



Bond strength and chemical interaction of self-adhesive resin cements according to the dentin region



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ABSTRACT

The aim of the study is to evaluate the effectiveness and level of chemical interaction of self-adhesive resin cements (SRCs) according to the dentin region. One hundred eight sound human third molars and three SRCs were selected: Bifix SE (Voco), Maxcem Elite (Kerr), and RelyX U200 (3M ESPE). Ninety human molars were used for the bond strength test and 18 teeth for the X-ray diffraction (XRD) characterization. A flat surface of superficial, deep, or axial dentin was exposed. For bond strength evaluation, 90 indirect composite resin restorations (10 mm in diameter, 2.0 mm-thick) were built and cemented with one of the SRCs according to the manufacturer's instructions. The restored teeth were then cut into sticks with cross-sectional areas of 0.8 mm² and tested in tensile at a speed of 0.5 mm/min (n=10). The results of bond strength were statistically analyzed by two-way ANOVA and Tukey's test ($\alpha=0.05$). The fractured specimens were classified under SEM. The remaining teeth were further sectioned in order to build dentin fragments with 2.0 mm² of area and 0.2 mm in thickness for XRD analysis. In general, significantly higher bond strength was found when bonding to axial and deep dentin compared to superficial dentin. Comparing the bonding effectiveness of the SRCs, taking into account the mean bond strength obtained in the 3 dentin regions, the study found no significant difference ($p > 0.05$). Although RelyX U200 showed similar bond strength irrespective of the dentin region ($p > 0.05$), the bonding results of the other 2 SRCs varied significantly ($p < 0.05$). There was a higher incidence of cohesive failure in the SRCs for all groups. The XRD analysis detected different perceptual reductions of hydroxyapatite crystallinity for all SRCs, indicating a particular chemical interaction in each experimental condition. Thus, it can be concluded that the bond strength and chemical interaction of the SRCs can vary significantly according to the dentin region.

1. Introduction

Over the last 2 decades, adhesive dentistry has undergone remarkable progress, thanks to continuous and rapidly evolving tooth-bonding technology. This evolution process has led to the development of an innovative category of resinous restorative materials, self-adhesive materials, which are able to directly interact with the dental hard tissues for bonding [1–5].

By using such particular adhesion approach, the self-adhesive resin cements (SRCs) has been outstanding. They are able to greatly simplify the cementation procedure by eliminating the need to pretreat the tooth structure, due to the incorporation of functional monomers that demineralize and infiltrate the tooth substrate, resulting in micromechanical retention [1,6]. Such functional monomers are generally esters originating from the reaction of a bivalent alcohol with methacrylic acid

and phosphoric/carboxylic acid derivatives. It has been suggested that such functional monomers also are able to provide chemical adhesion to a tooth via secondary reactions with the calcium present in the hydroxyapatite (HAp), contributing to the SRCs' performance in addition to micromechanical hybridization [1,6,7].

Since SRCs interact directly with the tooth for bonding, it is speculated that the inherent characteristics of the dentin, mainly considering their chemical and morphological regional variation, could influence adhesion effectiveness. The dentinal tubule's variability in terms of number, diameter, and changes in its orientation from the surface to the pulp chamber create a severe discrepancy in dentin within the same tooth [8–10]. As a consequence of these regional morphologic dentin particularities, the level of mineralization, and thus the calcium available for chemical interaction with the SRCs, is also variable [8].

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Therefore, the purpose of the present study is to investigate the bond strength and level of chemical interaction of SRCs in 3 different dentin regions: superficial, deep, or axial. The research hypotheses of the study are that the (I) bond strength and (II) chemical interaction of the SRCs will be negatively influenced by the dentin region.

2. Materials and methods

This study used 108 caries-free human third molars. Teeth were obtained and used in accordance with the local IRB (# 218/11) and with the informed consent of the donors. Teeth were stored in 0.5% chloramine-T solution at 4 °C and used within 1 month following extraction.

