INTRODUCTION

For successful endodontic treatment, not only choosing of filling technique, but also the choosing of the material used is crucial. In order to create a leak-proof filling, currently using a combination of endodontic sealer and gutta-percha. Gutta-percha is widely used because of its good physical and biological properties, but the lack of adhesiveness and flow makes the association with endodontic sealers necessary. According to ***Grossman***[(1)], an ideal root canal sealer should provide the following: an excellent seal when set, dimensional stability, a slow setting time to ensure sufficient working time, insolubility to tissue fluids, adequate adhesion with canal walls, and biocompatibility.

Natural products have been used for several years in folk medicine. Therapy with bee products (e.g. honey, pollen, Propolis, etc), is an old tradition that has been revitalized in recent research. Their beneficial effects allied to the current worldwide "back to nature" trend have led to greater attention being paid to these products Propolis is a resinous material collected by honey bees from various plant species. It has attracted increased interest due to its bioactivities such as anti-inflammatory, anti-tumor and antimicrobial activity against a wide range of pathogenic microorganisms. The precise composition of raw Propolis varies with the source. Flavonoid has been considered as the main primary biologically active component in Propolis.

Calcium silicate cements, well known as MTA. They have received greater attention in endodontics because they are able to set in presence of biological fluids, and their biocompatibility. They appeared interesting to develop endodontic sealers based on calcium silicate hydraulic cements.

Tech Biosealer Endo is a recently introduced MTA-based sealer. Its powder is a mixture of white Portland cement, calcium chloride, anhydrous calcium sulfate, phyllosilicate, sodium fluoride and bismuth oxide. Its liquid is composed of Dulbecco's phosphate buffered saline. It is become important to evaluate the characteristics of this sealer as any new dental product must be tested before being cleared for clinical use.

MTA-Fillapex is another MTA-based sealer, which is mainly composed of MTA, resin (salicylate, diluting, natural), bismuth oxide, nano-particulated silica and pigments. This sealer has been extensively evaluated for its physicochemical properties and biological response.

It was worth to estimate some physical properties and cytotoxicity of Propolis to be used as endodontic sealer (Flavonoid-based experimental sealer) and compare it to the newly introduced Tech Biosealer Endo in addition to MTA-Fillapex sealer.

REVIEW OF LITERATURE

1. Physical Properties:

A number of tests have been developed to assess the physical and technological properties of endodontic filling materials, such tests serve a number of purposes. They ensure that the materials are presented in a consistency and workability so that they are practical to use in a clinical situation, they provide a physical characterization of the material when mixed and set, and they may in some instances be helpful in anticipating how the material will perform clinically [2].

Chng et al [3] studied the physical properties and sealing ability of Viscosity Enhanced Root Repair Material (VERRM); and, compared them with Mineral Trioxide Aggregate (MTA). VERRM has a composition similar to mineral trioxide aggregate, with handling characteristics and consistency similar to commercially available materials such as IRM and Super EBA. The pH, setting times, solubility, radiopacity, dimensional change upon setting, and apical sealing ability of VERRM were evaluated and compared to that of ProRoot MTA (GMTA) and ProRoot MTA (Tooth Colored Formula) (WMTA). The results showed that VERRM had physical properties similar to WMTA. VERRM and WMTA showed significantly greater dye penetration than GMTA when used as a root-end filling material. There was no significant difference in depth of dye penetration between VERRM and WMTA. Further development of VERRM is indicated to produce a biocompatible root-end filling material with superior handling characteristics.

Islam et al [4] evaluated and compared the pH, radiopacity, setting time, solubility, dimensional change, and compressive strength of ProRoot MTA (PMTA), ProRoot MTA (tooth colored formula), white Portland cement, and ordinary Portland cement. Results showed that PMTA and Portland cement have very similar physical properties. However, the radiopacity of Portland cement is much lower than that of PMTA. Compressive strength of PMTA was greater than that of Portland cement.

