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Influence of primers on the properties of the adhesive interface between resin composite luting cement and fiber-reinforced composite

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ABSTRACT

Objectives: The purpose of this study was to characterize the adhesive interface formed due to the dissolving capability of 4 primer systems into pre-polymerized semi-interpenetrating polymer network (semi-IPN)-based fiber-reinforced composite (FRC) and luting cement.

Materials and methods: Semi-IPN FRC (everStick C&B, StickTech) prepregs stored for various durations (at 4 °C; 1, 1.5, and 3 years) were used to fabricate the specimens. FRC specimens (n = 10) were light-cured and treated with primers before adhering a luting cement onto them. Each age group was divided into four subgroups according to the primer used: no priming, a dimethacrylate adhesive primer, universal primer, and primer intended for composite surfaces. The degree of monomer conversion (DC%) of the luting cement; nanohardness, elastic modulus and structural information of the luting cement–FRC adhesive interface were measured.

Results: According to analysis of variance ($P \leq 0.05$), no statistical difference was observed in the DC% among the tested groups. However, both universal and composite primers showed increased nanohardness in 1- and 1.5-year-aged groups. The highest nanohardness (0.55 ± 0.21 GPa) and elastic modulus (14.27 ± 5.19 GPa) were observed in specimens of 1-year-aged FRC primed with the application of universal primer. Raman spectroscopy and scanning electron microscopy examination confirmed the presence of poly(methyl methacrylate) at the interface when the FRC prepregs were aged for 3 years before use.

Conclusion: Both primers improved diffusion of monomers of composite luting cement into the polymerized semi-IPN polymer structure and possible covalent binding with pendant methacrylate groups in the polymer matrix of FRC. The diffusing capability of universal and composite primers might increase the opportunity to form solid adhesive interface bonding between the FRC and composite luting cement.

1. Introduction

The evolution of adhesive dentistry in the 1990s has paved the way for resin composite materials to replace traditional metallic restorations (Vallittu, 1999). Chipping and fracture of veneering material (Garoushi et al., 2007), and the need for cutting significant amount of sound tooth structure for the fabrication of conventional fixed restorations are the major shortcomings associated with conventional materials (Freilich et al., 1998; Kolbeck et al., 2002). With the introduction of fiber-reinforced composites (FRC), directly and indirectly made minimally invasive restorations for the replacement of missing teeth have become possible (Vallittu, 2015; Vallittu et al., 2017).

The use of silanated glass fibers impregnated with a dental cement or resin matrix of FRC is promising owing to the surface chemistry, and this method has been successfully applied to a wide range of clinical applications (Behr et al., 2000; Khan et al., 2017). The resin matrix of dental FRCs is usually based on dimethacrylate polymers, such as bisphenol-A glycidyl methacrylate (*bis*-GMA) and urethane dimethacrylate, which are highly cross-linked polymer matrices. The high cross-link density of these polymer matrices has resulted in insufficient adhesion of composite luting cement and veneering composite. Thus, debonding and delamination of restorations occur (Uctasli et al., 2005;

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Lassila et al., 2005). To overcome problems related to the interfacial adhesion between composite luting cement and FRC, a semi-interpenetrating polymer network (semi-IPN) matrix was developed for FRC (Vallittu, 2009). It has been shown that combining a cross-linked *bis*-GMA resin system with poly(methyl methacrylate) (PMMA) yields a semi-IPN system for FRC, which can be adhered better to the composite luting cements and veneering composites (Lastumäki et al., 2002; Le Bell et al., 2004; Frese et al., 2014; Wolff et al., 2012).

Improved adhesion of composite luting cement to FRC is based on the capability of monomers of composite luting cement to dissolve the semi-IPN matrix of FRC. By curing the composite luting cement, an interface between the semi-IPN and cross-linked matrix of the composite luting cement is formed. In fact, this adhesive interface region is also an IPN system and it is called secondary-IPN (Behr et al., 2000).

Thus, the monomers diffuse into the linear polymer system of the semi-IPN FRC. The dissolution gradient is governed by the duration of exposure, monomers used in the resin composite, temperature, and polymeric structure of semi-IPN (Vallittu and Sevelius, 2000; Khan et al., 2018a; Chen et al., 1998). These semi-IPN FRCs are most useful when pre-fabricated restorations are used to attach the tooth surface, or in particular, when a restoration is required to be repaired (Wolff et al., 2012, 2011; Vallittu and Sevelius, 2000; Mannocci et al., 2005; Vallittu and Ruyter, 1997). A strong and durable interface can lead to high levels of stress transfer from the composite luting cement to the FRC-based prosthesis, and increase clinical success of the treatment (Wolff et al., 2012). Recently, we have reported the change in a semi-IPN structure during the shelf-life of the FRC prepreg. We observed that the PMMA used in the semi-IPN structure can be enriched to the surface of the FRC during long-term storage of the FRC prepreg before its use (Khan et al., 2018a). Some composite luting cements and specifically composed primers have been recently marketed to improve the bonding of composite luting cement with semi-IPN FRC. However, some of these primers contain a photo-initiator system whereas others do not. There is a concern that, although primers could have good dissolving capability of PMMA in the semi-IPN system, the adhesive interface layer might be left poorly polymerized even after curing the composite luting cement.