2.1. Microtensile bond strength evaluation and SEM fractographic analysis

Ninety human molars were selected. The teeth were x-rayed using a millimeter adhesive scale fixed on periapical X-ray film (X-Ray Mesh; Hager & Werken GmbH & Co. KG – Germany) in order to estimate the dimensions of the dental structures and guide the dentin's regional exposition. After that, flat dentin surfaces were produced on each tooth using a diamond-impregnated disc (Extac, Enfield, CT, USA) under water cooling in a specific cutter machine (Isomet 1000, Buehler, Lake Bluff, IL, USA). The sectioned teeth were then randomly assigned into 3 groups according to the exposed dentin region: superficial (1 mm below the dentine-enamel junction at the occlusal surface), deep (1 mm above the highest pulp horn), or axial (1 mm below the dentine-enamel junction at the buccal or lingual surface).

Composite overlays were constructed with a resin composite (3 M ESPE Filtek Z250, St. Paul, MN, USA) using Teflon molds (12 mm in diameter, 2 mm in thickness). After the composite overlay fabrication, both sides of the restoration were sandblasted with 50 µm aluminum oxide glass spheres (Sandblaster Micro Etcher, Buffalo Dental, San Ramon, CA) for 10 s on each side. The composite overlays were then ultrasonically cleaned in distilled water for 3 min. After that, silane primer (3 M ESPE RelyX Ceramic Primer, St. Paul, MN, USA) was applied to the sandblasted surfaces with a minisponge for 1 min and air dried.

The sectioned teeth of each group were assigned into 3 sub-groups according to the 3 SRCs used (n=10). The composition of the cements are listed in Table 1. Prior to cementation, the exposed dentin surfaces

Table 1
Description of the materials used in this study.

Resin cements	Manufacturer	Lot #	Composition
RelyX U200	3 M ESPE, St. Paul, Minnesota, USA	5355	Silane treated glass powder, substituted dimethacrylate 1-benzyl-5-phenyl-barbic-acid, calcium salt, silane treated silica, sodium p-toluenesulfinate, 1,12-dodecane dimethacrylate calcium hydroxide methacrylated aliphatic amine methacrylated aliphatic amine titanium dioxide
Maxcem Elite	Kerr Italia, Scafati, Italy	4791075	GPDM, co-monomers (methacrylate ester monomers), inert mineral fillers, Ytterbium Fluoride, activators, stabilizers and colorants
Bifix SE	Voco, GmbH, luxhaven, Germany	1420440	Aliphatic (UDMA), aromatic (BisGMA), and acid methacrylate, benzoyl peroxide (Initiator), amines (cat) and BHT (stabilizer).

GPDM, glycerol dimethacrylate dihydrogen phosphate; UDMA, urethane dimethacrylate; Bis-GMA, bisphenol A diglycidyl methacrylate; BHT, butylhydroxytoluene.

were abraded with #600-grit SiC paper for 15 s in order to standardize the smear layer [11]. The SRCs were manipulated according to the manufacturers' instructions and applied to the composite overlays, which were gently seated on the prepared dentin surfaces using finger pressure. Thereafter, the restored teeth were placed under a constant seating pressure of 3.0 kg for 3 min [12]. Excess cement was removed after setting and then light cured for 60 s on 4 different regions at the tooth/restoration margin and on the top of overlay using an LED light unit (Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein) with a radiant emittance of 1000 mW/cm².

The restored teeth were then stored in distilled water at 37 °C for 24 h. After storage, the specimens were sectioned to obtain bonded, stick-shaped specimens with a cross-sectional area of 0.8 mm² (± 0.2) using the "nontrimming" specimens and tested in tensile at a speed of 0.5 mm/min [13]. Statistical differences among the mean bond strengths of the experimental groups were investigated by two-way ANOVA (factors: resin cements and dentin region) and Tukey's test at a preset alpha of 0.05.

The fractured specimens were mounted on stubs with double-face carbon tape and desiccated in silica gel for 2 h [13]. The specimens were then sputtered (SCD 050; Balzers, Schaan, Liechtenstein) with a thin palladium-gold film (25 nm) for 100 s at 40 mA and examined by a scanning electron microscope (SEM; JEOL-5600 LV, JEOL Ltd., Tokyo, Japan) operating at 15 kV. The failure modes were classified according to the following categories [13]: Type I – cohesive failure in the resin cement; Type II – adhesive failure; and Type III – mixed failure: adhesive and in the resin cement. The schematic representation of the technique used for the microtensile bond-strength test is illustrated in Fig. 1.

