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Research Paper

The effect of polymerization mode on monomer conversion, free radical entrapment, and interaction with hydroxyapatite of commercial self-adhesive cements

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ABSTRACT

Objectives: This study evaluated the degree of conversion, the free radical entrapment, and the chemical interaction of self-adhesive resin cements mixed with pure hydroxyapatite, as a function of the polymerization activation mode among a variety of commercial self-adhesive cements.

Materials and methods: Four cements (Embrace WetBond, MaxCem Elite, Bifix SE, and RelyX U200) were mixed, combined with hydroxyapatite, dispensed into molds, and distributed into three groups, according to polymerization protocols: IP (photoactivation for 40 s); DP (delayed photoactivation, 10 min self-curing plus 40 s light-activated); and CA (chemical activation, no light exposure). Infrared (IR) spectra were obtained and monomer conversion (%) was calculated by comparing the aliphatic-to-aromatic IR absorption peak ratio before and after polymerization ($n=10$). The free radical entrapment values of the resin cements were characterized using Electron Paramagnetic Resonance (EPR) and the concentration of spins (number of spins/mass) calculated ($n=3$). Values were compared using two-way ANOVA and Tukey's post-hoc test ($\alpha=5\%$). X-ray diffraction (XRD) characterized the crystallinity of hydroxyapatite as a function of the chemical interactions with the resin cements.

Results: The tested parameters varied as a function of resin cement and polymerization protocol. Embrace WetBond and RelyX U200 demonstrated dependence on photoactivation (immediate or delayed), whereas MaxCem Elite exhibited dependence on the chemical activation mode. Bifix SE presented the best balance based on the parameters analyzed, irrespective of the activation protocol.

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Conclusions: Choice of polymerization protocol affects the degree of conversion, free radical entrapment, and the chemical interaction between hydroxyapatite and self-adhesive resin cement mixtures.

1. Introduction

Resin cements are a class of dental materials of choice for bonding metal, ceramic and indirect composite restorations. These resin-based materials are generally classified as a function of their activation reaction as self-cured (chemically activated), light-cured (photoactivated), or dual-cured (a combination of both activation reaction) (Burrow et al., 1996). Based on interaction with tooth substrates, resin cements can be also classified into three categories: etch-and-rinse, self-etch, and a recently developed group of resin cements known as self-adhesive systems (SLCs) (Carvalho et al., 2004; Pegoraro et al., 2007). The main objective of the introduction of SLCs was to overcome the drawbacks of other types of cements used to join indirect restorations to tooth preparations (Radovic et al., 2008). These materials require no technique-sensitive steps, such as acid etching, priming, or bonding (De Munck et al., 2004). The adhesion strategies employed with SLCs also allow the formation of secondary reactions between the self-adhesive resin and hydroxyapatite, forming chemical bonds (De Munck et al., 2004). This innovative bonding mechanism represents an important characteristic when compared to other resin cements, which are essentially micromechanical in nature (Van Meerbeek et al., 1993).

Resin-based cements are also subjected to the oral environment, in spite of the thin layer that results from seating indirect restorations. The polymerization process starts with light exposure or through a self-curing mechanism, if no light is present. Considering this clinical scenario, the polymerization protocol of resin cements is of paramount importance in the subsequent restoration performance (Svizero et al., 2013). It is claimed that the best mechanical properties are achieved when base and catalyst pastes are mixed and immediately photoactivated (Pegoraro et al., 2007). On the other hand, the chemical cure mechanism proceeds slowly and is expected to ensure polymerization in those areas where light is unable to reach (Pereira et al., 2010). As the polymerizing network develops further, the rate of radical propagation eventually becomes limited by diffusion, and the polymerization rate decelerates, providing only a limited conversion, even in the presence of unreacted monomer and free radicals (Halvorson et al., 2002). Conversely, under a delayed photoactivation condition, the cements is chemically activated at first and the polymerization reaction progresses slowly, especially in areas where the curing light is unable to reach the material (Pereira et al., 2010). In this way, a higher end conversion would be expected. Increased degree of conversion has been strongly correlated with improved mechanical properties of resin-based materials (Ferracane and Greener, 1986). Previous studies focused on the influence of different activation protocols in conventional resin cements (Pereira et al., 2010; Svizero et al., 2013). However, studies are necessary to understand the influence of these protocols for the SLCs that present distinctive formulations, low initial pH, dual-cure polymerization, and the ability to interact with hydroxyapatite.

Concerns have been expressed over the chemical composition of the self-adhesive resin cements, specifically regarding the need for balanced formulae due to the polymerization reaction occurs in an acidic environment (Di Hipolito et al., 2012; Vaz et al., 2012). This category of resin cement presents methacrylate monomers that contain phosphoric acid esters that simultaneously demineralize and infiltrate both the smear layer and the underlying dentin, providing micromechanical bonding (Gerth et al., 2006). At the same time, it is important that the pH be neutralized in order to avoid impacting the end conversion, considering the effect of both new methacrylate monomers formulation and the technology to initiate polymerization (Vaz et al., 2012). On the other hand, it has been claimed that a glass ionomer concept was added to the formulation in order to neutralize the initial low pH, which increases from 1 to 6 (Radovic et al., 2008). Thus, the comprehension of the dynamic process in which the demineralization/monomer permeation process and the polymerization kinetics coexist in this category of material is of paramount importance.

Clinically, restorative materials must set in a reasonably short time, in order to be practical, and immediate photoactivation may optimize the initial cement properties necessary to withstand clinical stresses that affect indirect restorations cemented to the remaining tooth structure (Pereira et al., 2010). It is claimed that immediate photoactivation limits the time available for polymer growth and thus inhibits the formation of a rigid polymer network (Neves et al., 2005). On the other hand, the chemical activation protocol is expected to provide the resin cement optimal mechanical properties over time, in areas where polymerization light energy is unable to reach, improving the overall polymerization of the cement at that location (Camilotti et al., 2008; Sideridou et al., 2003). However, different polymerization protocols may affect the resin cements in different ways, depending on a variety of parameters tested (Pereira et al., 2010; Svizero et al., 2013). Some resin cements depend on immediate photoactivation, whereas others seem more dependent on the chemical activation mode. In this way, it is important to evaluate this new category of dual-cure resin cements, considering among others their particular acidic characteristics. Another concern is related to the analysis of the biocompatibility of dental materials, in that the nature and amount of components released during their clinical application are most important. Monomer-release studies are commonly investigated using different solvents such as water, saliva, and organic solvents (Sideridou et al., 2003).