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ORIGINAL ARTICLE

Application of mercury intrusion porosimetry for studying the porosity of mineral trioxide aggregate at two different pH

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Abstract

Objective. To evaluate a novel method of detecting and comparing the porosity of white Mineral Trioxide Aggregate and Portland cement at two different pH. ***Materials and methods.*** Cylindrical specimens ($n = 120$) were prepared from hydrated ordinary white Portland Cement (WPC) ($n = 60$) and white Mineral Trioxide Aggregate (WMTA) ($n = 60$) and exposed to environments with pH of 4.4 ($n = 30$) or 7.4 ($n = 30$). The pore size distribution and total pore volume were detected using Mercury Intrusion Porosimetry. Data were analyzed by analysis of variance and post-hoc Tukey or Tamhane test ($p = 0.05$). ***Results.*** The pore volume of WMTA was significantly lesser than WPC at both pH ($p < 0.05$). The surface tension of mercury was taken as 480 (N/m) and the contact angle 141.3° for both materials. Pores were consistently found in all specimens. Total pore volumes for WPC and WMTA (cubic centimeter/gram) were 0.1954 and 0.1023, respectively, while the diameter of the pores ranged from 50–100 Å and 20–50 Å, respectively. ***Conclusions.*** Mercury Intrusion Porosimetry technique is a promising and reliable technique for assessing the porosity of endodontic materials.

Key Words: *leakage, mineral trioxide aggregate, mercury intrusion porosimetry, porosity*

Introduction

The goal of endodontic treatment is to eliminate oral pathogens from the root canal and periapical tissues and to thereby maintain long-term periapical health. Penetration of microorganisms from the oral cavity into the filled root canal system is termed coronal leakage, while infiltration of the apical segment of the root by molecules like peptides that support microbial metabolism is termed apical leakage. In essence, there are three routes of leakage—material–tooth interface, core material–sealer interface and within the material itself, i.e. porosity. The rate of ingress of a medium into the filling material would be influenced by the distribution of the pores in the material, particularly the size and connectivity. In addition, porosity is directly related to leakage behavior of root filling material [1]. The techniques that have been used in the past to check the permeability of root canal filling material [2] are complex and not reproducible [3].

The term porosimetry includes the measurements of pore size, volume, distribution, density and other porosity-related characteristics of a material. The porosity of a material affects its physical properties and, subsequently, its behavior in its surrounding environment, and thereby helps in understanding the formation, structure, and potential use of many substances. Although porosity of a material may not have a direct influence on its leakage characteristics, it may have an impact upon numerous other factors including adsorption, permeability, strength and density [4–8].

Mercury intrusion porosimetry (MIP) has been used for the past several years to study the pore structure of Portland cement [9–11]. Mercury behaves as a

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non-wetting liquid towards most substances and does not penetrate into the openings and cracks of these substances and one must apply pressure to make it to do so. If a sample of a porous solid is sealed into a vessel, tapered into a capillary tube, evacuated, filled with mercury and then placed under increasing pressure, the mercury penetrates into the pores and its level in the capillary decreases. If the decrease of the level is registered in dependence on the pressure, a porosimetric curve is obtained, indicating how large a volume penetrated into the pores of the sample at a given pressure.

Mineral trioxide aggregate (MTA) is a commonly used material in endodontics. This material serves to seal the communicating pathways between the root canal system and the external surface of the tooth [12]. This study was to evaluate the pore size distribution of white Mineral Trioxide Aggregate (WMTA) and white Portland cement (WPC), at two different pH (7.4 and 4.4) using MIP. The null hypotheses were: (a) there is no difference in pore size and distribution between WMTA and WPC and (b) pH has no effect on the leakage of WMTA and WPC.

Materials and methods

Specimen preparation

Tooth-colored ProRoot MTA powder (Dentsply Tulsa Dental, Tulsa, OK; batch 083006) and ordinary WPC (Saveh white cement, Saveh, Iran) were used in this study. Each cement powder was mixed with appropriate liquid according to the manufacturer's instruction and packed into a cylindrical glass tube with an internal diameter of 4 mm and a height of 6 mm using a non-surgical manual MTA carrier (Dentsply, TulsaDental , US). A hand condenser (Hu-Friedy, Chicago, IL) was checked to make sure the tip would fit the length. One operator condensed WMTA using hand pressure according to previous studies [4,13]. The filled cylindrical glass tubes were stored at 37°C and 100% relative humidity for 72 h to ensure that cement hydrates completely. All specimens were weighed on a precision scale (accuracy: 0.001 g).