2.2. X-ray diffraction (XRD) analysis

Eighteen human teeth were selected and sectioned as previously described for the microtensile test, exposing superficial, deep, and axial dentin. Then, a square area (2.0×2.0 mm) of each sample was obtained using high-speed and cylindrical medium-grit diamond bur. The surface area of the specimens was previously standardized by using abrasive discs (Sof-lex, 3 M, ESPE, USA) mounted in a hand piece at low speed.

The dentin slices were then manually abraded by using a sequence of SiC sandpaper with decreasing grits (#A80, #150, and #600) until reaching a thickness of 0.2 mm. After that, the dentin samples were placed in an ultrasound apparatus in 90% ethanol solution for 5 min in order to eliminate waste sanding and other possible contaminants that could interfere in the XRD analysis.

The specimens were then evaluated in an X-ray diffractometer (DMAX Ultima+ Rigaku International Corporation, Tokyo, Japan) using CuKα radiation operating at 40 kV and 20 mA. Scans were performed from 10° to 80° (2θ) at a step size of 0.02° and a scan speed of 2°/min. Qualitative phase analysis was performed by using the Joint Committee on Powder Diffraction – International Center for Diffraction Data (JCPDS– ICDD) databases. The dentin samples were initially tested in order to guarantee the absence of cement to establish the individual chemical composition of each specimen. After this initial characterization, the specimens received a 1 mm thick cement layer opposite the side initially evaluated. After 3 min of chemical reaction, the SRCs were photoactivated for 20 s (LED light unit - Bluephase, Ivoclar Vivadent, Schaan, Liechtenstein; 1000 mw/cm²). The specimens were then tested again on the same side of the first characterization. Thus, it was possible to verify the chemical interaction of each SRC with the different regions of dentin by comparing the hydroxyapatite peak intensity at (211) between the first and second characterization of the same sample. The results were expressed in the reduction of peak intensity percentage.

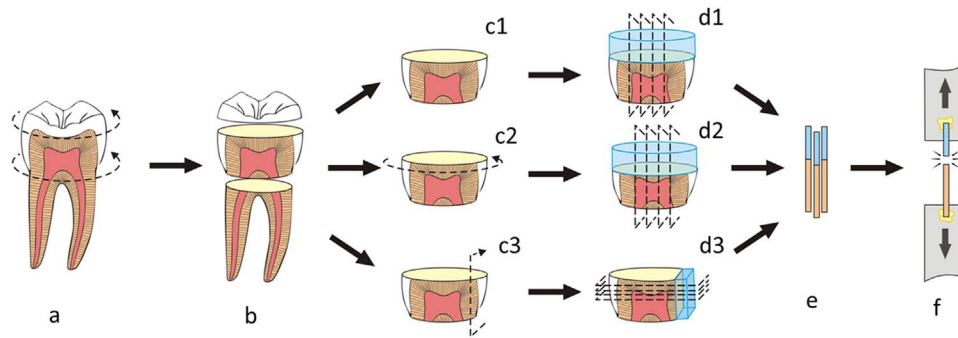


Fig. 1. Schematic representation of the technique used for the microtensile bond-strength test. The teeth were sectioned in order to (a) remove the occlusal enamel and root portion and (b) expose superficial (c1), deep (c2), and axial (c3) dentin surfaces. An indirect restoration was cemented on superficial (d1), deep (d2), and axial (d3) dentin surfaces and then sequentially sectioned into sticks (e), which were tested in tension until failure (f).

Table 2
Microtensile bond strength in MPa (standard deviation) of the experimental groups according to the dentin region.

Self-adhesive resin cements	Dentin region		Axial
	Superficial	Deep	
RelyX U200	25.25 (3.57) a A	23.12 (3.31) a A	24.58 (5.17) a AB
Maxcem Elite	20.10 (5.53) b AB	28.44 (3.49) a A	21.74 (6.68) ab B
Bifix SE	14.71 (7.22) b B	22.10 (7.59) b A	30.36 (7.14) a A

(n = 10).
Within the same row, different lower case letter: significant (p < 0.05).
Within the same column, different upper case letter: significant (p < 0.05).

