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A castor oil-containing dental luting agent: effects of cyclic loading and storage time on flexural strength

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ABSTRACT

Favorable results in the use of castor oil polyurethane (COP) as pulp capping, membrane material, sealer, mouthwash and in bone repair, associated with the fact that *Ricinus communis* is not derived from petroleum and it is abundant in Brazil, encourage researches in the development of luting agents. Objectives: This study compared the flexural strength (FS) of a castor oil-containing dental luting agent with a weight percentage of 10% (wt%) of calcium carbonate (COP10) with RelyX ARC (RX) after mechanical cycling (MC) and distilled water storage. Material and Methods: Sixty-four specimens (25x2x2 mm) were fabricated and divided into two groups, COP10 and RX (control). Each group was divided into 4 subgroups (n=8) according to the storage time, 24 hours (24 h) or 60 days (60 d), and the performance (MC+FS) or not (only FS) of the mechanical cycling test. The FS (10 kN; 0.5 mm/min) and MC tests (10,000 cycles, 5 Hz, 0.5 mm/min) were carried out using an MTS-810 machine. The data were analyzed using ANOVA (α=0.05). Results: The obtained FS (MPa) values were: COP10 24h- 19.04±2.41; COP10 60d- 17.92±3.54; RX 24h- 75.19±3.43; RX 60d- 88.77±6.89. All the RX specimens submitted to MC fractured, while the values for COP10 after MC were as follows: COP10 24h- 17.90±1.87 and COP10 60d- 18.60±1.60. Conclusions: A castor oil-containing dental luting agent with a weight percentage of 10% (wt%) of calcium carbonate is resistant to mechanical cycling without decreases in flexural strength. However, mean COP10 showed only about 25% of the RelyX ARC mean flexural strength.

Keywords: Biocompatible materials. Polyurethanes. Dental cements. Material resistance. Aging.

INTRODUCTION

Polymers are biocompatible materials of natural or synthetic origin that can be prepared by different methods[34]. In dentistry, various polymers are used, such as silicone, methyl methacrylate and polyurethane. Currently, vegetable-polyurethane, which combines the versatility of polymer formulation while addressing the global concern towards producing new biomaterials from sustainable resources, has become one of the most studied biomaterials[3]. The use of vegetable-polyurethane derived from castor oil (COP) in the health science fields has been studied, and COP has shown favorable results in tests for biocompatibility[22]. Castor oil is a new material that is globally available, and it has received much attention in recent years because of its availability on a large commercial scale[23].

The COP is a biocompatible, antimicrobial, osteointegrable and absorbable, osteoconductive and osteoinductive[13]. In dentistry, the use of this polymer has been studied in direct pulp capping[5], as a membrane material[22], as a sealer[31], as a mouthwash[28], as bone prosthesis and in alveolar healing[7] and bone reconstruction[20]. In clinical research focusing on human dental alveoli, Jowett, et al.[19] (1988) showed that this polyurethane has good biocompatibility for use both in soft and hard tissue, has osteoinductive properties, and can be bactericidal and fungicidal when combined with calcium carbonate.

The versatility of the polyurethane derived from castor oil as well as the aforementioned positive aspects support the study of COP as a dental luting agent. Although a wide range of dental luting agents is commercially available, the selection of a luting agent to be used for a given restoration should not be an arbitrary choice. It must be based on a basic knowledge of the materials available, the type of restoration to be placed, and the requirements defined by the patient[17] based on the functional and biological needs[2] of a particular clinical situation, including handling characteristics such as working time, setting time, consistency and ease of removal of excess material[33]. As such, no single dental luting agent is considered ideal, and new products should be studied. It is important to characterize the mechanical, physical and biological properties of COP. When compared with zinc phosphate cement, the COP, with the addition of calcium carbonate, presented better diametral tensile strength values and was associated with better film thickness[6]. The addition of calcium carbonate is responsible for conferring radiopacity to COP[29]. Moreover, this filler provides the release of calcium ions, facilitating ion exchange at the bone/resin matrix interface[15], which may be beneficial in subgingival restoration margins. The COP dental luting agents are deemed strong enough to resist masticatory stresses and provide retention similar to that of zinc phosphate cement, a permanent cementation material[29].

