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ORIGINAL ARTICLE

The Effect of a Setting Accelerator on the Physical and Mechanical Properties of a Fast-set White Portland Cement Mixed with Nano-zirconium Oxide

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ABSTRACT

Objective: This study compared the effects of calcium chloride dihydrate ($CaCl_2.2H_2O$) on the physical properties and push-out bond strength of white Mineral Trioxide Aggregate (WMTA) and an experimental Malaysian Portland cement mixed with nano-zirconium oxide (nano-ZrO) [(radiopaque Malaysian Portland cement (RMPC). Mineral Trioxide Aggregate (MTA) was the first calcium silicate cement (CSC) introduced in dentistry, but up to date, it is an expensive cement with long setting time and causes tooth discolouration. Although Portland cement has been introduced as a potential substitute to MTA, it still faces some challenges such as long setting time and lack of sufficient radiopacity.

Methods: Four groups [WMTA, RMPC, fast-set WMTA (FS-WMTA) and fast-set RMPC (FS-RMPC)] were prepared. Initial setting time was evaluated using Vicat apparatus. The pH was measured at seven-day intervals. For discolouration potential, cements were packed in the pulp chamber of 46 extracted maxillary incisors. Spectrophotometric readings were obtained at seven-day intervals, and the rate of colour change (ΔE) was recorded. For the push-out bond strength testing, cements were applied in 48 sectioned root samples, and the test was performed using universal testing machine at crosshead speed of 0.5 mm/min until bond failure. Statistical analysis was done according to the nature of each group of data using SPSS 26.

Results: Addition of $CaCl_2.2H_2O$ decreased the initial setting times of both RMPC and WMTA significantly ($p<0.05$). The pH values of FS-WMTA and FS-RMPC were comparable to their non-accelerated counterparts ranging from 10 to 12. Discolouration effect was more obviously observed with WMTA and FS-WMTA with time compared to RMPC formulations. Push-out bond strength of the two materials also showed an increase with the addition of the accelerator, however, only FS-WMTA showed statistically significant difference compared to WMTA ($p<0.05$).

Conclusion: The addition of $CaCl_2.2H_2O$ improves the physical and mechanical properties of the newly formulated RMPC and WMTA. The RMPC formulation overcomes the discolouration potential of WMTA.

Keywords: Calcium chloride, discolouration, mineral trioxide aggregate, portland cement, pH, push-out bond strength, setting time

HIGHLIGHTS

- Calcium chloride decreases setting time and increases push-out bond strength of both radiopaque Malaysian white Portland cement and WMTA.
- WMTA causes more tooth discolouration compared to both accelerated and non- accelerated radiopaque Malaysian white Portland cement.
- Radiopaque Malaysian white Portland cement could be a cheaper potential substitute for WMTA which can solve the discolouration problem reported with WMTA in an accelerated or non-accelerated form.

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INTRODUCTION

Calcium silicate-based cements (CSCs) have long been identified as one of the most favourable materials for use in dentistry (1). Mineral trioxide aggregate (MTA) was the first CSC introduced in dentistry in 1993 (2, 3). It has a wide range of clinical applications such as vital pulp therapy, repair of perforation defects, root-end filling material and regenerative endodontic procedures (4, 5).

MTA was initially introduced as a grey-coloured cement (GMTA), but because of the potential for discolouration, tooth-coloured white MTA (WMTA) was introduced later for applications in areas with aesthetic concerns (6). WMTA has been considered the material of choice in several endodontic procedures due to its favourable biological properties (7, 8), with high rates of clinical success (9, 10). Despite being a clinically successful material, WMTA has drawbacks such as long setting time, discolouration potential, poor handling properties and being an expensive material (9, 11).

Due to the long setting time of MTA, several setting accelerators (such as calcium chloride dihydrate ($CaCl_2.2H_2O$), calcium nitrite/nitrate and calcium formate) have been suggested as potential additives (12–15). However, such additives can change the physical and biological properties of the material (13, 15, 16).

WMTA is composed of 80% refined Portland cement (PC) and 20% bismuth oxide (BO), where BO was added as a radiopacifier (17). WMTA has smaller particle size compared to Portland cement and both were proven to have acceptable biological properties (15,18). However, PC lacks radiopacity due to the absence of BO, which makes it difficult to differentiate it from the tooth structure (19). Because of the discolouration potential of WMTA and other bismuth-containing materials (20), several radiopacifying agents such as zinc oxide, barium sulfate, niobium oxide, calcium tungstate, strontium fluoride and zirconium oxide (ZrO) have been added to PC and examined as potential substitutes for WMTA (19, 21, 22).