3. Results

3.1. Bond strength and fracture analysis

Table 2 displays the results of the microtensile bond strength test according to the different SRCs and dentin regions. RelyX U200 showed equivalent bond-strength means, irrespective of the dentin region (p > 0.05). Bifix SE exhibited similar bond strength to superficial and deep dentin (p > 0.05); on axial dentin, the bond strength was significantly higher than the other groups (p < 0.05). Maxcem Elite reached significantly higher bond strength in deep dentin than those

attained in superficial dentin (p < 0.05); the bond strength on axial dentin was intermediate, not significantly different from the other groups (p > 0.05).

Comparing the performances of the SRCs, considering the same dentin region (Table 2), the results of the 3 SRCs were similar in deep dentin (p > 0.05). In superficial dentin, the bond strength produced by Rely X U200 was similar to Maxcem Elite (p > 0.05) but higher than the results obtained by Bifix (p < 0.05). When the bond strength to the axial dentin was compared, a significantly higher mean bond strength was reached using Bifix SE (p < 0.05); the bond strengths of Rely X U200 and Max Maxcem Elite were statistically similar (p < 0.05).

The failure pattern distribution (%) as analyzed by SEM can be observed in Fig. 2. The Type I fracture pattern was predominant for all groups. When individually analyzing the performance of each SRC, the incidence of Type I fracture was similar on superficial and axial dentin but higher than that observed for deep dentin. The resin cement Bifix SE showed the lowest incidence of Type I fracture, regardless of the dentin region, when compared to those produced by the other SRCs evaluated.

3.2. XRD analysis

Representative diffractograms of all the groups, illustrating the crystallinity of elements present in the samples before and after application of the SRC on the dentin, are shown in Figs. 3–5. A reduction of diffraction peak at (211), which represents the crystalline phase of the hydroxyapatite, was observed in all groups after the

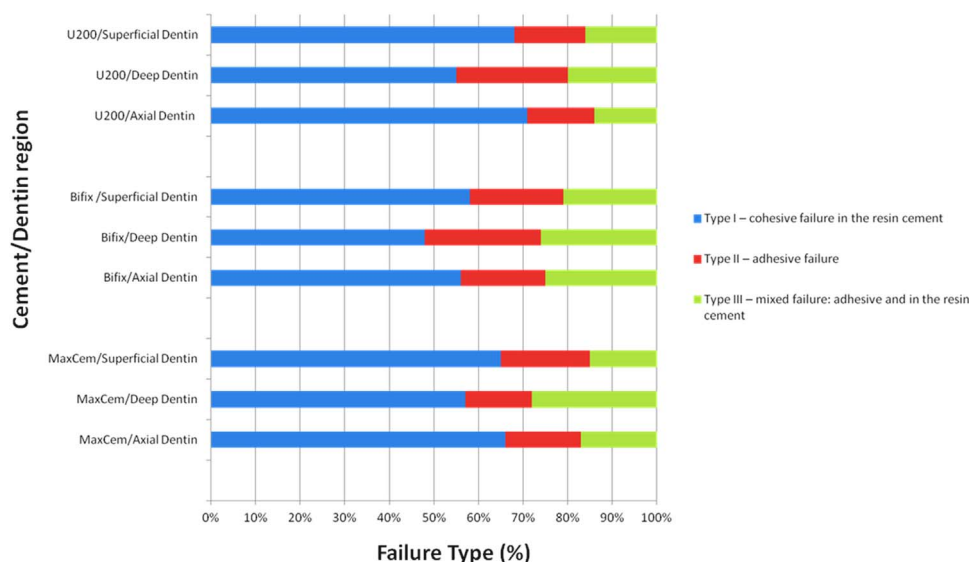


Fig. 2. Distribution (%) of the fracture modes.

