when bonded following the worst-case scenario onto class-I cavity-bottom dentin. Self-cured Su-O bonded more effectively to cavity-bottom dentin, as also did CentionN when it was bonded using the separately applied and light-cured universal adhesive UA. Since self-adhesive bulk-fill composites are relatively new materials, more *in-vitro* experiments, among which also research to fully elucidate the underlying mechanisms of self-adhesiveness, but also short- as well as long-term clinical data are highly needed.

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Table 1 The different restorative materials examined in this study.

Materials	Code batch no.	Type	Composition	Application	Filler loading
Surefil One (Dentsply Sirona)	**Su-O** 1807004175	Self-adhesive bulk fill composite	aluminum-phoshor-strontium-sodium-fluoro-silicate glass, highly dispersed silicon dioxide, ytterbium fluoride, polycarboxylic acid, bifunctional acrylate, acrylic acid, iron oxide pigments, water, titanium dioxide pigments, camphorquinone, stabilizer, self-cure initiator	**1.1** Light-cure for 20 s with an output of 1200 mW/cm^2. **1.2** Self-cure for 6 min (prior to further specimen processing).	77 wt% 58 vol%
Fuji II LC Improved (GC)	**Fuji2LC** 171012A	Resin-modified glass-ionomer	2-hydroxyethyl methacrylate, polybasic carboxylic acid, urethane dimethacrylate, dimethacrylate, calcium-aluminum-fluoro-silicate glass, others	Light-cure up to 1.8-mm thickness for 20 sec with an output of 1200 mW/cm^2.	76 wt%
Cention N (Ivoclar Vivadent)	**CentionN** W94184	'Alkasite' restorative	**Liquid:** dimethacrylates, initiators, stabilizers and additives **Powder**: calcium fluoro-silicate glass, barium glass, calcium-barium-aluminium fluoro-silicate glass, iso-fillers, ytterbium trifluoride, initiators and pigments.	**1.** Application of AdheSE Universal in self-etch mode. **2.** The mixing ratio for larger cavities: 2 measuring scoops of powder and 2 drops of liquid (corresponding to a weight ratio of 4.6:1) **3.** Light-cure up to 4-mm thickness for 20 sec with an output of 1200 mW/cm^2	78.4 wt% 57.6 vol%

Table 2 EDS analysis of elements (mean and standard deviation in wt%) detected in the different restorative materials investigated.

	C	Ca	N	O	F	Na	Zn	Al	Si	Sr	Zr	P	Ba	Yb
Su-O	28.2±0.9	0.3±0.6	4.8±1.2	9.5±2.3	3.5±0.7	0.6±0.3	-	7.1±0.8	13.9±0.3	10.6±0.3	-	16.0±0.7	-	5.5±1.7
Fuji2LC	19.7±3.1	0.6±0.1	-	26.9±0.6	8.6±0.7	-	0.2±0.2	11.4±0.4	13.8±0.7	17.8±1.0	1.3±1.5	-	-	-
CentionN	19.0±1.9	7.7±1.8	-	28.2±1.0	4.9±0.6	-	1.5±0.3	2.5±0.2	16.6±0.5	-	-	-	11.2±0.7	8.6±0.7

The grey-marked columns were discussed in detail in the Discussion section.