Two pieces of gauze soaked in butyric acid buffered at pH values of 4.4 or synthetic tissue fluid (1.7 g of KH_2PO_4, 11.8 g of Na_2HPO_4, 80.0 g of NaCl and 2.0 g of KCl in 10 L of H_2O (pH = 7.4) were placed on two separate vials. Each experimental group was placed in one vial for 3 days and the acid soaked pieces of gauze were replaced every day with fresh ones to ensure a sufficient acidic environment within the vials.

Mercury intrusion porosimetry

The pore size distribution of the specimens was measured with Mercury Intrusion Porosimetry (MIP) in high pressure mode (Porosimeter 2000, Carlo Erba Instruments, Italy). Mercury intrusion porosimetry is based on the premise that a non-wetting liquid (one having a contact angle greater than 90°) will only intrude capillaries under pressure. The relationship between the pressure and capillary diameter was calculated using the formula [14,15]: $P = -4\gamma \cos\theta/d$, where P = pressure, γ = surface tension of the liquid, θ = contact angle of the liquid and d = diameter of the capillary. The pore size distribution was determined from the volume intruded at each pressure increment and total porosity was determined from the total volume intruded.

Data presentation and analysis

The variable assessed in this study was pore volume (in cm^3/g). Statistical analyses of the data were done using ANOVA. Equality of variances was assessed using Leven statistics. If an equality of variance existed, post-hoc Tukey test was employed to identify significant difference between groups. If variances did not exhibit equality, a post-hoc Tamhane test was employed. The alpha-type error was set at 0.05 for all statistical analyses.

Results

The MIP curves showing the volume of mercury intruded to the sample vs pore-size distribution were registered. Surface tension for mercury was 480 (N/m) and contact angle between material and mercury was about 141.3°. One major peak could be observed in the pore size distribution curves for both and results indicated that total pore volume (cm^3/g) is 0.1954 for WPC and 0.1023 for WMTA.

The maximum total pore volume was observed in WPC at pH of 4.4 (0.2005 ± 0.0006 cm^3/g), while the least pore volume was seen in WMTA at a pH of 7.4 (0.1025 ± 0.0004 cm^3/g). There was significant difference in the pore volume of all the groups (ANOVA, post-hoc Tamhane test, $p < 0.05$, Figure 1).

Discussion

The present study assessed the suitability of mercury intrusion porosimetry in studying porosity of MTA at two different pH. Namazikhah et al. [5] were the first to conclusively establish that the surface microhardness of MTA decreased at acidic pH. They suggested that this was due to the porous microstructure of the cement. Nevertheless, the authors stated that, with the technique employed (SEM), it was not possible to objectively assess or grade the degree of porosity of the material. Having knowledge of the porosity of root filling materials can help in drawing firm deductions as to which filling material would perform better in the clinical scenario. It has been suggested that the greater the porosity of the cements, the lower is their sealing ability [5,6].

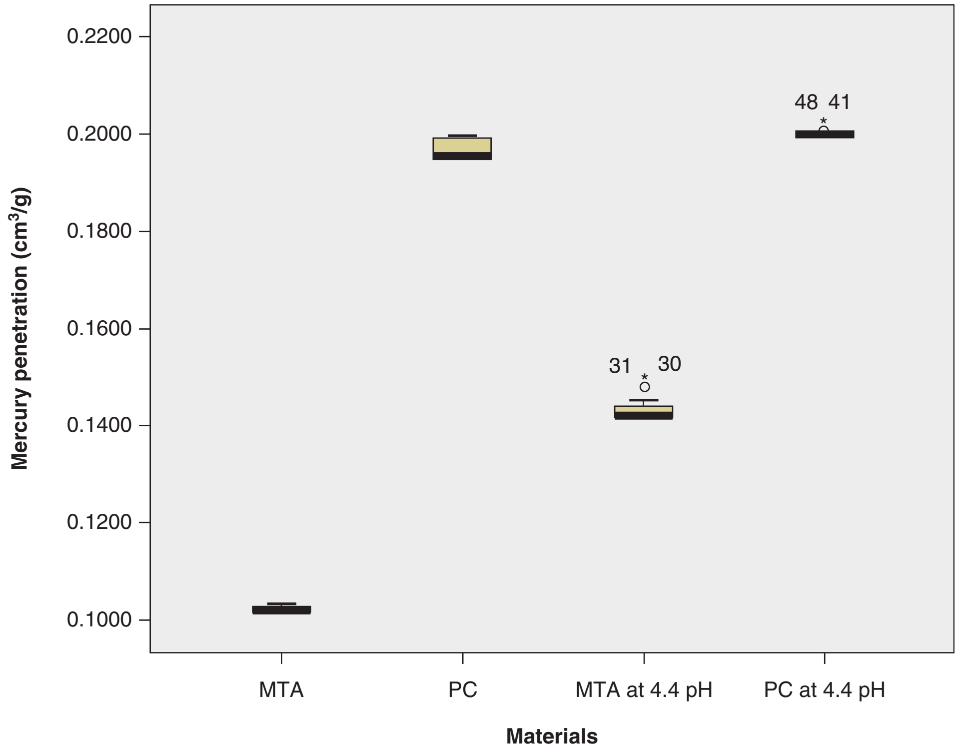

Figure 1. Box plots of the mean ± SD, minimum and maximum amounts of porosity of the specimens, as well as the variance in each experimental group.