A new formula of a Malaysian Portland cement (MPC) is being developed and tested, this formula has nano-ZrO as a radiopacifier, which is also expected to affect the physical and mechanical properties of the cement. This study aimed to compare the physical, mechanical and aesthetic properties of a fast-set and normal-set new Portland cement formulation (mixed with nano-ZrO), WMTA and fast-set WMTA. The null hypothesis was that the addition of $CaCl_2.2H_2O$ as a setting accelerator does not affect the physical, mechanical, and aesthetic properties of WMTA and the newly formulated radiopaque Malaysian white Portland cement.

MATERIALS AND METHODS

An ethical approval [IRB Ref no. DF RD2020/0115/2124(L)] was obtained from Medical Ethics Committee, Faculty of Dentistry, Universiti Malaya for this study.

Sample Size Calculation

Ps Power and sample size calculation software ver. 3.1 was used to calculate the sample size for both discolouration potential and push-out bond strength (23). For discolouration experiment, 10 samples were allocated for each group (five central incisors and five lateral incisors) (as per sample size calculation, mean=2.5, SD=1.4, (24) alpha=0.05, power=0.9 – sample size calculation = 9; 10% was added for sample loss). For push out bond strength, 12 samples were allocated for each group (as per sample size calculation, mean=5.38, SD=3.17, alpha=0.05, power=0.9 – sample size calculation=9; (20% were added for sample loss).

For measuring the setting time and pH value, three specimens were prepared for each material, and for pH measurement, three readings were taken for each sample (12, 14). Preparation of each experimental cement group was done following the proportion as stated in Table 1. Randomised grouping of the study samples was conducted using online Research Randomizer (25).

Preparation of Materials

In this study, powders of White ProRoot MTA (WMTA) (Dentsply Maillefer, Ballaigues, Switzerland) and Malaysian white Portland cement (MWPC) (Aalborg, Ipoh, Malaysia) were used. The MWPC powder was sieved using a 20 µm test sieve (Retsch, Haan, Germany) to obtain a homogenous powder size (15). To generate radiopaque Malaysian white Portland cement (RMPC), nano-zirconium oxide (nano-ZrO) of particle size 20 nm (US Research Nanomaterials, Houston, USA) was added to MWPC powder in a ratio of 20% nano-ZrO: 80% MWPC19. For fast-set groups, calcium chloride dihydrate ($CaCl_2.2H_2O$) was used as a setting accelerator (Sigma Aldrich, Taufkirchen, Germany) (15).

A pilot study was performed to select the optimal weight of the setting accelerator (0.1, 0.15 and 0.2 g $CaCl_2.2H_2O$) that would result in a clinically relevant setting time (less than 25 mins). Results showed that the most suitable setting time could be obtained when 0.15 g $CaCl_2.2H_2O$ is mixed with 1 gm of RMPC resulting in fast-set RMPC (Fs-RMPC). The same ratio

TABLE 1. Preparation of different powder groups

Material	Proportion
RMPC	0.8 g sieved MWPC+0.2 g of 20 nm nano-ZrO+210-µl distilled water
Fast-set RMPC (FS-RMPC)	0.8 g sieved MWPC+0.2 g of 20 nm nano-ZrO+0.15 g of $CaCl_2.2H_2O$+210 µl distilled water
WMTA	1 g ProRoot WMTA+liquid provided by the manufacturer
Fast-set WMTA (FS-WMTA)	1 g WMTA+0.15g of $CaCl_2.2H_2O$+liquid provided by the manufacturer

RMPC: Radiopaque Malaysian white Portland cement, MWPC: Malaysian white Portland cement, nano-ZrO: nano-Zirconium oxide, WMTA: white mineral trioxide aggregate, $CaCl_2.2H_2O$: Calcium chloride dihydrate

was used with WMTA by adding 0.15 g of $CaCl_2.2H_2O$ to 1gm WMTA to obtain fast-set WMTA (FS-WMTA).

All powders were weighed by using an analytical balance (Sartorius, Gottingen, Germany) with sensitivity of 0.001 g – 420 gm. Table 1 shows ratios used to prepare normal-set and fast-set WMTA and RMPC. A pilot study was conducted to obtain a consistency that can be easily manipulated and condensed for MPC and RMPC by mixing different ratios of powder to liquid (distilled water), while for WMTA, manufacturer's instructions were followed. Table 1 summarizes powder composition for each group.