Carvalho-Junior et al [5] proposed smaller dimensions for samples used in solubility and dimensional change tests of root filling materials on the basis of ANSI/ADA specification no. 57. Volume, mass, and density of the test samples were determined, and 6 different samples of smaller dimensions were proposed for each test. Endofill and AH Plus were used. For the solubility test, 2 samples were weighted, stored in distilled and deionized water for 24 hours, dried, and weighted again. Solubility was determined as percentage weight loss. For dimensional change, samples heights were measured before and after immersion in deionized water for 30 days. They concluded that smaller dimensions for test samples used in solubility and dimensional change tests are a viable alternative, decreasing the amount of filling material necessary for executing these tests.

Gandofi et al [6] investigated the setting times and the linear expansion between the initial and final setting times of experimental accelerated calcium-silicate cements and ProRoot MTA after immersion in deionized water, phosphate-buffered saline (PBS), [20% Fetal bovine serum (FBS)/80% PBS] or hexadecane oil. Different compound such as sodium fluoride, strontium chloride, hydroxyapatite, and tricalcium phosphate were separately added to a basic experimental calcium-silicate cement to test their effect on setting and expansion. They concluded that:(1) the setting time of CSC may be effectively reduced; (2) the expansion is a water dependent mechanism owing to water uptake (no expansion occurred in oil); (3) a correlation between setting time and expansion in water and PBS exists; (4) fluorine-containing cement showed a significant expansion in water and in PBS.

Tanomaru-Filho et al [7] evaluated calcium ion release and pH of Sealer 26, white MTA, Endo CPM Sealer (CPM1), Endo CPM Sealer in a thicker consistency (CPM2), and zinc oxide and eugenol cement. Ten disc samples were placed in polyethelene tubes and immersed in 10 ml of distilled water. After 3, 6, 12, 24, and 48 hours and 7, 14, and 28 days, the water pH was determined, and calcium release was assessed by atomic absorption spectrophotometry. Results showed that Sealer 26 presented greater hydroxyl ion release up to 12 hours. Sealer 26, MTA, CPM1, and CPM2 showed similar results from 24 hours until 28 days. Zinc oxide and eugenol cement presented the lowest hydroxyl ion release at all observation periods.

Camilleri [8] evaluated properties of MTA as a sealer. MTA was mixed with water at powder/liquid ratios of 4 and 3.33 and an addition of 2ml to 20 ml of water-soluble polymer. The resultant MTA sealer was tested for radiopacity using methods suggested by ISO 6876 (2002), using pulp canal sealer as control. Results showed that the resultant cement sealer had a lower radiopacity than pulp canal sealer but greater than the 3mm thickness of Al specified by the ISO. It was concluded that the addition of a water-soluble polymer to MTA did not alter the hydration characteristics of the material and resulted in a material with improved properties suitable for use as endodontic sealer cement.

Chiang [(9)] comparatively examined physicochemical and biocompatible properties of 20 wt% bismuth oxide (Bi_2O_3)-containing dicalcium silicate cement and white-colored mineral trioxide aggregate (WMTA). The radiopacity, setting time, diametral tensile strength, pH value, morphology, and phase composition of the cements with and without Bi_2O_3 were measured after mixing powders with water. Cement biocompatibility was evaluated by incubating the cement specimens with MG63 human osteoblast-like cells. He concluded that the dicalcium silicate cement with 20 wt% Bi_2O_3 showed shortened setting time and good biocompatibility and thus may have the potential to be alternative to MTA.

Camilleri and Gandolfi [(10)] evaluated the radiopacity of calcium silicate cements containing different radiopacifier. The chemical composition of the alternative radipacifying materials and bismuth oxide was determined using energy dispersive X-ray analysis. The radiopacity of each material was determined using an aluminum step-wedge and densitometer as recommended by international standards. A commercial MTA and CSC were used as controls. They concluded that Silver/tin alloy and gold powder imparted the necessary radiopacity to calcium silicate-based cement. Barium sulphate was also a suitable radiopacifier together with a lower concentration of silver/tin alloy and gold powder that achieved the radiodensity recommended by ISO 6876.

Camilleri and Mallia [(11)] evaluated the setting time, early age restrained dimensional stability, fluid uptake, microstructure and porosity of a root canal sealer based on MTA (MTAS) and compared it to pulp canal sealer (PCS). Setting time was determined according to ISO 6876; 2002. Vertical dimensional change was measured over a period of 7 days from setting time using a linear variable differential transducer. Fluid uptake was evaluated in Hank's balanced salt solution, and porosity was investigated using light optical microscopy. They concluded that the new MTA-based sealer demonstrated adequate setting time and was dimensionally stable.