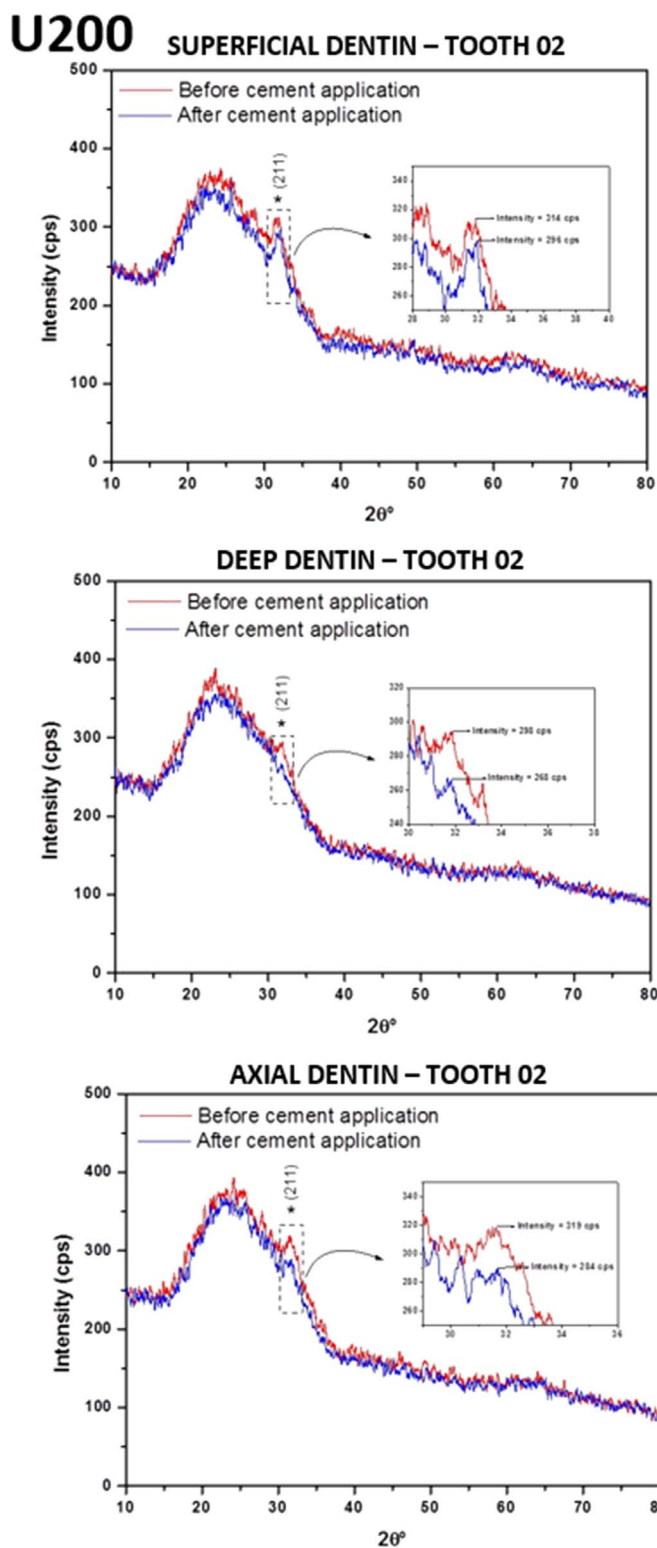


Fig. 3. Representative diffractograms illustrating the reduction of the crystallinity considering the intensity of the HAp (211) diffraction peak in the 3 dentin regions (superficial, deep and axial dentin) after the application of the SRC, U200.

application of the SRC at different intensities.

The percentage reduction of the intensity of HAp (211) diffraction peak in function of the dentin region is displayed in Table 3. The results from the deep and axial dentin were similar and higher than that of superficial dentin, which is an indication of a higher chemical interaction in these dentin regions.