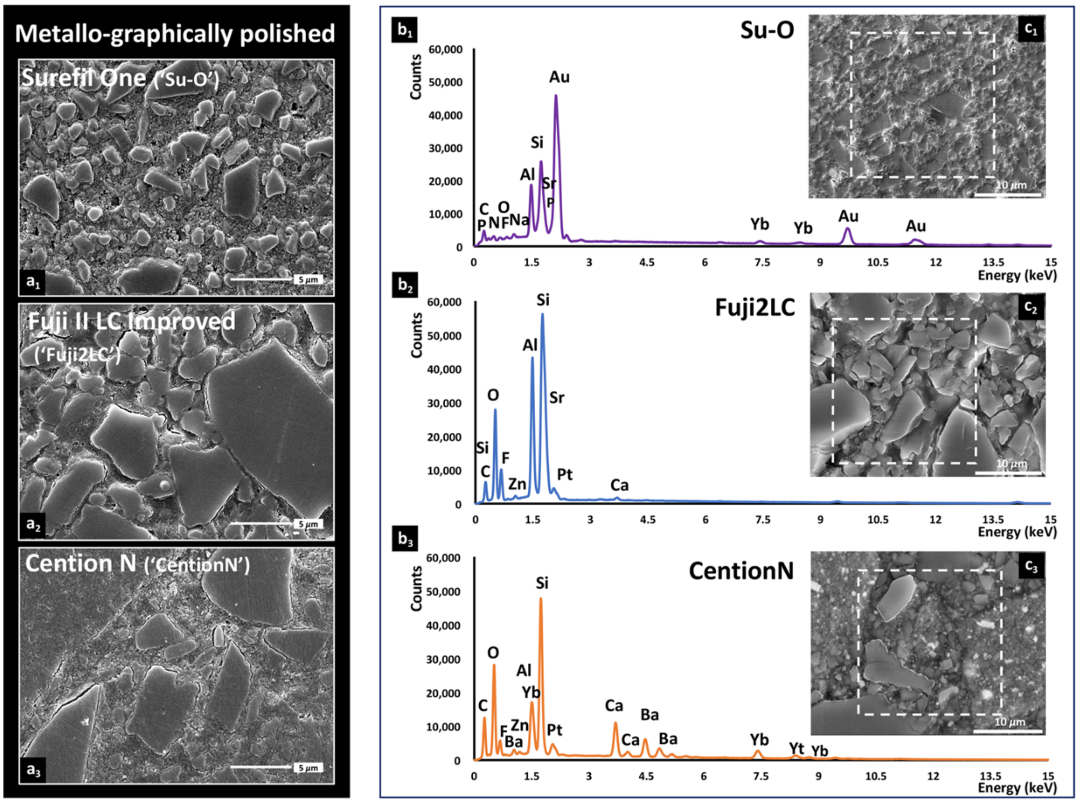

Fig 1 SEM photomicrographs and EDS spectra of the three restorative materials investigated. Metallo-graphically polished surfaces are shown for the self-adhesive bulk-fill composite restorative Surefil One ('Su-O') (Dentsply Sirona) in **(a_1)**, the resin-modified GIC Fuji II LC Improved ('Fuji2LC') (GC) in **(a_2)**, and the alkasite restorative Cention N ('CentionN') (Vivadent Ivoclar) in **(a_3)**. Representative SEM-EDS spectra and high-magnification SEM photomicrograph of the material surfaces are presented in **(b_1)** and **(c_1)** for Su-O, in **(b_2)** and **(c_2)** for Fuji2LC, and in **(b_3)** and **(c_3)** for CentionN. The white square in the high-magnification SEM photomicrograph represents the selected 20×20 µm area, at which the EDS spectra were captured. The elements Au and Pt were detected, which should be attributed to the gold and platinum sputter-coating to make the specimens conductive for SEM.