Initial Setting Time Measurement

The four groups of cements were mixed packed into moulds with diameter 15 mm and height 3 mm. Three samples were prepared for each group of cement to obtain an average measurement (12). Vicat Apparatus Model NL 3012 X/ 003 (NL Scientific, Selangor, Malaysia) with a plunger and needle with diameter of 1.12 mm using a 300 g weight was used to test initial setting time of each cement. Samples were tested and time was recorded at an interval of 15 minutes except for FS-WMTA and FS-RMPC which were tested at 2 minutes interval. Samples were wrapped with moist gauze and incubated at 37°C in an incubator (IN 450, Memmert, Germany) in between testing. The time when no indentation can be seen on the surface of the cement was recorded as the initial setting time of the cement.

pH Values Measurement

Powders were mixed as previously mentioned and the paste was condensed in a silicon mould to generate 6 capsules of each material with dimensions of 2 mm height and 5 mm diameter. Capsules were then placed in incubator in 99% humidity for 24 hours. After that, every 2 capsules were transferred in 15 ml centrifuge tube and submerged in filtered water of average pH 6.8. Three tubes were prepared for each material, in addition to one control tube containing only water without capsules. Tubes were stored in incubator at 37°C and pH was tested using pH meter (pH 700, Eutech instruments, Germany) at 0, 1, 7, 14, 28, 60 and 90 day intervals (21). Before measuring, the pH meter electrode was calibrated using standardized solutions of pH 4, 7 and 10. At the time of measuring, the readings were recorded, then the water was changed by fresh one and pH was measured again. In between readings, the electrode was flushed with distilled water and dried to avoid solutions contamination. Tubes were then sealed and returned to the incubator till the next reading day.

Discolouration Potential Examination

Samples collection

Forty extracted permanent single-rooted maxillary central (n=20) and lateral (n=20) incisor teeth with single canals were collected from clinics of faculty of dentistry, Universiti Malaya, Malaysia where teeth were extracted for reasons not related to the study. Inclusion criteria were to include non-carious teeth, teeth without coronal restorations or cracks. Second round of exclusion was done using cone beam computed tomography scans (CBCT) (Kodak 9000 3D, Kodak Carestream Health, Trophy, France, software used is Carestream Health, New York, USA) with exposure of 63 kV, 6.3 mA, 10.8 s, voxel size of 0.076 mm and field of view of 100 mm ×100 mm ×100 mm. Pulp chamber sizes, canal spaces and labial dentine thickness of the collected teeth were examined. Pulp chamber with large pulp stones and narrow canal spaces were excluded. Teeth having dentine thickness with an average of 2.2 mm (±0.2 mm) at the cemento-enamel junction (CEJ) level were included where the mean labial dentine thickness of lateral incisors was 2.07±0.18 mm compared to 2.4±0.24 mm for central incisors. Teeth were disinfected in Chloramine-T solution for 24 hours and then stored into normal saline until testing.

Preparation of samples

Access cavity was done, and the pulp tissues were removed from pulp chamber. Root canals were negotiated using K-file #15. Irrigation of the roots was performed using 3 ml of 2.5% sodium hypochlorite (NaOCl) for 1 min, followed by 3 ml of 17% Ethylenediaminetetraacetic acid (EDTA) (26), and again irrigated with 3 ml of 2.5% NaOCl for 1 min. One ml of saline was used to wash the canal in between each irrigant. No attempt was made to enlarge the canals to preserve the coronal dentine thickness of the teeth as measured in CBCT imaging. The canals and pulp chamber were dried with paper points and cotton pallets. Damp cotton pallet soaked with saline was packed until CEJ level.

Experimental setup for colour assessment

Colour measurements were done using a spectrophotometer (CM5, Konica Minolta, Tokyo, Japan) before the cement placement and repeated three times for each sample. Cements were placed for a thickness of 2 mm and covered with a damp cotton pallet until setting. After one day, 1 mm of glass ionomer cement (Riva Self cure, SDI, Bayswater, Australia) was placed on top of the cement and the cavity was sealed with resin composite (Amelogen Plus, Ultradent, South Jordan, USA). Readings were recorded immediately after cement placement as baseline (T0), then samples were again stored in saline and kept in incubator. Colour change was assessed at different time intervals after 1 day (T1), 1 week (T2), 2 weeks (T3), 4 weeks (T4), 6 weeks (T5),8 weeks (T6) and 17 weeks (T7).

Colour assessment using spectrophotometer

To reproduce tooth positioning while taking readings on a spectrophotometer device, beading wax was used to stick the tooth at a fixed and reproducible position by the same operator. The reading was taken three times and an average was obtained from the three readings. After each analysis, specimens were stored back in saline solution and incubated at 37°C. The colour change was being assessed by CIE L*a*b system. The rate of lightness is indicated by the range of 'L' from 0 (black) to 100 (white) whereas 'a' and 'b' represent colour change in green-red and blue-yellow axes respectively. Lastly, the discolouration rate (ΔE) was calculated us-

ing the following equation: $\Delta E=(\Delta L)^2+(\Delta a)^2+(\Delta b)^2)1/2$ (20). At week 17, the samples were sectioned at longitudinal sections using a high-speed precision sawing machine (Metkon, Turkey) and examined under a stereomicroscope (Olympus corporation, Japan).