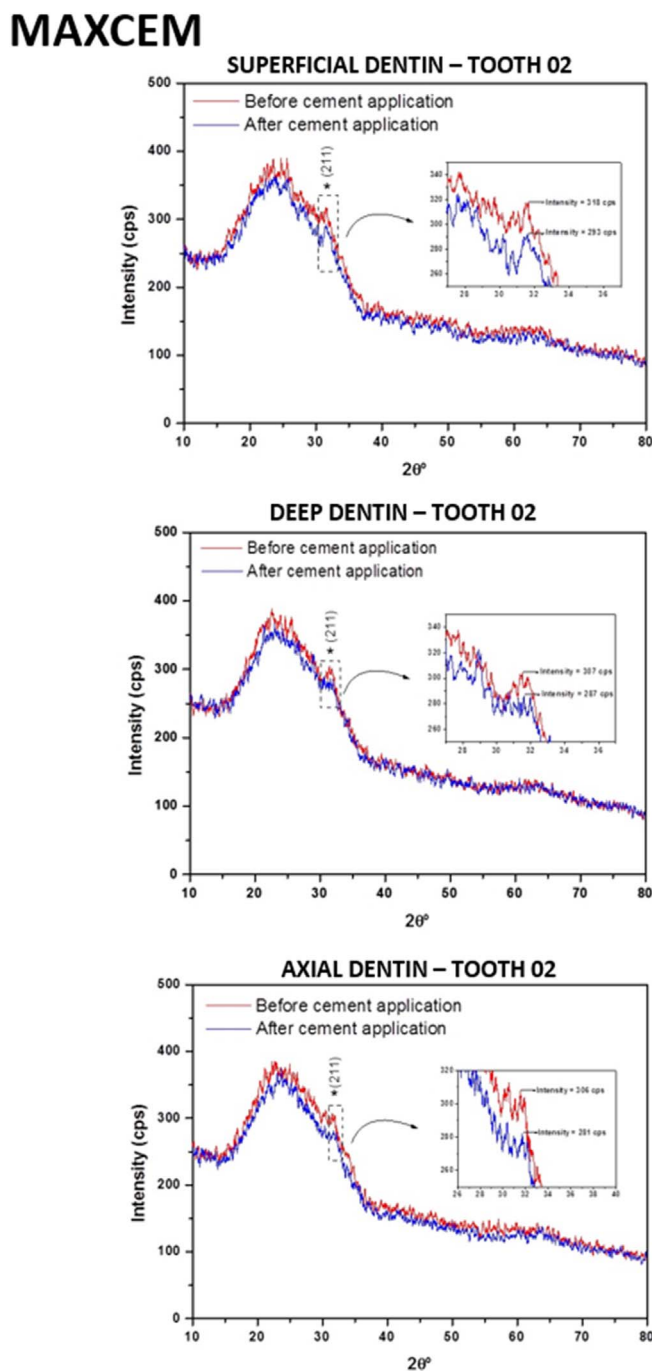


Fig. 4. Representative diffractograms illustrating the reduction of the crystallinity considering the intensity of the HAp (211) diffraction peak in the 3 dentin regions (superficial, deep and axial dentin) after the application of the SRC, Maxcem Elite.

4. Discussion

SRCs have been used increasingly due to their simplified clinical application and efficiency, as demonstrated in several *in vivo* [14,15] and *in vitro* studies [16,17]. Nevertheless, it is important to consider that there is currently a wide variety of commercial brands of SRCs available in the dental market that present distinct chemical formulations. Accordingly, each SRC has particular interactions with the dentin that determine its individual bonding effectiveness. In the present study, Rely X U200 showed a more regular bonding performance, with the same magnitude of bond strength regardless of the bonding region. On the other hand, the bond strength of the other 2 SRCs evaluated