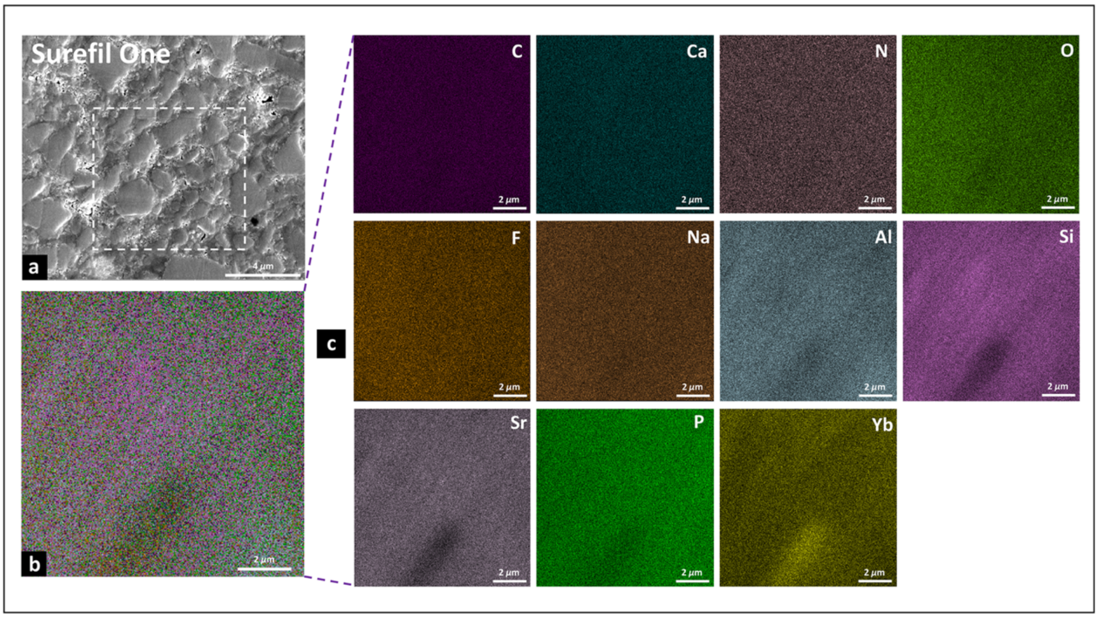

Fig 2 SEM/EDS mapping of the self-adhesive bulk-fill composite Su-O, with an SEM photomicrograph presented in **(a)**, indicating the selected EDS mapping area of 10×10 µm, the superimposed EDS map in **(b)**, and individual maps for C, Ca, N, O, F, Na, Al, Si, Sr, P and Yb in **(c)**, with the higher color intensity indicating higher element content. In particular, C, O, Si and P were detected more intensively.

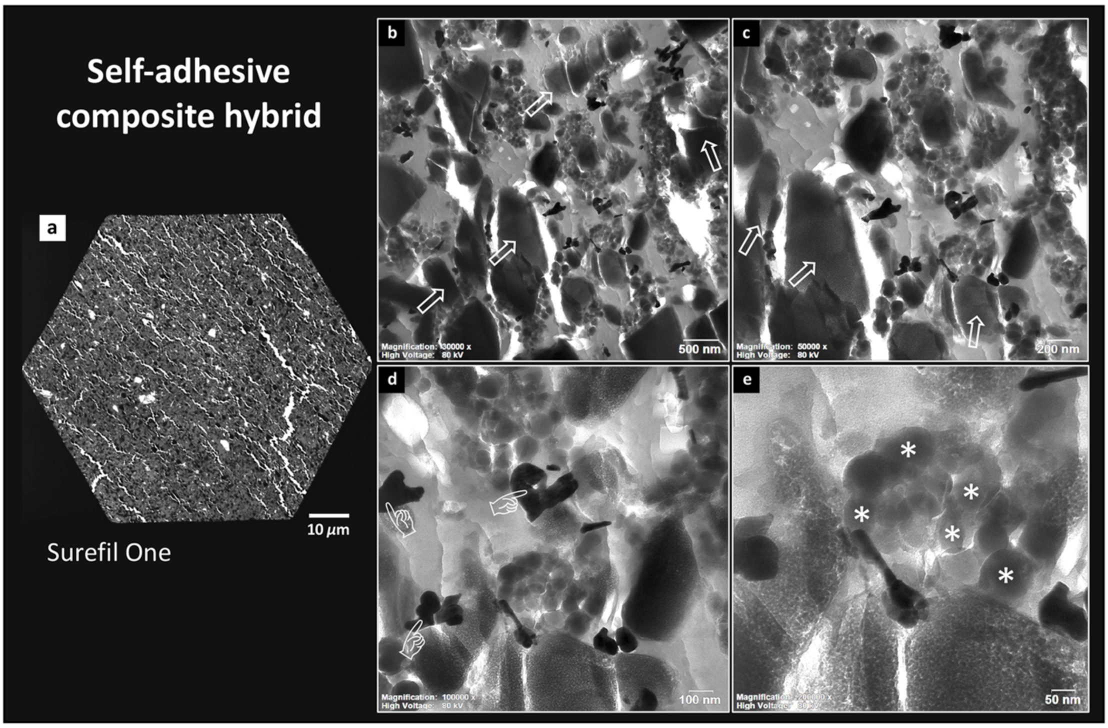

Fig 3 TEM photomicrographs of the self-adhesive bulk-fill composite Su-O at low magnification in **(a)** and at increasingly higher magnification in **(b-e)**. Open white arrows: Al-P-Sr-Na-F-Si glass with an irregular polyhedral shape; Handpointers: irregular and strongly electron-dense YbF particles with a size of around 200 nm; asterisks: highly dispersed SiO_2 filler particles.