Push-out Bond Strength Examination

Samples collection

Forty-four maxillary central and lateral incisors with clinically sound root surfaces were collected and scaled to remove calculus and subsequently soaked in saline.

Preparation of samples

The samples were mounted vertically in a mould with diameter 20 mm using cold-cure epoxy resin (Mirapox A and B; Miracon, Selangor, Malaysia) according to the manufacturer's instructions with a ratio of 100:30 (Part A: Part B). The samples were left to set for 24 hours.

After setting, the mounted roots of the teeth were sectioned transversely to get 1 mm sections of the middle root area (27). A slow speed round bur with diameter 0.9 mm was used to prepare a standardized cavity preparation in the centre of the root samples. The samples were immersed in order in 2.5% NaOCl, 18% EDTA, for 3 minutes in each solution (27), then another rinse of 2.5% NaOCl was done to remove the organic and inorganic components of the smear layer. The samples were rinsed copiously with saline after every immersion.

Cements of the four groups were mixed and packed into the cavity preparations using a plugger. The samples were wrapped with a moist gauze individually, sealed in a plastic container, and incubated in an incubator at 37°C for 24 hours.

Push-out bond strength testing

After 24 hours, the samples underwent push-out test using Universal Testing Machine (Shimadzu, Kyoto, Japan) fixed with a 0.8 mm diameter cylindrical stainless-steel plunger. An increasing compressive load was applied onto the cement at a crosshead speed of 0.5 mm/min until bond failure. The maximum force (N) needed to push-out the cement from the canal was recorded at the point where there is a sharp drop in the stress-strain curve or when there is complete dislodgement of the cement from the cavity.

Push-out bond strengths in MPa of the cements were calculated by dividing the maximum force (N) needed to push the cement out of the samples by the debonded area of the root canal filling (mm^2). The debonded area was calculated using the formula (27):

Debonded area (mm^2) = 2π r*h, where π is a constant=3.14, r is the radius of the cavity and h is the height of the cavity.

Statistical Analysis

Statistical analysis was done using SPSS ver. 26 (SPSS, Chicago, IL, USA). Shapiro-Wilk test was performed, and all the data were found to be normally distributed. Subsequently, data were analysed using One way analysis of variance (ANOVA) test with the level of statistical significance set at 0.05 ($p<0.05$) followed by Tukey post-hoc test. All data were homogenous, except for push out bond strength where data showed non-homogenous presentations, therefore, Kruskal-Wallis test was performed ($p=0.05$), followed by Mann Whitney test ($p=0.008$) and medians+interquartile ranges were used instead of means+standard deviations.

TABLE 2. Comparison between mean initial setting time of the tested cements using Tukey post hoc test, different letters are significantly different ($p<0.05$)

Groups	Mean initial setting time (min)	SD	p
WMTA	123.75[a]	12.44	0.006
RMPC	91.67[b]	2.36	
FS-WMTA	8.50[c]	0.41	
FS-RMPC	24.00[c]	2.45	

SD: Standard deviaton, WMTA: white mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

RESULTS

Setting Time Measurement

As shown in Table 2, the shortest setting time was obtained by FS-WMTA (8.50±0.41 min), followed by FS-RMPC (24.00±2.45 min) with no significant difference. WMTA recorded the longest setting time (123.75±12.44 min) followed by RMPC (91.67±2.36 min). In the presence of $CaCl_2.2H_2O$, the initial setting time of both RMPC and WMTA decreased significantly in which RMPC was found to set faster by 73.82%, while WMTA set faster by 93.13%.

pH Value Measurement

As demonstrated in Tables 3 and 4, the pH values recorded for the four materials were compared at all time intervals and were found to be significantly higher than the control group. On day 0 (immediate submersion of material), the pH values of all materials were significantly different, where the highest result was recorded by FS-RMPC (10.5) while the lowest was recorded by RMPC (9.1).

The pH values were recorded high in all days, starting day 1 till day 90 for all materials. Within the same day intervals, some materials showed statistically significant differences (Tables 3, 4). Similar observations were recorded before and after changing the immersion medium. (Figs. 1, 2).