BIFIX

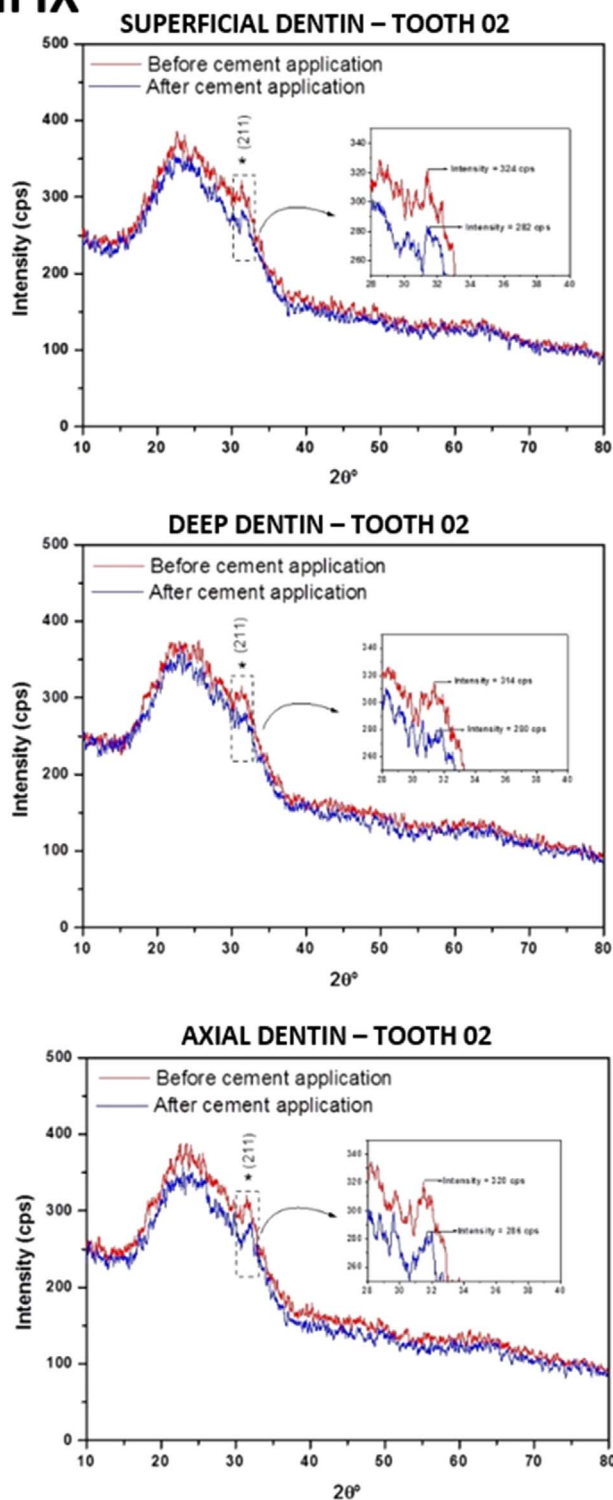


Fig. 5. Representative diffractograms illustrating the reduction of the crystallinity considering the intensity of the HAp (211) diffraction peak in the 3 dentin regions (superficial, deep and axial dentin) after the application of the SRC, Bifix SE.

significantly varied according to the dentin region, leading to the rejection of Research Hypothesis I.

The interaction between SRCs and dentin creates a micromechanical interlocking that is considered the fundamental principle of adhesion to the tooth substrate, based on an exchange process by which inorganic tooth material is exchanged for synthetic resin [18,19]. This process involves 2 phases. One phase consists of removing calcium

Table 3

Percentage reduction of the intensity of HAp (211) diffraction peak in function of the dentin region.

Dentin region	Percentage reduction
Superficial dentin	6.3%
Deep dentin	8.0%
Axial dentin	8.3%

phosphates, by which microporosities are exposed at the dentin surface. The subsequent so-called hybridization phase involves infiltration and subsequent in situ polymerization of resin within the produced microporosities. Similarly to how micromechanical interlocking is believed to be a prerequisite to achieving good bonding within clinical circumstances, the potential benefit of additional chemical interactions between functional monomers and tooth-substrate components has regained attention recently [20–22].

According to the “Adhesion-Decalcification” concept, specific functional monomers within SRCs can ionically interact with HAp [23,24]. Commonly, esters originating from the reaction of a bivalent alcohol with methacrylic acids and phosphoric/carboxylic acid derivatives are used. Such molecules are able to etch/infiltrate the dentin and react with HAp, generating calcium ions with a reduced binding energy. These ions act as an electron acceptor, enabling chemical interaction with the composite. This way, the micromechanical interlocking and chemical binding with HAp are thought to synergistically provide the ultimate adhesion of the material [1,6].

Besides the functional monomers, there are other components of the SRCs that are key to their bonding performance. For example, rheological modifiers were incorporated in RelyX U200 in order to increase the flowability of the cement, which is thought to improve the wettability of the cement to the substrate. In fact, the mean bond strength of RelyX U200 to dentin is significantly higher than its predecessor (RelyX U100), [25] and the only difference between them is the rheological behavior (3M ESPE – Technical Product Profile). In the case of Maxcem Elite and Bifix SE, the manufacturers incorporated the monomers GPDM (glycerol dimethacrylate dihydrogen phosphate) and Gly-DMA (glycerol dimethacrylate), respectively (Table 1), which is speculated by the authors to favor the wettability potential of the cements to dentin due to the hydrophilic character of such monomers.

