EDAX and FTIR Characterization and Setting Time of an Experimental Nanoparticle Incorporated Root-end Filling Material

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The evolution of calcium silicate based cements in the field of dentistry has been rewarding. It offers a plethora of advantages with respect to physicochemical and biological properties. However, the extended setting time and limited antibacterial activity in these cements is quite a concern. This study aimed to develop a fast-setting nanoparticle incorporated root-end filling material for use after periapical surgeries. With the incorporation of the silver nanoparticles, and using calcium chloride as the liquid component, the desirable study outcome was achieved. The setting time was significantly reduced when compared to the commercially available root-end filling material.

Keywords Calcium silicate; Setting time; Scanning electron microscope; Fourier transform infrared spectroscopy; Calcium chloride

I. INTRODUCTION

Over the years, a continuous quest has been going on in search of an ideal filling material with an exemplary combination of physicochemical and biological properties along with the cost effectiveness of the material [1]. With regard to the root end filling material following periapical surgery, this search has been unending [2].

With the advent of calcium-silicate based mineral trioxide aggregate (MTA), most of the ideal properties of a root end filling material have almost been satisfied. However, drawbacks such as a long setting time and limited antibacterial activity coupled with the extremely high cost, have compelled the researchers to develop newer materials with ideal properties [3, 4].

Calcium-silicate cements and other Portland-based cements (PC) are mainly composed of hydrophilic particles of dicalcium silicate and tricalcium silicate. They are hydraulic cements able to set in presence of blood or other fluids [5]. Numerous efforts have been made to modify these calcium silicate cements with the addition of various additives. The addition of 10% calcium chloride to MTA and PC has been reported to reduce the setting time and increase compressive strength [3, 6]. The addition of silver nanoparticles to MTA has been shown to improve its antimicrobial efficacy [7, 8].

The aim of this study was to develop a novel fast-setting nano root-end filling material based on calcium silicate with the addition of silver nanoparticles and calcium chloride. The objective was to determine the constituent elements in the novel cement and determine its setting time.
II. MATERIALS AND METHOD

Solid state reaction technique was used to synthesize the calcium silicate based powder. Preparation of the experimental calcium silicate based powder was done from pure oxides of powders and silver nanoparticles (20 nm) which was weighed on an analytical balance and mixed manually in a porcelain mortar with 98% ethanol for 2 h. Further the experimental powder was subjected to sintering using a hot air oven at 100 °C for 24 h. The final powder was passed through a 250-μm mesh to attain a homogeneous powdered mixture.

A. EDAX SEM and FTIR for chemical constitution determination

Energy dispersive analysis by X-rays (EDAX) in the scanning electron microscope (SEM) (Zeiss Gemini) was carried out to determine the constituent elements of the powder. Fourier transform infrared spectroscopy (FTIR) measurements were recorded with a Brukers Alpha 400 model FTIR spectrometer using the KBr pellets technique. Spectra were obtained in the transmission mode from the pressed KBr discs between 500 and 4000 cm⁻¹ wave-numbers.

B. Preparation of the liquid component

Aqueous solution of 10% calcium chloride was prepared by mixing 10 g of a calcium chloride powder in 100 mL of distilled water using a magnetic stirrer (REMI 2MLH). Calcium chloride was added in distilled water in small increments every 5 min until all the particles were dissolved.

C. Powder–liquid ratio

Mixing 0.2 g of powder with 0.14 mL of liquid, produced a material of desired putty consistency, which was easily workable. A mixing time of 1 min was sufficient to achieve the desired consistency.

D. Determination of setting time

Initial and final setting times of the experimental material were carried out at Department of Dental Materials, Yenepoya (Deemed to be) University, using a Gilmore needle apparatus according to specifications recommended by ISO 9917-1. Freshly mixed cement with the determined powder–liquid concentration was prepared and placed in the specially made molds of 10 mm diameter by 1 mm height. To determine the initial setting, a Gilmore needle with 100 g mass and 2 mm diameter was carefully placed vertically on the surface of the cement one minute after mixing. This process was repeated every 30 s until there was no indentation on the surface of the cement. Final setting time was determined when the Gilmore needle with 400 g mass and 1 mm tip diameter failed to produce an indentation in the cement. The test was repeated 10 times for the experimental material. A similar test was carried out to determine the setting time for commercially available white ProRoot MTA (Tulsa Dental Products, USA). The results were tabulated for statistical analysis and comparison of variables.

III. RESULTS

A. EDAX SEM analysis

EDAX analysis of the experimental material showed the presence of calcium, silica, aluminum, magnesium, bismuth, silver, oxygen, and carbon, as shown in Table 1. The particles were coarse and irregular. By examining the spectra of energy dispersive X-ray spectroscopy (EDS) scans, it is clear that there are pronounced peaks for calcium, silica, and oxygen as shown in Figure 1.

B. FTIR analysis

Major absorption bands that were seen (Figure 2) include a 3442.25-cm⁻¹ band assigned to H−O−H stretching (generally known as a water band), a 1637.25-cm⁻¹ band assigned to a carbonyl band (C=O), and 1442.38 and 708 cm⁻¹ bands attributed to carbonate stretching vibrations.