Discolouration Potential

The means ΔE of all groups are presented in Figure 3. There was no significant difference in the discolouration rate between different materials at each of the time intervals from day 1 till week 8, even though an increase in ΔE was observed over time in all groups ($p<0.05$). An exception was observed at week 17, FS-WMTA showed significantly the highest mean ΔE (15.56) followed by FS-RMPC (14.6); both

TABLE 3. Comparison of mean pH values of each group before changing medium within each day using one way ANOVA followed by Tukey post hoc test, means with different letters within different row are statistically different (p<0.05)

	Control	WMTA	RMPC	FS-WMTA	FS-RMPC	p
Day 0	7.14+0.18^{a}	9.34+0.18^{b}	9.10+0.21^{c}	9.69+0.21^{d}	10.50+0.06^{e}	<0.001
Day 1	7.3+0.1^{a}	11.51+0.15^{b}	11.7+0.23^{b}	11.68+0.33^{b}	11.65+0.18^{b}	<0.001
Day 3	6.82+0.12^{a}	12.12+0.14^{b}	12.24+0.26^{bc}	12.44+0.18^{bc}	12.26+0.74^{c}	<0.001
Day 7	7.23+0.12^{a}	11.69+0.23^{b}	11.49+0.17^{b}	11.96+0.14^{c}	11.92+0.14^{c}	<0.001
Day 14	6.28+0.14^{a}	12.13+0.13^{bf}	11.69+0.18^{c}	12.26+0.09^{df}	11.95+0.10^{e}	<0.001
Day 28	6.7+0.35^{a}	12.21+0.05^{b}	12.16+0.07^{b}	12.31+0.07^{c}	12.38+0.05^{c}	<0.001
Day 60	6.87+0.21^{a}	12.56+0.10^{b}	12.76+0.09^{cd}	12.65+0.12^{bc}	12.79+0.022^{d}	<0.001
Day 90	6.67+0.15^{a}	12.49+0.03^{b}	12.6+0.08^{c}	12.67+0.71^{c}	12.69+0.05^{c}	<0.001

ANOVA: Analysis of variance, WMTA: White mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

TABLE 4. Comparison of mean pH values and standard deviations of each group after changing medium within each day using one way ANOVA followed by Tukey post hoc test, means with same letters within different row are statistically different (p<0.05)

	Control	WMTA	RMPC	FS-WMTA	FS-RMPC	p
Day 0	7.13+0.18^{a}	9.34+0.18b	9.10+0.21^{c}	9.69+0.21^{d}	10.50+0.06^{e}	<0.001
Day 1	7.3+0.1^{a}	10.36+0.12^{b}	10.06+0.16^{cd}	10.14+0.1^{bc}	9.88+0.29^{d}	<0.001
Day 3	6.94+0.06^{a}	9.31+0.28^{b}	10.35+0.28^{c}	10.46+0.37^{c}	9.67+0.54^{b}	<0.001
Day 7	6.75+0.19^{a}	10.19+0.23^{b}	9.91+0.11^{c}	10.45+0.20^{d}	10.13+0.14^{bc}	<0.001
Day 14	6.65+0.04^{a}	10.2+0.16^{b}	10.34+0.18^{b}	10.24+0.13^{b}	10.38+0.08^{b}	<0.001
Day 28	6.82+0.10^{a}	9.65+0.17^{b}	10.05+0.18^{c}	10.09+0.39^{c}	10.01+0.07^{c}	<0.001
Day 60	7.1+0.2^{a}	9.91+0.25^{b}	10.90+0.46^{c}	9.84+0.10^{b}	10.29+0.04^{d}	<0.001
Day 90	6.9+0.15^{a}	10.22+0.20^{b}	10.32+0.44^{b}	10.18+0.29^{b}	10.29+0.27^{b}	<0.001

ANOVA: Analysis of variance, WMTA: White mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

cements were significantly different from RMPC (9.24) and the control group (6.34). It was observed that from 1 week until 17 weeks interval, RMPC consistently showed the least colour change (mean ΔE).

Table 5 shows the mean values and standard deviations for central and lateral incisors separately in all groups. As for the central incisors, no significance difference could be detected at all time intervals between different materials. Only after