Corroborating with previous studies, the XRD analysis confirmed that chemical interaction exists between the 3 SRCs and dentin, irrespective of the dentin region (Figs. 3–5). To get to this finding, the crystal structure of dentin specimens was previously characterized with XRD analysis. In this analysis, XRD patterns indicated the coexistence of an inorganic, crystalline phase, related to hydroxyapatite - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ - and an organic, amorphous phase (seen as a broad hump in the baseline) at 2θ between 15° and 35° , which corresponds mostly to the presence of collagen fibers. Similar results were obtained for both dentin specimens tested, irrespective of the dentin region. Then, the cements were applied onto the dentin specimens according with the manufacturer’s instructions. After cement photoactivation, the specimens were positioned again in the apparatus in the same way as previously characterized. The intensities of HAp peaks related to (211) plane at $\sim 31.5^\circ$ in 2θ before and after application of 3 SRCs were determined. As previously mentioned, a reduction of peak intensity of (211) plane was observed in all experimental groups after the application of the SRCs. This reduction indicates a less crystalline hydroxyapatite and it is related to the decrease in calcium concentration, i.e. chemical consumption of Ca^{2+} ions [20]. This somehow confirms the possible chemical interaction of hydroxyapatite present in both regions of dentin and the SRCs evaluated.

In general, the chemical interaction was found to be material dependent and was varied significantly according to the dentin region, leading to the acceptance of Research Hypothesis II. This result is

supposed to be directly related to the amount of calcium ions (Ca^{2+}) available for bonding, which varies significantly according to dentin region. The superficial dentin has higher amount of intertubular dentin compared to the deep dentin, which has more tubules with larger diameters and thicker peritubular dentin [8–10]. Since it is more mineralized, theoretically, the peritubular dentin could provide higher amounts of calcium available for bonding. The axial dentin has a similar condition; although the diameter of the dentin tubules is not as large as that of observed in deeper dentin, the section orientation exposes a comparable area of peritubular dentin. Therefore, the above described heterogenic characteristics of dentin seem to determine the chemical interaction of the different SRCs tested on dentin (Table 3).

Several chemical analytical tools have been used to investigate the chemical interaction of restorative materials and dental hard tissues; infrared spectroscopy (IR) is most frequently used [26,27]. However, IR is not able to provide irrefutable evidence of chemical bonding [28–30]. Although the reaction of carboxyl groups with calcium can be detected using this method, it is not possible to distinguish between carboxyl groups of the acidic monomer that chemically interacted with calcium at the HAp interface and those that merely participated in gelation through reaction with calcium ions extracted from HAp. On the other hand, the XRD analysis used in the present study can specifically investigate the level of chemical bonding by comparing the hydroxyapatite diffraction peaks of the dentin before and after the interaction with an SRC [28,29]. In this case, the chemical bonding occurring within the material is not taken into consideration, which makes the SRCs/dentin-interaction-level investigation more accurate [21]. Another important aspect of the using XRD analysis is that the incidence of X-ray was performed on the opposite side of the bonding interface. Considering the X-ray incidence at the bonding surface, the analysis after the cementation procedure would be impaired, as the SRCs contain radiopaque components hindering the X-ray transposition until reaching the underlying dentin, which would jeopardize the identification of the HAp crystallinity.

Based on the analysis of the results displayed in Tables 2 and 3 it can be speculated that it seems that higher bond strength means are obtained in dentin regions exhibiting higher levels of chemical interaction with the SRC (deep and axial dentin). Therefore, the chemical interaction of SRCs to dentin seems to contribute significantly to the bond strength and can be considered a plausible explanation for the good performance of SRCs. In addition, the functional monomers found in the SRCs chemically interact with Ca ions from the demineralized dentin, creating a 3-dimensional cross-linking that allows the formation of an insoluble adhesive layer, which was claimed to favor long-term bonding durability [31,32].

5. Conclusions

Within the limitations this study, the following conclusions can be drawn:

1. The bond to different dentin regions was proven to be affected by the individual characteristics of the SRCs tested.
2. There is a chemical interaction in the interfacial area formed between the dentin/SRCs.
3. Based on the parameters evaluated, Rely X U200 provided more optimal characteristics than the others, improved bond strength and higher chemical interaction with dentin, regardless of the region.

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