In the oral cavity, the chewing forces applied to restorative materials result in cycles of mechanical impulses that lead to material fatigue and, consequently, fracture. These impulses can be simulated in the laboratory by performing mechanical cycling, which approaches the physiological conditions generated by the chewing cycle[24]. Fixed partial dentures are more likely to be subjected to bending forces than to other types of stress[10,25,26]. As such, the flexural properties of the restorative material are more important than their tensile, shear and compressive strengths. Moreover, the flexural strength test is considered the most appropriate for simulating the clinical situation of material fatigue[4,32] because the concentration of masticatory forces causes flaws and microcracks in the dental luting agent prior to the fracture or displacement of the restoration material[11]. The mechanical properties of resinous materials are directly related to the quantity and type of inorganic particles[8], degree of cure and percentage of silane-treated filler[12], with the flexural strength being directly proportional to amount of filler particles[30]. Most current *in vitro* studies include cycling testing with dynamic loads in order to assess the influence of stress on the material[16,21].

The aim of this study was to assess the behavior of COP under masticatory stress simulated by mechanical cycling. The flexural strength of COP with a weight percentage of 10% (wt%) of calcium carbonate was analyzed with and without the performance of the mechanical cycling test as well as with storage in distilled water. The results were compared with the results for RelyX ARC. The null hypothesis was that there is no difference between the flexural strength of COP10 and that of RelyX ARC.

MATERIAL AND METHODS

The procedure of the study is summarized in Figure 1. For the COP10 group, 32 specimens were fabricated with the castor oil-containing dental luting agent (Castor Oil Polyurethane - COP, Poliquil Araraquara, Chemical Polymers Ltd, Araraquara, SP, Brazil) with a weight percentage of 10% (wt%) of calcium carbonate ($CaCO_3$). For the control group, named RX, 32 specimens were fabricated with the resin cement RelyX ARC (3M ESPE, Sumaré, SP, Brazil). Each group was randomly divided into 4 subgroups (n=8) according to the storage time in distilled water, 24 hours (24 h) or 60 days (60 d), and the performance or not of the mechanical cycling (MC) test.

The COP was provided in a sachet containing polyol, prepolymer and calcium carbonate[6]. This polyurethane has the following highly reactive groups in the ricinoleic acid structure: a carbonyl group on the first carbon, a double bond (or unsaturation) on the ninth carbon and a hydroxyl group on the twelfth carbon. This combination of a hydroxyl group and unsaturation occurs exclusively in the castor oil molecule[14]. Prepolymer was synthesized from methylene diphenyl diisocyanate (MDI) and was prepolymerized with the polyol while preserving 20% of free isocyanate. When these two components were mixed, the moisture-curing kinetics was determined by the polymerization reaction between the isocyanate and hydroxyl groups. The stoichiometric ratio between the polyol and the prepolymer was equal to 1:0.66.

For the COP10 specimens, the material was manually mixed in the sachet for 2 minutes. It was then mixed with a spatula on a Teflon plate for an additional 2 minutes to obtain the final consistency[6]. The material was inserted into a Teflon matrix (2x2x25 mm) positioned between two Teflon plates. This apparatus was placed in a mechanical press under constant load and stored in saturated water vapor in a container lined with wet paper at 37°C for one hour[9].

For the RX group, the cement was manipulated according to the instructions of the manufacturer, dispensed on the Teflon matrix (2x2x25 mm) and cured with light at three points along its length on both sides for 40 seconds each[10]. The matrix was placed in a mechanical press under constant load and stored in saturated water vapor in a container lined with wet paper at 37°C for one hour[9].

After the initial storage period of 1 hour, all the samples were removed from the matrix and polished with 200 grit silicon carbide sandpaper (3M ESPE). Then, they were measured at three points using a digital caliper (500-144B, Mitutoyo Sul America Ltd, Suzano, SP, Brazil) to verify the width and thickness. A variance of ±0.2 mm was accepted. The samples were immersed in distilled water at 37°C for the specified periods according to the subgroups.

All samples were subjected to 3-point bending test, which was conducted in a universal testing machine (MTS 810, Material Test System, Eden Prairie, MN) equipped with the Test Work 4 software, at a crosshead of 0.5 mm/min[18] and with a 10 kN load cell. The FS values were calculated in MPa according to the following formula: $\sigma=3Pl/2bd^2$ (σ=flexural strength, P=maximum load at fracture point, l=distance between the supports, b=width of the samples, d=thickness of the samples). The MC procedure was carried out under conditions equivalent to those used for the FS test. Samples were submitted to 10,000 cycles at a frequency of 5 Hz and a cross-head displacement of 0.5 mm. The initial load was 60% of the mean FS value previously obtained. After completing the MC, samples were submitted to FS. Normality distribution within each sample was done using Kolmogorov-Smirnov test, and the comparison between the experimental