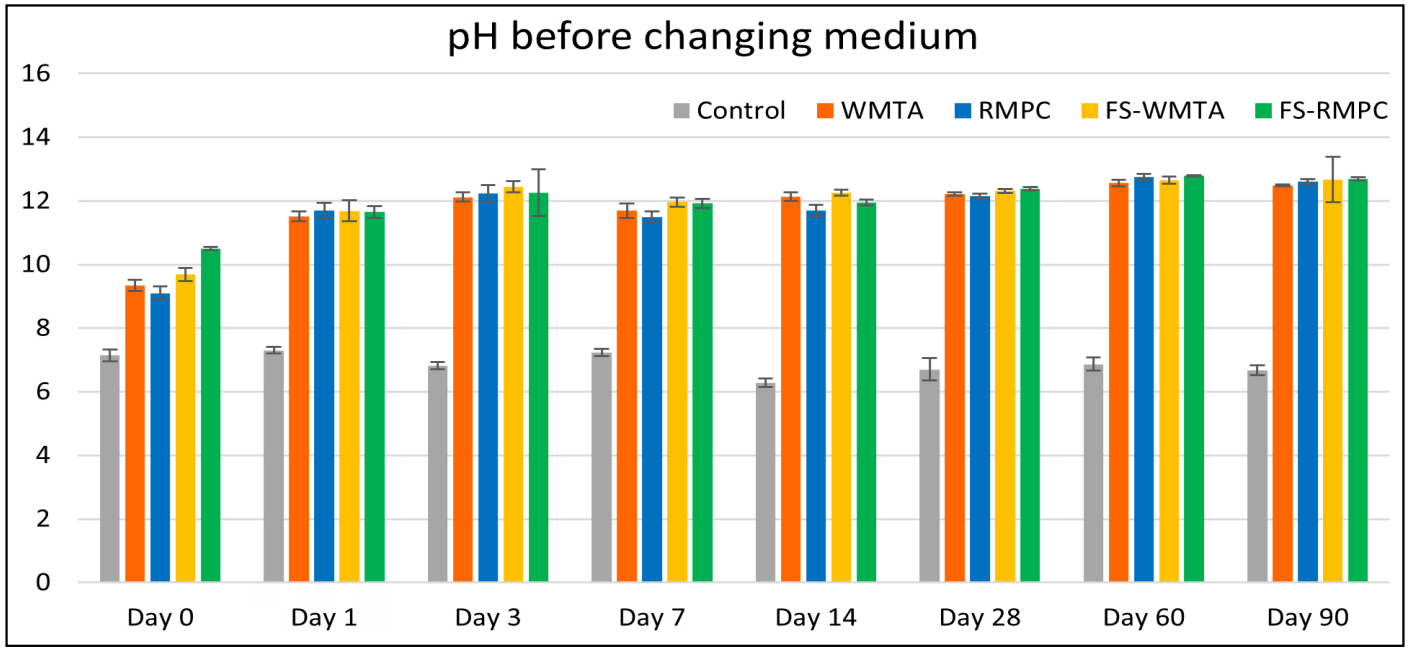

Figure 1. Mean pH values and standard deviations before changing medium (p<0.05)

WMTA: white mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

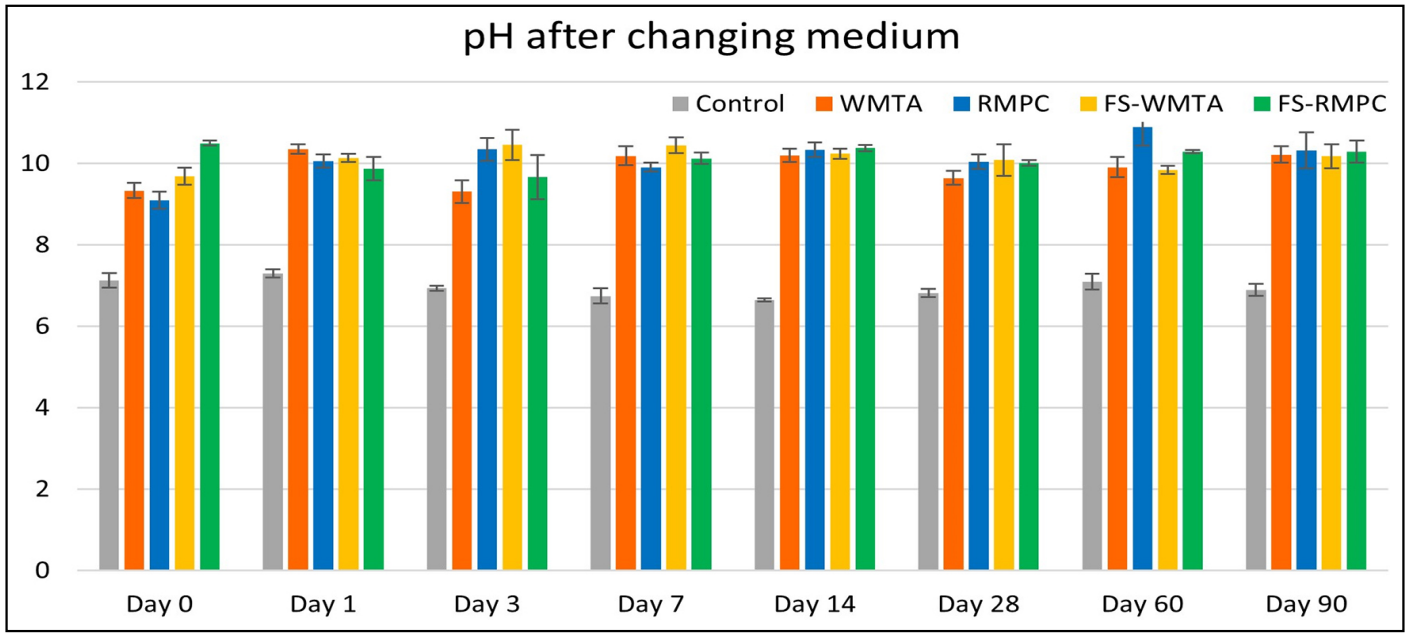

Figure 2. Mean pH values and standard deviations after changing medium ($p<0.05$)