Taddei et al [(12)] investigated commercial (white ProRoot MTA, White and Grey MTA-Angelus) and experimental (WTC-Bi) accelerated calcium-silicate cement with regards to composition, hydration products and bioactivity upon incubation for 1-28 days at 37c, in DPBS. Deposits on the surface of the cement and the composition changes during incubation were investigated by micro-Raman and ATR/FT-IR spectroscopy, and pH measurements. Vibrational techniques disclosed significant difference in composition among the unhydrated cement, which significantly affected the bioactivity as well as pH, and hydration products of the cement. Results showed that after one day in DPBS, all the cement were covered by a more or less homogeneous layer of B-type carbonated apatite. The experimental cement maintained a high bioactivity, only slightly lower than the other cement and appears a valid alternative to commercial cements, in view of it adequate setting time properties.

Massi et al ***[13]*** evaluated the setting time, pH, and calcium ion release of MTAS compared with white Portland cement, white MTA Angelus, and AH Plus. Each material was analyzed using Gilmore-type needles for setting time evaluation. Polyethylene tubes with the materials were immersed in distilled water for the measurement of pH (digital pH meter) and calcium release. The evaluations were performed at 3, 6, 12, 24, and 48 hours and 7, 14, and 28 days. MTAS showed higher calcium release at all experimental periods, a greater increase in pH up to 48 hours and the longest setting time. They concluded that the MTAS presented favorable properties for its indication as a root canal sealer.

Vidotto et al ***[14]*** compared MTA Fillapex radiopacity with the radiopacity of Endométhasone-N, AH Plus, Acroseal, Epiphany SE and RoekoSeal. Five cylindrical samples of each sealer were used, constructed with the aid of a matrix. On an occlusal film, a sample of each sealer was placed along with an aluminum stepwedge and five radiographic shots were taken. The radiographic images were digitized and each sample’s gray scales were compared with each shade of the aluminum stepwedge, by using software. They concluded that MTA Fillapex was the third most radiopaque sealer among all tested sealers. Also, MTA Fillapex has the radiopacity degree in agreement with ADA specification No. 57 (1983).

Aguilar et al [15] evaluated the radiopacity of calcium aluminate cement (EndoBinder) with 3 different radiopacifiers (bismuth oxide, zinc oxide, or zirconium oxide) in comparison with gray mineral trioxide aggregate (GMTA), white MTA, and dental structures (enamel and dentin). Eighteen test specimens of each cement with thicknesses of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mm were made. To compare the radiopacity of the cements with that of dental structures, slices of first molars with specific. One occlusal radiograph for each tested cement was taken. They concluded that the bismuth oxide was the most efficient radiopacifier for EndoBinder, providing adequate radiopacity in all studied thicknesses, as recommended by ISO 6876, being similar to GMTA.

Kuga et al [16] evaluated pH and calcium releasing of MTA-Fillapex, and compared with gray and white MTA. Polyethylene tubes with the materials were immersed in distilled water for the measurement of pH (digital pH meter) and calcium release. After 24 hours, 7 days and 14 days, the water pH was determined, and calcium release was assessed by atomic absorption spectrophotometry. In results, concerning to pH, the materials present similar behaviors among each other at 24 hours. At 7 and 14 days, MTA-Fillapex provided significantly lower pH values than the other materials. Regarding to calcium releasing, at 24 hours and 7 days, MTA-Fillapex provided lower releasing than the other materials. After 14 days, differences were found between MTA-Fillapex and gray MTA.

Borges et al [17] tested the solubility of four calcium silicate-containing endodontic materials (iRoot SP, MTA-Fillapex, Sealapex and MTA-Angelus (MTA-A)) compared to AH Plus, together while comparing the changes in the surface structure and elemental distribution, as well as the percentage of ion release. Solubility was tested according to ANSI/ADA Specification 57 and the water used was submitted to atomic absorption spectrophotometry. The outer and inner surfaces of samples of each material were analyzed by means of scanning electron microscopy and energy-dispersive spectroscopy. AH Plus and MTA-A showed similar solubility. High levels of Ca^{2+} ion release were observed in all groups except AH Plus sealer. All surfaces showed morphological changes.