Table 1: Atomic percentile of the constituent elements in the powder component as observed under EDAX SEM.

| Element   | Weight percentage (atomic %) |
|-----------|------------------------------|
| Calcium   | 12.39                        |
| Silica    | 5.21                         |
| Aluminum  | 0.44                         |
| Magnesium | 0.43                         |
| Bismuth   | 0.12                         |
| Oxygen    | 54.26                        |
| Carbon    | 27.13                        |
| Silver    | 0.03                         |

Figure 1: EDAX spectrum of the powder component showing pronounced peaks for calcium, silicon, and oxygen.
carbonate signal indicates that calcium carbonate is present in the experimental cement. Bands at 1104.14 and 873.40 cm\(^{-1}\) are assigned to Si–O–Si and Si–O–Al bonds, respectively. An unresolved weak band at 500 cm\(^{-1}\) arises from bismuth oxide vibrations. A peak at 2928.39 cm\(^{-1}\) is assigned to C–H stretching vibration.

Asymmetric and symmetric stretching vibrations for respective bands at 1587.29 and 1422.38 cm\(^{-1}\) and C=O stretching at 1637.25 cm\(^{-1}\) attribute to presence of the carbonate ions in the powder sample. Disappearance of symmetric and asymmetric stretching upon addition of the calcium chloride solution suggests the interaction of the calcium ions with the carbonate that leads to accelerated setting process. Furthermore, disappearance of the 1104.14 and 873.40-cm\(^{-1}\) bands is attributed to the siloxane linkage indicating the formation of the calcium layer on the cement surface (Figure 3).

### C. Setting time

The mean has been estimated and the corresponding confidence intervals are reported for both the groups at the initial and final setting time as shown in Table 2. Since the initial setting time and the final setting time of the groups are non-overlapping, there is statistically significant difference between the groups.

| Variables       | n  | Mean (min) | SD    | Min. | Max. | 95% CI     |
|-----------------|----|------------|-------|------|------|------------|
| Initial setting time |    |            |       |      |      |            |
| Experimental cement | 10 | 6.50       | 0.6667| 5.5  | 7.5  | (6.023, 6.977) |
| MTA             | 10 | 25.10      | 0.9661| 23.5 | 26.5 | (24.409, 25.791) |
| Final setting time  |    |            |       |      |      |            |
| Experimental cement | 10 | 32.25      | 1.7834| 28.5 | 35.0 | (30.974, 33.526) |
| MTA             | 10 | 171.00     | 1.4720| 168.0| 172.5| (169.947, 172.053) |

### IV. DISCUSSION

This study was conducted to characterize and evaluate the initial and final setting time of a laboratory manufactured nano root-end experimental cement. The ultimate goal of incorporating silver nanoparticles and calcium chloride to calcium silicate based cement was to enhance its biological and physicochemical properties [3]. Addition of silver nanoparticles to MTA and Portland cement have yielded favourable results in terms of antibacterial activity against E. faecalis biofilm [4]. Studies have also shown an accelerated setting time and improved sealing ability with calcium chloride as an additive in MTA and Portland cement [2, 3, 9].

Several studies have been conducted to examine the similarities in the chemical constitution with the routinely studied root end filling materials, MTA and Portland cement. MTA and Portland cement is mainly composed of calcium, silica, magnesium, aluminum, and oxygen, with the exception of Portland cement lacking bismuth oxide [10]. The chemical composition of the experimental cement powder, also showed a similar composition to MTA, with the addition of silver and carbon. Also, scanning electron microscopy revealed that the experimental cement consisted of irregular coarse particles in a wide variety of sizes. On the contrary, previous studies of MTA have shown a homogenous particle size [10, 11]. The FTIR spectrum of the experimental powder obtained in this study showed...
different stretches of bands at different peaks. The water band (H−O−H) was seen at 3442.25 cm\(^{-1}\). The 1637.25-cm\(^{-1}\) band showed the presence of carbonyl bond. The carbonate stretching vibrations at 1442.38 and 708 cm\(^{-1}\) indicated that calcium carbonate was present in the experimental powder. Minor amounts of calcium carbonate phases usually occur in calcium silicate based cements and are found to occur due to the atmospheric hydration and carbonation of calcium oxide in the mixture [12]. Upon the addition of calcium chloride to the powder component, the stretching vibrations seemed to have disappeared suggesting the interaction of calcium ions with the carbonate that leads to accelerated setting process. Further, siloxane linkage indicating the formation of calcium layer on the cement surface could be attributed to the disappearance of the bands at 1104.14 and 873.40 cm\(^{-1}\) [13].

Regarding the set time, the results showed that the experimental nano cement had a shorter setting time (initial and final) in comparison with the commercially available MTA. The drastic difference in the setting time is due to the presence of calcium chloride and silver nanoparticles in the novel cement. One possible explanation for the accelerated setting was calcium chloride and its capacity to form aggregated lumps of hydrophobic colloids, thus easing the diffusion of ions and water through the initial calcium silicate hydrate layer due to an increased pore diameter, thus increasing hydration rate and hastening the final set [6]. Another reason could be the ability of silver nanoparticles to penetrate the cement porosities, thus speeding up the silicate hydration and thereby decreasing the set time. Our results were consistent with previous findings of studies which used calcium chloride as a substitute for distilled water to reduce the setting time [7].

V. CONCLUSION

Experimental nanosilver incorporated calcium silicate cement with calcium chloride as the liquid component is a suitable substitute for MTA and a potential root-end filling material with regard to the setting time. Further research is being carried out to evaluate the cytotoxicity and antibacterial activity of this material.

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