WMTA: white mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

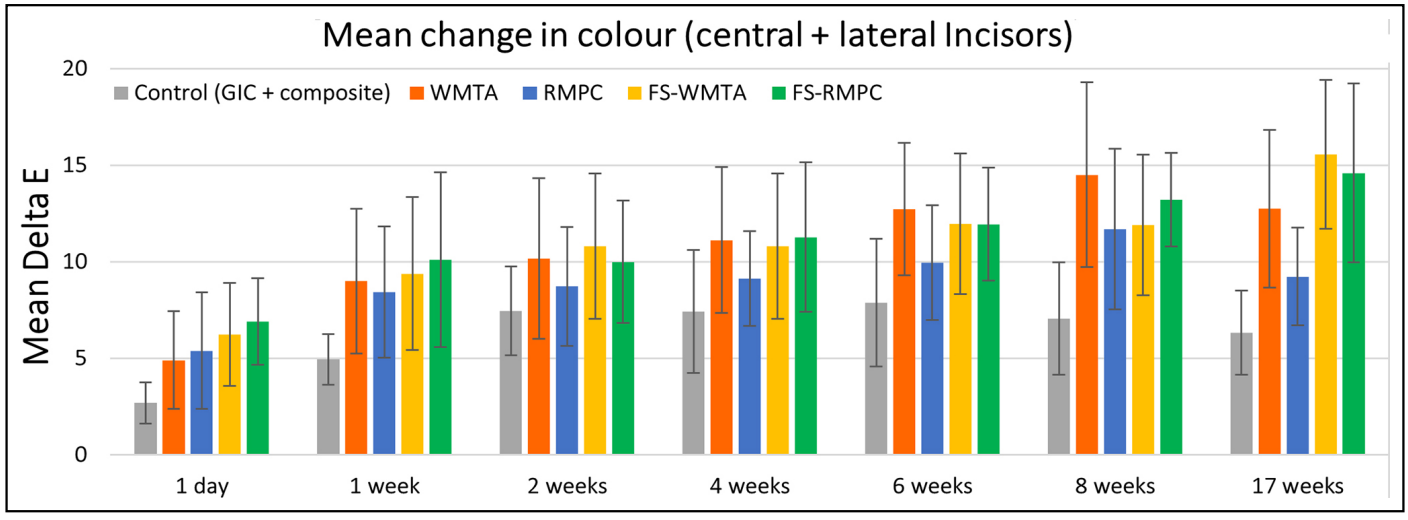

Figure 3. ΔE average in all groups (both central & lateral teeth) at different time intervals

GIC: Glass Ionomer cement, WMTA: white mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

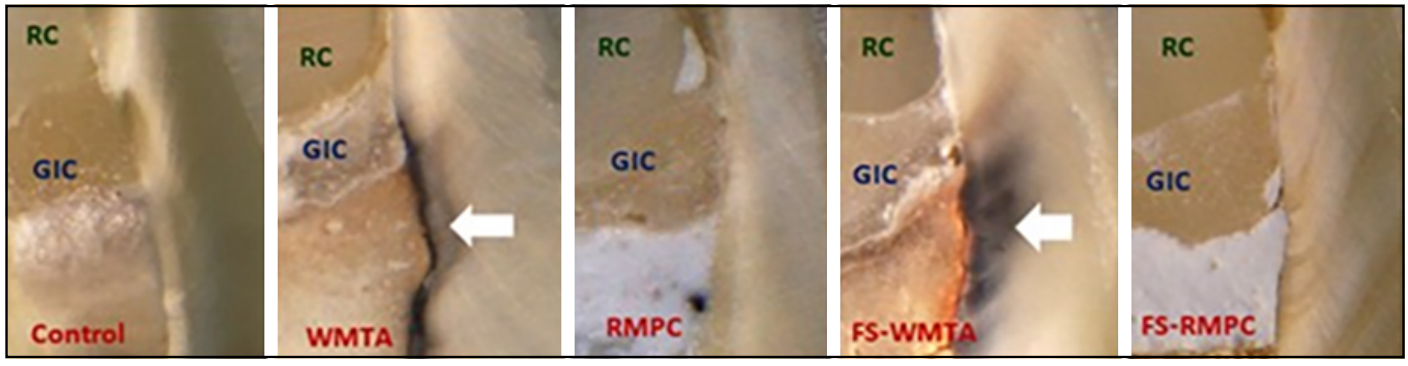

Figure 4. Stereomicroscope capture Comparing the degree of discolouration caused by each material after 17 weeks of storage (RC: Resin composite, GIC: Glass Ionomer cement), white arrows show tooth discolouration caused by the cements applied