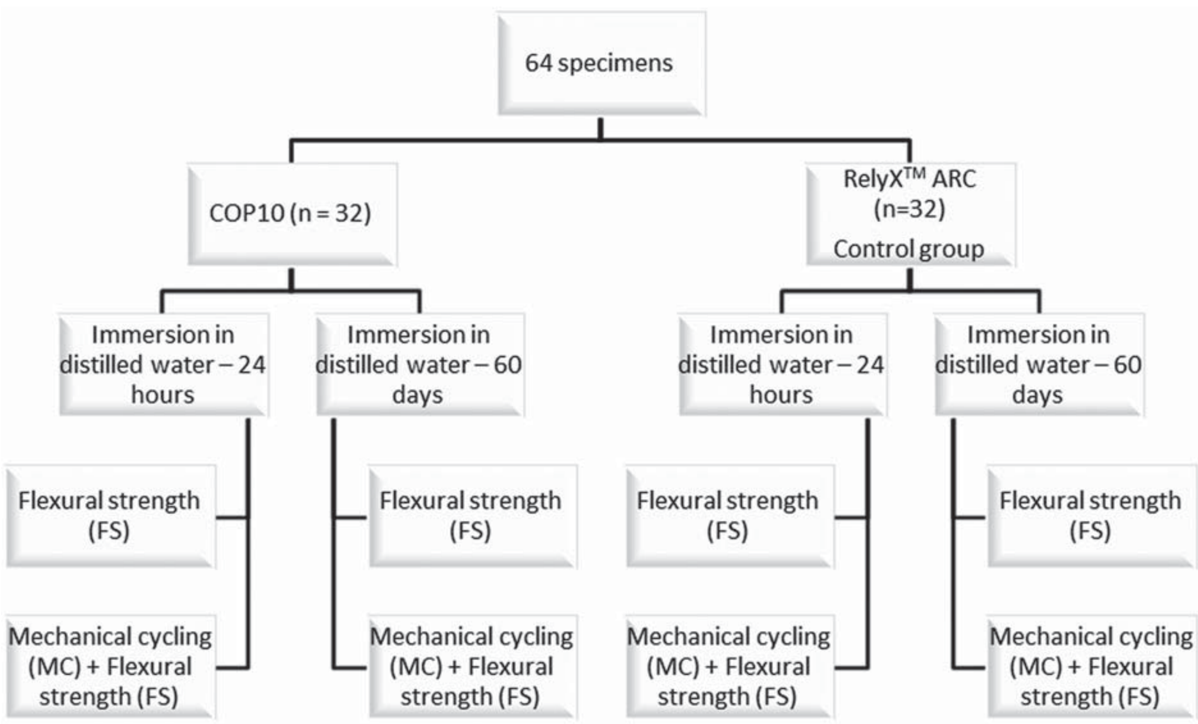

Figure 1- Flow chart of the study

Table 1- Means (MPa) and standard deviations of flexural strength values of luting agents according to storage time and performance of mechanical cycling test

	COP10		RX	
	24 hours	60 days	24 hours	60 days
Without mechanical cycling	19.04±2.41[a]	17.92±3.54[a]	75.19±3.43[b]	88.77±6.89[c]
With mechanical cycling	17.90±1.87[a]	18.60±1.60[a]	*	*

* Specimens did not resist the mechanical cycling
Identical superscript letters were not significantly different

subgroups was performed using analysis of variance (ANOVA) adopting a significance level of 5% (α=0.05).

RESULTS

The FS values are shown in Table 1. The COP10 specimens had mean only about 25% of the RelyX ARC. The RX samples did not resist the mechanical cycling and fractured before the 10,000 cycles were completed. Two-way ANOVA among the subgroups of COP10 reveals no significant differences among the FS values as a function of either the “mechanical cycling” ($F_{1,28}$=0.068; p=.0795) or “storage time” ($F_{1,28}$=0.0558; p=.8150). One-way ANOVA identified significant differences between 24 h and 60 days of RelyX ARC storage ($F_{1,14}$=24.860, p<.0002); it was observed that storage increased the flexural strength of the RX samples (Table 1).

DISCUSSION

In this study, the null hypothesis was rejected because the FS of the COP10 was significantly different from that of the RelyX ARC, a commercially available and most widely used resin cement. Two clinical situations were assessed using conditions designed to simulate the oral environment: aging was simulated by storage in aqueous medium[12], and chewing forces were simulated by mechanical cycling[24]. The calcium carbonate filler was used because previous studies have shown its ability to provide radiopacity to the COP and to supply bactericidal and fungicidal properties to the cement, properties that can be a key factor in the selection of a dental luting agent. The addition of 10% calcium carbonate showed good results regarding diametral tensile strength and film thickness[6].