Dhani et al [18] evaluated and compared the pH, setting time, hardness and chemical composition of white ProRoot MTA with gray and white Portland cements and a novel composition of Portland cement with bismuth oxide. Results showed that the chemical composition of white Portland cement, gray Portland cement, modified Portland cement and MTA were very similar in powder and bound form. The only difference obtained was the presence of bismuth ions in MTA and modified Portland cement and iron in gray Portland cement. All the cements tested showed no difference in pH values at 2 mins, 30 mins and 60 mins. All the cements showed similar setting time except gray Portland cement showed higher setting time. The hardness values of all the cements were same except white Portland cement showed significant higher value.

Banava et al [19] compared two types of MTA (ProRoot MTA and Angelus MTA) in terms of setting time and surface porosity. Primary setting time was evaluated according to ISO 6876: 2001 standard using Gilmore needle system. After final setting, surface porosity of samples was assessed using an electron microscope. Results showed that primary setting times of materials in two groups differed significantly, and microscopic investigations revealed better surface properties in ProRoot MTA compared with those in Angelus MTA. They concluded that Angelus MTA had shorter primary setting time compared with ProRoot MTA, but ProRoot showed better surface properties and less porosity after final setting.

Vitti et al [20] compared physicochemical properties of MTA Fillapex and AH Plus. The working time and flow were tested according to ISO 6876:2001 and the setting time according to ASTM C266. Ten disc samples were placed in polystyrene-sealed container with 20 mL of deionized water at 37°C. At 1, 7, 14 and 28 days, the samples were removed from the solutions and blotted dry for solubility and water absorption tests. MTA Fillapex showed the lowest values of flow, working and setting times, solubility and water absorption. The solubility and water absorption increased significantly over time for both sealers. They concluded that MTA Fillapex showed suitable properties to be used as an endodontic sealer.

Vitti et al [21] evaluated the calcium release, pH, flow, solubility, water absorption, setting and working time of three experimental root canal sealers made by mineral trioxide aggregate

(MTA) and different calcium phosphates (CaP). The materials were composed of a base and a catalyst pastes mixed in a 1:1. The base paste was made by 60% bismuth oxide and 40% butyl ethylene glycol disalicylate. Three different catalyst pastes were formulated containing 60% MTA or 40% MTA + 20% CaP (hydroxyapatite HA or dibasic calcium phosphate dehydrate DCPD), 39% Resimpol 8 and 1% titanium dioxide. MTA Fillapex was used as control. Results showed that all cements showed basifying activity and released calcium ions. MTA Fillapex showed the highest values of flow and working/setting times and the smallest values of solubility and water absorption. They concluded that all experimental materials showed satisfactory physicochemical properties to be used as endodontic sealers in clinical practice .

Zhou et al [(22)] evaluated the physical properties of MTA Fillapex and Endosequence BC in comparison with AH Plus, ThermaSeal, GuttaFlow, and Pulp Canal Sealer. ISO 6876/2001 specifications were followed. The pH change of freshly mixed and set sealers was evaluated at one day and 5 weeks. The viscosity was investigated at different injection rates at room temperature using a syringe-based system. The flow, dimensional change, solubility, and film thickness of all sealers were in agreement with ISO 6876/2001 recommendations. The Endosequence BC sealer exhibited the highest value of solubility. The MTA Fillapex and Endosequence BC sealers presented an alkaline pH at all times. The viscosity of the tested sealers increased with the decreased injection rates.

Akbari et al [23] evaluated the effect of addition of nano-SiO2 to MTA on the setting time and its physical properties. Two concentrations (8% and 10%) of nano-SiO2 were added to the white MTA powder. After mixing with water, the setting time, compressive strength, and flexural strength were investigated and compared with pure MTA. They concluded that the addition of 8% and 10% of nano-SiO2 to MTA accelerated the hydration process, reduced the setting time, and had no adverse effect on the compressive and flexural strength of MTA.