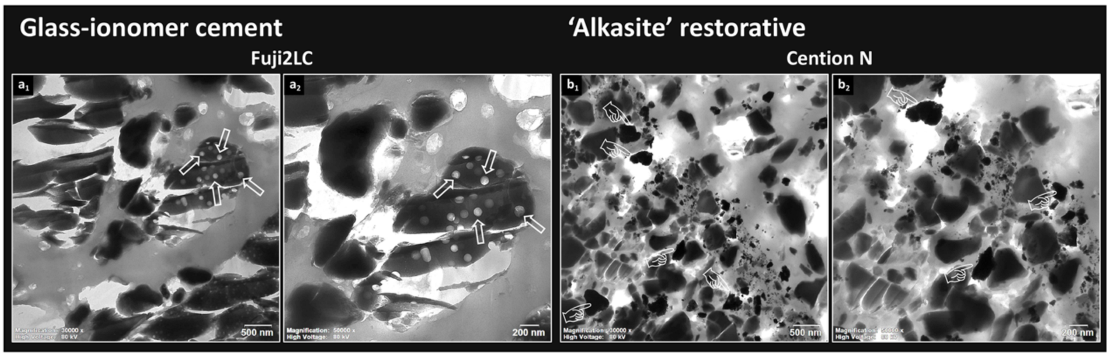

Fig 4 TEM photomicrographs of Fuji2LC at low and higher magnification in **(a_1)** and **(a_2)**, respectively, and likewise of CentionN in **(b_1)** and **(b_2)**, respectively. Open with arrows: electron-lucent globules within relatively large GIC glass filler; Handpointers: electron-dense 150-200 nm YbF particles.

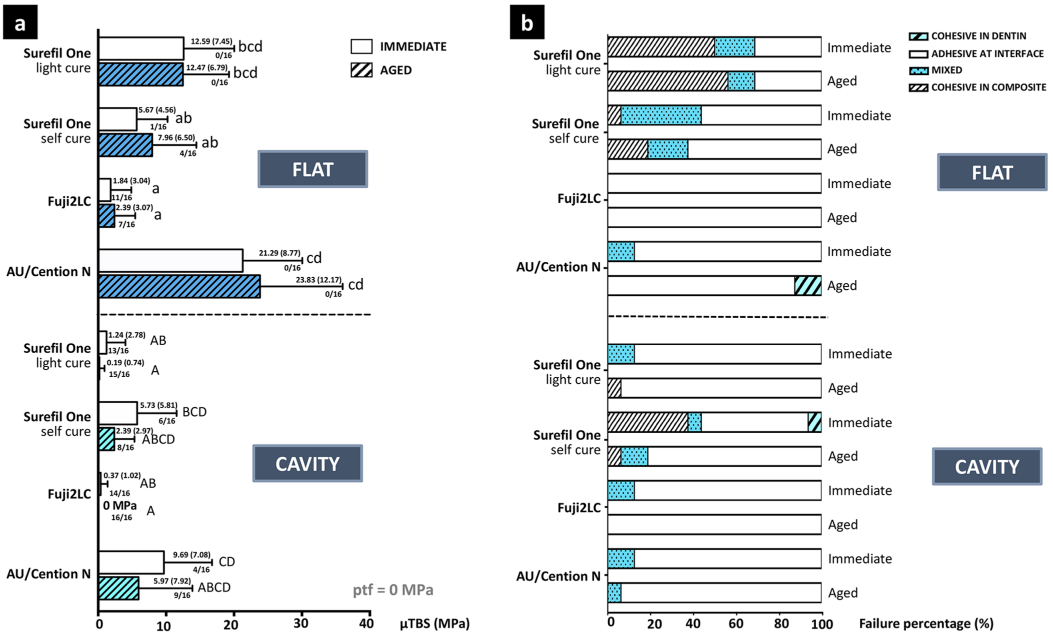

Fig 5 'Immediate' and 'aged' µTBS of the three restorative materials to flat ('FLAT') and class-I cavity-bottom dentin ('CAVITY') in **(a)**, with the failure analysis data of all (micro)µ-specimens

graphically presented in **(b)**. Besides the mean µTBS, the standard deviation is given within brackets, along with the number of pre-test failures (ptfs) per total number of µ-specimens. µTBSs with the same small (bonded to FLAT dentin) or capital letter (bonded to CAVITY dentin) are not statistically significantly different (p>0.05). The predominant failure mode recorded was adhesive interfacial failure for all experimental groups, except for light-cured Su-O when bonded to flat dentin and tested both immediately and upon aging.