The mechanical properties of resinous materials are directly related to the quantity and type (composition, shape, size and distribution) of the inorganic particles[8], degree of cure and percentage of silane-treated filler[12], with the flexural strength being directly proportional to the amount of filler particles[30]. The results of this study showed that, for both storage times, the flexural strength of the COP10 group was lower than that of the RelyX ARC group. This result can be explained by differences in the type and amount of filler particles in both cements.

The RelyX ARC is composed of the following: 1) an organic matrix composed of monomers, polymerization inhibitors, color modifiers and an initiator/activator system; 2) a zirconia/silica inorganic filler of approximately 67.5% by weight; 3) organo-silane as a bonding agent between the organic matrix and the filler. In contrast, the COP10 is composed of the following: 1) a matrix that results from the polymerization of polyester from vegetable polyol with linear aliphatic diisocyanates; 2) 10% (wt%) of calcium carbonate by weight as an inorganic filler. Thus, aside from the differences between the amount and type of filler, the absence of a bonding agent, which could result in the consequent failure in the linking-up of the inorganic particles with the resin matrix, could be a key factor in the lower flexural strength of the COP10. However, even though the FS mean for COP10 was only about 25% of that of RelyX ARC, the FS values were similar or slightly less than those found for luting agents such as zinc phosphate (18 MPa), glass ionomer cement (15-36 MPa) and resin-modified cement (22 MPa)[2].

The specimens made from the resin cement RelyX ARC did not achieve the FS values reported by ISO Specification 4049 for light-cure composites (86±6 – 155±7 MPa) in 24 hours[18]. However, after 60 days of storage in distilled water, this dental luting agent showed an 18% increase in FS in comparison with the values obtained after 24 hours. It has been shown in the literature that mechanical resistance results can vary as a result of different filler compositions, extent of cure and testing method used[12]. According some authors[10,12,26], increases in FS, even in the presence of water, could be the result of significant residual or continued polymerization that may occur in dual-cure cements.

On the other hand, after 60 days, the flexural strength of the COP10 specimens remained statistically similar to that observed after 24 hours of storage. According to the manufactures of the COP, after 1 hour, the cement has acquired strength, although it can continue to present residual polymerization for up to 36 hours after the initial mixing, thought most of the isocyanate-hydroxyl reaction is completed in 24 hours. As such, in this study, the residual polymerization that occurred between 24 and 36 hours of storage was not sufficient to significantly increase the FS values. Moreover, considering that the specimens were immersed in distilled water and that the free isocyanates may have reacted with water molecules, it was interesting that there was no decrease in FS, i.e., the long-term effect of water storage did not affect the FS of the COP10, similarly to the COP applied as an endodontic filler that had a reduced solubility in both artificial saliva and deionized water[31].

The results of the MC test show that the RelyX ARC fractured before 10,000 cycles. This finding may be the result of the large amount of zirconia/silica filler (67.5 wt%) incorporated into the matrix[17]. This amount of filler may have influenced the fracturing of the material without the occurrence of behaviour elastic. In comparison, the COP10 showed no change in FS after mechanical cycling, possibly due to the higher elasticity provided by the proportion of polymeric matrix/filler present. The failure potential of a cemented restoration under forces is related to the mechanical properties of the individual parts (periodontal ligament, tooth, luting agent and restoration)[32]. Despite reports of success of RelyX ARC[1,27], current literature shows that the comparisons based on adhesive properties and clinical data proving the longevity of crown and fixed partial dentures (FPD) cemented with RelyX ARC are still limited. Then, this *in vitro* study was carried out as a preliminary study to investigate and compare the behavior of the COP10 under tension, without the influence of the individual parts[32]. Future studies will be designed to assess the flexural (monotonic and fatigue) behavior of crowns or FPD cemented with these two materials in order to enhance the knowledge about COP10 and RelyX ARC.

Despite the limitations inherent to an *in vitro* study as well as the lower FS values of the COP10 that were observed, this dental luting agent can still be considered a promising material due to its characteristics related to biocompatibility, elasticity, mechanical strength and versatility in being modified in terms of composition and structure according to specific requirements[34]. Moreover, *Ricinus communis* is a plant easily found in Brazil with great potential in the manufacturing of products derived from its oil. As such, future studies should be conducted to assess COP containing higher concentrations of $CaCO_3$ and the addition of other fillers, such as zirconia/silica, as well as certain bonding agents. These modifications may improve its mechanical resistance, causing it to have properties similar to those of commercially available resin cements.

CONCLUSION

A castor oil-containing dental luting agent with a 10% weight percentage (wt%) of calcium carbonate resisted mechanical cycling without decreases in flexural strength. However, the COP10 showed lower flexural strength values than the RelyX ARC.

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