Previous methods like dye leakage [16], protein leakage [1] and bacterial leakage [17] tests had been developed to evaluate the permeability of endodontic materials, but all of them evaluate microleakage across the system including dentin, dentin/filling interface and filling material. Unfortunately, they did not provide reliable and reproducible information about leakage across the endodontic material [7].

Surface porosity of mineral trioxide aggregate has been evaluated by scanning electron microscopy [4,8]. This method, although reliable for evaluating surface porosity, cannot relate to the bulk of these materials. Previous studies have shown close dependency between surface porosity and microleakage. Bulk porosity shows a high correlation to leakage and permeability of these materials and hence may be a main factor in leakage assessments [18].

Mercury intrusion porosimetry has been used in a recent study for evaluating the pore size distribution of MTA and calcium aluminate [19]. To the knowledge of the authors, this study is the second one applying the MIP for evaluating the biomaterials. This technique is based on the capillary law for liquid penetration into small spaces. As the applied pressure increases, pore size is calculated and the corresponding volume of mercury required to fill these pores is measured. These measurements, taken over a range of pressures, give the pore volume vs pore size distribution for the sample [20].

Mercury porosimetry provides a characteristic of the pore space geometry based on the curvature of a meniscus in the pore space. Other techniques that use the presence of a meniscus to characterize porous media are suction (drainage and re-imbibition of a wetting liquid) and capillary condensation or evaporation in sorption experiments. Furthermore, all transport phenomena in porous media characterize the pore space in some way; molecular diffusion, viscous flow, heat conductivity and others [21].

Previous studies have declared that MTA has higher than or at least equal leakage behavior to PC [2,22]. Therefore in this study the total pore volume of WPC and WMTA was measured. Despite the lack of significant differences in chemical compositions of WMTA and WPC, the comparison of numerical data showed that the total pore volume and its dimensions were greater in WPC than in WMTA specimens. Consequently, the first null hypothesis needs to be rejected. These findings may be attributed to the filler effect of bismuth oxide, which is insoluble in water, but reacts in alkaline media [23] and may influence the pore-size and distribution of WMTA to some extent. This bismuth oxide may accommodate in the pore space, produce a uniform mass against the mercury penetration and therefore decreases pore volume in total mass.

In this study, MTA was exposed to acid-soaked pieces of gauze to simulate the clinical scenario of inflammation. The samples were exposed for no longer than 3 days to the acidic solution to simulate the situation in which the initiating and perpetuating factors of inflammatory process are removed by appropriate treatment. Butyric acid was used in the present study to simulate the effect of by-products of anaerobic bacterial metabolism [1,24]. The results of the present investigation showed that WMTA showed more leakage and pore volume at a pH of 4.4 than at 7.4, which is in agreement with previous reports [5,6]. The second null hypothesis was rejected based on this finding. The acidic environment alters the hydration reaction and brings about considerable changes in the microstructure of the hydrated cements. Furthermore, MTA releases soluble fractions in both short- and long-term to maintain the pH of the surrounding environment at a high level [5,25]. These factors could be implicated in the increased porosity at acidic pH.

The MIP technique does have some disadvantages. The specimens should have adequate mechanical properties so that the sample is not mechanically destroyed by the pressure of the mercury. On the basis of the data available, it may be speculated that samples will be damaged only if the porosity is very high or have significant numbers of closed pores [26]. Meanwhile, in the current research none of the specimens deformed due to high pressure. WMTA was selected in the present study due to the fact that it possesses adequate mechanical properties that are comparable with PC after setting [27].

Collectively, it can be assumed that geometry of the pore structure may be approximated by a three-dimensional network and hence it is necessary that the pores be interconnected in order to allow the flow of fluids through the pores in root filling materials. Although the geometry of the pore space can be observed directly by scanning electron microscopy (in two dimensions) [28] and in a limited pore size range by the scatter scattering of X-rays [29], these measurement techniques give fundamentally different kinds of information about the pore space and in most cases are not comparable with each other.

Also, it seems that mercury intrusion porosimetry is a feasible and suitable method for determining the porosity of MTA. Further research is warranted on the application of this technique on other endodontic materials.

Declaration of interest: The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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