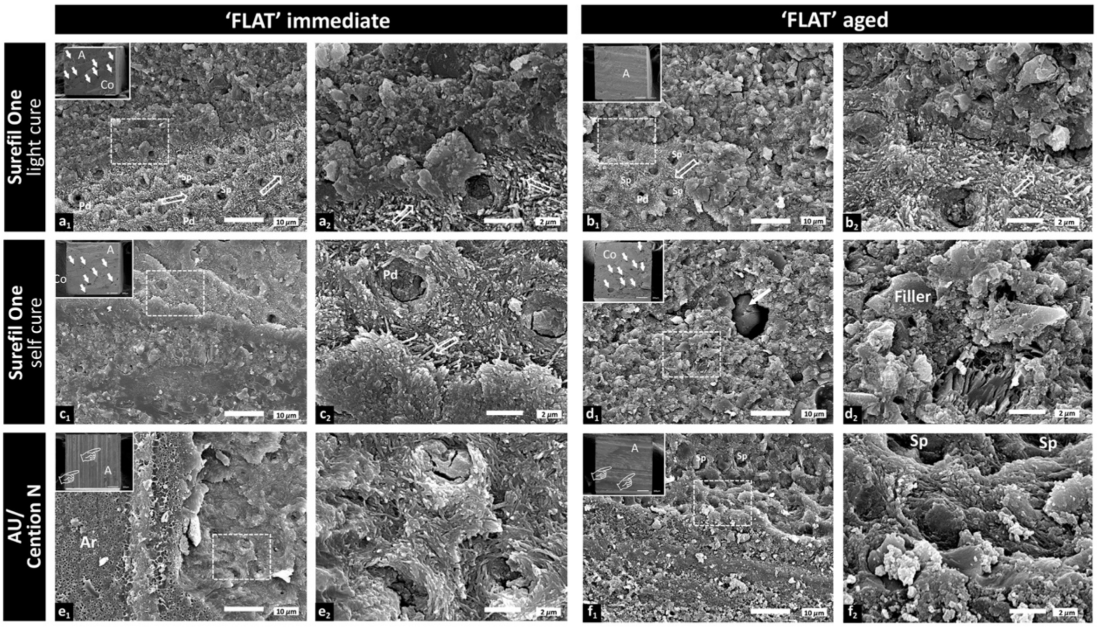

Fig 6 Representative SEM photomicrographs illustrating the fractured dentin sides of the three different experimental materials bonded to flat ('FLAT') dentin upon 1w water storage and 50k TC. **(a$_1$)** Fractured surface of an 'immediate' light-cured Su-O µ-specimen, revealing a mixed failure mode exhibiting a particle-filled substance that remained attached to dentin along with cohesively fractured dentin with clear collagen-fibril exposure (open white arrows). Dentin remained covered with smear debris and was potentially infiltrated by resin. The low-magnification image in the insert (90× original magnification) revealed some interfacial porosities (arrows). **(a$_2$)** Higher magnification of the white rectangle in (a$_1$), confirming the particle-filled substance, most likely representing smear-layer parts potentially mixed with Su-O fragments. **(b$_1$)** Fractured surface of an 'aged' light-cured Su-O µ-specimen, revealing a similar interfacial structure as observed in (a$_{1,2}$). No interfacial porosities were detected in the