Tanomaru-Filho et al [24] evaluated the radiopacity and flow of different endodontic sealers: AH Plus, Endo CPM, MTA Fillapex, Sealapex, Epiphany, and Epiphany SE. For the radiopacity test, six specimens measuring 10 mm in diameter and 1 mm in thickness were fabricated from each material. They were radiographed on an occlusal film alongside an aluminum step wedge. Radiographs were digitized to determine the radiopacity equivalence in millimeters of aluminum. Results showed that AH Plus and Epiphany SE presented the greatest radiopacity (12.5 mm Al and 12.0 mm Al, respectively), followed by Epiphany (9.6 mm Al) and Fillapex (8.9 mm Al). Endo CPM (5.46 mm Al) and Sealapex (5.51 mm Al) presented lower radiopacity. MTA Fillapex presented significantly higher values of flow than other sealers (33.11 mm and 844.9 mm2). AH Plus, Epiphany, and Epiphany SE had similar values. Endo CPM (21.05 mm and 342.8 mm2) and Sealapex (19.98 mm and 352.5 mm2) presented the lowest flow values. They concluded that all sealers presented radiopacity and flow values according to ISO and ANSI/ADA recommendations.

Borges et al [(25)] evaluated solubility, pH, electrical conductivity, and radiopacity of AH Plus and MTA FillApex. In addition, the surfaces morphologies of the sealers were analyzed by using scanning electron microscopy. For pH test, the samples were immersed in distilled water at different periods of time. The same solution was used for electrical conductivity measurement. The solubility and radiopacity were evaluated according to ANSI/ADA. Results showed that MTA FillApex presented higher mean value for solubility and electrical conductivity. No significant difference was observed in the mean values for pH reading. AH Plus presented higher radiopacity mean values. MTA FillApex presented an external surface with porosities and a wide range of sizes. They concluded that the materials fulfill the ANSI/ADA requirements when considering the radiopacity and solubility. AH Plus revealed a compact and homogeneous surface with more regular aspects and equal particle sizes.

Prati and Gandolfi [(26)] reviewed the most important investigations of the last 20 years and analyze their impact on hydraulic calcium silicate cements (HCSCs) use in clinical application. HCSCs, well-known as MTA, were developed more than 20 years ago. Their composition is largely based on Portland cement components (di- and tri-calcium silicate, Al- and Fe-silicate). They have important properties such as the ability to set in moist, biocompatibility, adequate mechanical properties, etc. Their principal limitations are long setting time, low radiopacity and difficult handling. New HCSCs-based materials containing additional components (setting modulators, radiopacifying agents, drugs, etc.) have since been introduced and have received a considerable attention from laboratory researchers for their biological and translational characteristics and from clinicians for their innovative properties.

2. **Adaptability:**

Almas et al [(27)] compared the texture changes of dentinal surfaces after the application of Propolis and saline. Twenty-four recently extracted human premolar teeth were classified as sound, periodontally involved and with recession. Forty-eight, 3 x 3 mm dentin disc specimens were prepared and only 24 specimens were treated with Propolis (pH 8.5) and saline (pH 6). The remaining specimens were divided into four categories i.e.: (1) no application of any material (control); (2) Propolis for 60 seconds; (3) Propolis for 120 seconds and (4) saline for 60 seconds. All specimens were prepared for SEM. Results showed that Propolis partially occluded the dentinal tubules with some smear layer in sound specimens, a few wide opened tubules in periodontally involved teeth and occluded tubules in samples with recession. While in those groups treated with Propolis for 120 seconds, there was dentinal tubules occlusion.

Gandolfi et al [(28)] evaluated physical properties (workability, expansion, setting time, pH and radiopacity), sealing ability and marginal adaptation of experimental silicate cement (CS) and compare it with (MTA and CVI). A mineral cement silicate-based was modified by addition of components to expansion control, to setting time increase and to improve the radiopacity. The sealing ability and the adhesion to the root canal were also checked by SEM. Results showed that the modifications on basic material (Ca and Al silicate) caused variations on pH (during 24 hours), on setting time and on workability. SEM analyses showed a good marginal adaptation for CS and a good sealing ability.