Therefore, the aim of this study was to evaluate the dissolving capability and solidification of the dissolved surface layer of the semi-IPN polymer matrix FRC by photo-activated cross-linking of the composite luting cement on top of the FRC. According to the previous finding of the change in the PMMA gradient of the surface of the semi-IPN FRC during its shelf-life, this study also investigated FRC prepregs stored for various durations before their use.

2. Materials and methods

The materials used in this study are listed in Table 1. A semi-IPN-based prepreg of FRC (everStick C&B, Stick Tech Ltd., Turku, Finland) was selected and stored at 4 °C for different durations—1, 1.5, and 3 years—before fabricating the test specimens. Ten specimens (n = 10) of dimensions 5 × 3 × 1 mm^3 were prepared from each aging group. Each aging group was divided into four subgroups according to the primer used to pretreat the surface of the FRC: no pretreatment, pretreatment with a light-curing dimethacrylate adhesive primer (StickRESIN, GC, Leuven, Belgium), universal primer (G-Multi Primer, GC, Tokyo, Japan), and primer intended for composite substrates (Composite Primer, GC, Leuven, Belgium) (Table 1).

A mold made of silicone putty (Affinis Putty, Coltene Whaledent) was used to prepare the specimens and standardize their shapes and thicknesses. The FRC prepreg was cut off, placed inside the silicone mold, and pressed against two glass plates to obtain an even surface. The FRC was subsequently light-polymerized using a hand-held light-polymerizing unit for 40 s with an irradiance of 1150 mW/cm^2 (Elipar S10; 3M ESPE). Subsequently, a single coat of the primer for each subgroup was applied on the FRC using a fine micro-brush. The specimens were thereafter stored under a light-protection shield (Viva Pad®, Ivoclar Vivadent AG, Schaan, Liechtenstein) for 3 min to allow the monomers to dissolve the surface of the FRC. Subsequently, the specimens were light-polymerized for 20 s following the manufacturers' instructions. After the FRC specimens were treated with the primers, a resin composite luting cement (G-CEM LinkAce, GC, Tokyo, Japan) was applied on their surface using the silicone mold to maintain the same thickness for all specimens. A Mylar sheet and a glass plate were used to achieve a smooth surface. The specimens were subjected to a final light-polymerization for 40 s. They were thereafter polished with a 1200-grit silicon carbide paper under running water.

2.1. Fourier-transform infrared spectroscopy (FTIR) evaluation

The degree of monomer conversion (DC%) of the resin luting cement was evaluated using Frontier FTIR spectrometer (PerkinElmer, Waltham, MA, USA) in the attenuated total reflectance (ATR) mode. As a control measurement for DC%, a sample of the resin composite luting cement (LinkAce, GC) of thickness 0.3 mm was placed on the ATR sensor (ZnSe-crystal) to measure the DC% at the bottom. The upper surface of the specimen (n = 6) was covered with a Mylar sheet and a glass slide of thickness 1 mm was pressed slightly against the ATR to establish a good contact with the specimen. The light source was placed in contact with the glass slide. The photo-polymerization was performed using a hand-held light-polymerizing unit for 40 s.

Four groups were prepared to evaluate the differences in the DC% compared with the control group and they were classified as follows: a. FRC without the application of primers on which a luting cement (LinkAce, GC) was applied; b. FRC treated with StickRESIN followed by the application of the luting cement; c. FRC treated with G-Multi Primer followed by the application of the luting cement; d. FRC treated with Composite Primer followed by the application of the luting cement. The luting cement side was always placed on the ATR sensor. The FRCs of the specimens of each group were photo-polymerized for 40 s; subsequently, the primer was applied and left on the surface of the FRCs for

Table 1
Materials used in the fabrication of the specimens.

Brand	Manufacturer	Composition	Lot. No.
everStick C&B[1]	StickTech - GC	bisphenol A-glycidyl methacrylate, poly(methyl methacrylate), substituted methacrylate (< 0.5%), hydroquinone (< 0.5%) photoinitiator system	1612081
everStick C&B[2]	StickTech - GC	-do-	1606291
everStick C&B[3]	StickTech - GC	-do-	1412081
StickRESIN	GC	(1-methylethylidene)bis[4,1-phenyleneoxy(2-hydroxy − 3,1-propanediyl)] bismethacrylate (25–50%), 2,2′-ethylenedioxydiethyl dimethacrylate 25–50%, 2-dimethylaminoethyl methacrylate (0.1–0.5%), photoinitiator system	5411810
Composite Primer	GC	2-hydroxyethyl methacrylate (30–60%), tetrahydrofurfuryl methacrylate (10–30%), urethane dimethacrylate (10–30%), photoinitiator system	1704031
G-Multi Primer	GC	ethyl alcohol (90–100%), phosphoric acid ester monomer (1–5%), dimethacrylate component (1–5%)	1602041
G-Cem LinkAce	GC	urethane dimethacrylate (25–50%), dimethacrylate (5–10%), phosphoric acid ester monomer (1–5%), dual-curing initiator system	1702024

everStick[1]: 1-yr aged; everStick[2]: 1.5-yr aged; everStick[3]: 3-yr aged.