low-magnification image in the insert (90× original magnification). **($c_{1,2}$)** Fractured surface of an ‘immediate’ self-cured Su-O µ-specimen, revealing a similar mixed failure mode as revealed for light-cured Su-O, along with some interfacial porosities observable in the low-magnification image in the insert (90× original magnification, arrows). **($d_{1,2}$)** Fractured surface of an ‘aged’ self-cured Su-O µ-specimen, revealing most likely a mainly cohesive failure mode with part of the restorative material having remained attached to the dentin side, along with some interfacial porosities observable in the low-magnification image in the insert (90× original magnification, arrows). **($e_{1,2}$)** Fractured surface of an ‘immediate’ AU/CentionN µ-specimen, revealing an interfacial failure mode with bur scratches clearly visible (handpointers) in the low-magnification image in the insert (90× original magnification). Failure seems to have occurred close to the actual interface with areas of fractured dentin (e_2) adjacent to areas covered by the adhesive resin (Ar). Abundant tiny micro-pores were detectable in Ar, most likely representing water droplets absorbed through osmosis in Ar. **(f_1)** Fractured surface of an ‘aged’ AU/CentionN µ-specimen, revealing an interfacial failure mode with bur scratches (handpointers) detectable in the low-magnification image in the insert (90× original magnification). Areas of fractured dentin can be observed next to areas covered by a particle-filled substance, most likely representing smear-layer fragments. A: adhesive failure; Ar: Adhesive resin; AU: Adhese Universal; Co: composite; Pd: peritubular dentin; Sp: smear plug.

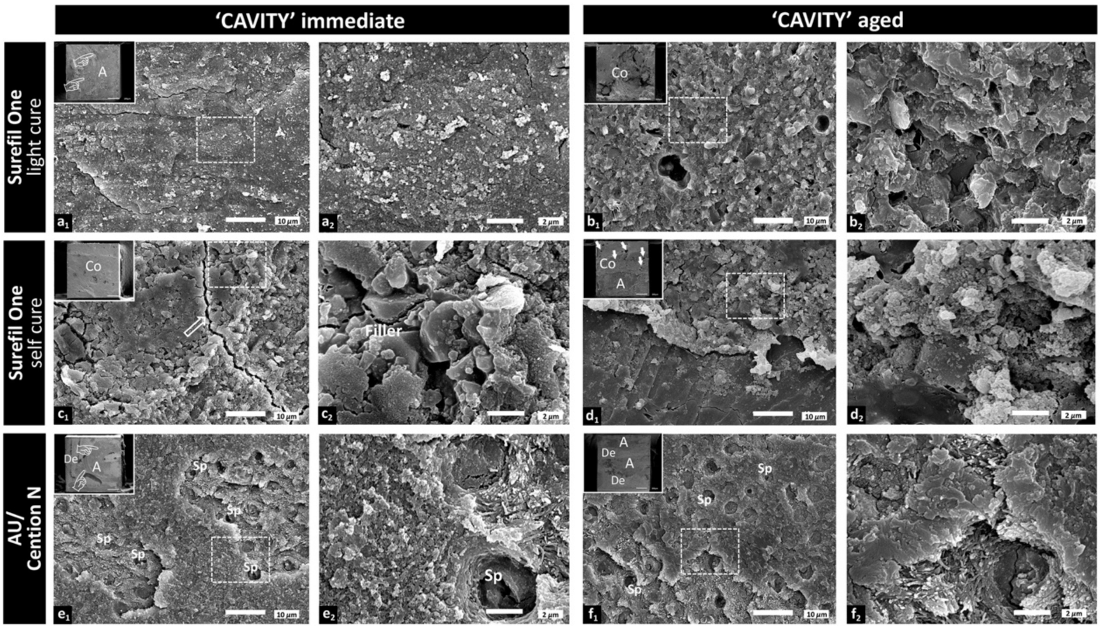

Fig 7 Representative SEM photomicrographs illustrating the fractured dentin sides of the three different experimental materials bonded to class-I cavity-bottom dentin ('CAVITY') upon 1w water storage and 50k TC. **(a$_1$)** Fractured surface of an 'immediately' light-cured Su-O μ-specimen, revealing most likely an interfacial failure mode, as based upon observation of circular bur scratches (handpointers) in the low-magnification image in the insert (90× original magnification). **(a$_2$)** Higher magnification of the white rectangle in (a$_1$), revealing most likely smear-layer fragments potentially mixed with Su-O filler particles. **(b$_{1,2}$)** Fractured surface of an 'aged' light-cured Su-O μ-specimen, revealing a cohesive failure mode within Su-O. This special cohesive failure with partially fractured flat surface could be ascribed to apply two layers of Su-O, which was not common and may be happened when a thin layer of Su-O was bonded onto the cavity and the Capsule Extruder could not continue to squeeze out more material. **(c$_1$)** Fractured surface of an 'immediate' self-cured Su-O μ-specimen, revealing a cohesive failure within Su-O. The crack detected within Su-O (open white arrow) should most likely be attributed to a dehydration artifact. **(c$_2$)** Higher magnification of the white rectangle in (c$_1$), revealing fractured fragments entailing smaller filler particles (asterisk). **(d$_{1,2}$)** Fractured surface of an 'aged' self-cured Su-O μ-specimen, revealing a mixed failure mode with most likely smear-layer parts that were potentially mixed with Su-O fragments and together remained attached to dentin, along with some interfacial porosities (arrows) observable in the

low-magnification image in the insert (90× original magnification). **(e$_1$)** Fractured surface of an 'immediate' AU/CentionN µ-specimen, revealing a mixed failure mode with large parts having fractured at the actual interface, as based upon observation of circular bur scratches (handpointers) in the low-magnification image in the insert (90× original magnification). **(e$_2$)** Higher magnification of (e$_1$), having exposed dentin tubules obstructed by smear plugs. **(f$_{1,2}$)** Fractured surface of an 'aged' AU/CentionN µ-specimen, revealing a mixed failure mode with large fractured parts with exposed dentin tubules. A: adhesive failure; AU: Adhese Universal; Co: composite; De: dentin; Sp: smear plug.

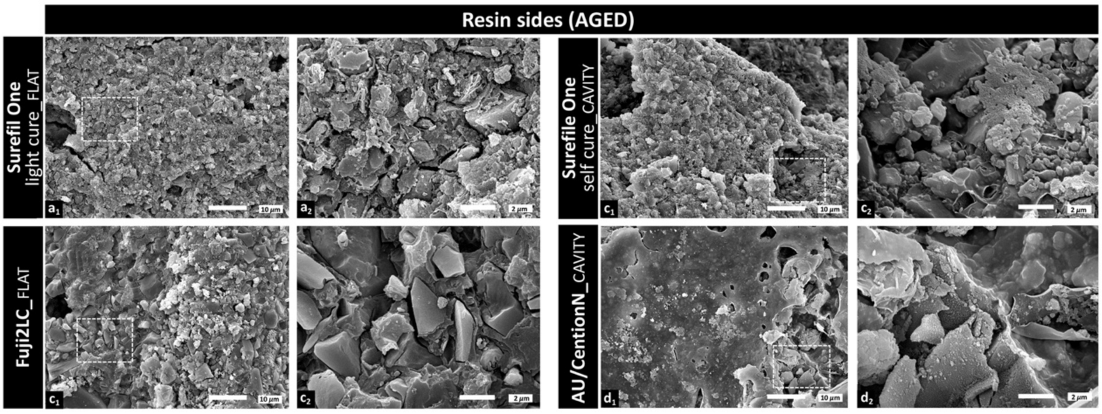

Fig 8 Representative SEM photomicrographs illustrating the fractured resin sides of 'aged' µ-specimens of the different experimental materials bonded to flat dentin ('FLAT') or class-I cavity-bottom dentin ('CAVITY'). **(a$_1$)** Cohesively fractured light-cured Su-O (2000× original magnification). **(a$_2$)** Higher magnification (9000× original magnification) of the white rectangle in (a$_1$), revealing filler particles in different sizes, ranging from less than 1 µm to around 5 µm. **(b$_1$)** Cohesively fractured self-cured Su-O (2000× original magnification), revealing some porosities within Su-O. **(b$_2$)** Higher magnification of the white rectangle in (b$_1$), revealing filler particles in different sizes, ranging from around 0.5 µm to 5-6 µm. **(c$_1$)** Cohesively fractured Fuji2LC. **(c$_2$)** Higher magnification of the white rectangle in (c$_1$), revealing the size of most filler particles being around 3-5 µm. **(d$_1$)** Fractured AU/CentionN µ-specimen. **(d$_2$)** Higher magnification of the white rectangle in (d$_1$), revealing that the filler particle size of CentionN was larger than the ones of Su-O and Fuji2LC.