WMTA: white mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

TABLE 5. Mean and standard deviation (SD) for the colour change (ΔE) of central and lateral incisors from different tested groups at all time intervals. Comparison done using One way ANOVA followed by Post Hoc Tukey test where (*) indicates a significant difference within the same row for either centrals or laterals at p<0.05

Time	Central incisors					Lateral incisors			
	Control	WMTA	RMPC	FS-WMTA	FS-RMPC	WMTA	RMPC	FS-WMTA	FS-RMPC
1 Day	2.69±1.07	3.65±1.89	3.69±0.85	4.83±3.13	5.5±1.91	6.16±2.64	7.11±3.54	7.66±1.09	8.33*±1.62
1 Week	4.94±1.3	7.07±3.70	5.97±1.31	6.93±3.71	6.89±2.47	10.92±2.90	10.89±3.02	11.83*±2.56	13.33*±3.77
2 Weeks	7.46±2.3	8.01±3.46	6.34±1.13	10.12±5.01	7.88±2.76	12.33±3.93	11.12±2.38	11.49±2.38	12.12±1.91
4 Weeks	7.41±3.18	9.67±3.46	7.21±0.94	10.12±5.01	9.3±2.65	12.59±3.85	11.08±1.81	11.49±2.38	13.25±4.12
6 Weeks	7.89±3.3	11.44±3.31	7.58±1.42	11.58±4.94	11.22±3.21	14.02*±3.37	12.34±1.94	12.36±2.26	12.67±2.75
8 Weeks	7.06±2.9	12.3±2.74	8.22±1.81	11.52±4.92	12.01±2.44	16.73*±5.64	15.19*±2.32	12.31±2.28	14.45*±1.88
17 Weeks	6.34±2.18	11.16±3.02	7.52*±1.83	15.94*±4.90	11.60*±2.23	14.35*±4.71	10.96±1.94	15.17*±3.03	17.61*±4.53

ANOVA: Analysis of variance, WMTA: White mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

17 weeks of storage, FS-WMTA showed significantly higher discolouration compared to both control group and RMPC (p<0.05). For lateral incisors, significant differences were observed at different time intervals compared to the control group while no significant difference was found between different materials at the same time interval (p<0.05). RMPC had the least discolouration values for both central and lateral incisors. It has been observed that the colour change for lateral incisors in WMTA group was more obvious compared to RMPC group (Fig. 4), which corresponds to the higher mean value of ΔE though the difference was not statistically significant (p>0.05).

Push-out Bond Strength

Data showed non-homogenous presentations, therefore, Kruskal-Wallis test was performed (p=0.05), followed by Mann Whitney test (p=0.008). Results are shown in Table 6. FS-RMPC yielded the highest push-out bond strength with a mean strength of (8.29±5.52 MPa) followed by FS-WMTA (6.88±5.86 MPa), RMPC (6.36±4.72 MPa) and WMTA (2.16±1.47 MPa). In general, the addition of $CaCl_2.2H_2O$ increased the push-out bond strength of both WMTA and RMPC. Statistical analysis showed that both FS-RMPC and FS-WMTA had significantly higher push-out bond strength compared to WMTA (p<0.05).

TABLE 6. Mean, standard deviation, median and interquartile ranges of push-out bond strength values of the test groups. Same letters are not significantly different (Median and IQR were used for Kruskal Wallis and Mann-Whitney U tests, p=0.008)

Groups	Mean push-out bond strength (MPa)	SD	Median	IQR	p
WMTA	2.16	1.47	1.96[a]	1.81	0.006
RMPC	6.36	4.72	5.68[ab]	6.32	
FS-WMTA	6.88	5.86	5.79[b]	4.89	
FS-RMPC	8.29	5.52	8.81[b]	7.88	

IQR: Interquartile range, MPa: Mega Pascal, SD: Standard deviation, WMTA: White mineral trioxide aggregate, RMPC: Radiopaque Malaysian white Portland cement, FS-WMTA: Fast set- white mineral trioxide aggregate, FS-RMPC: Fast set- Radiopaque Malaysian white Portland cement

DISCUSSION

WMTA is a material of favourable biocompatibility and sealing ability with desirable clinical outcomes when used for perforation repair, vital pulp therapy, root-end filling and regenerative endodontic procedures (5, 6). However, it has drawbacks such as long setting time, tooth discolouration, high cost and difficult handling characteristics (5, 20, 28).

Research has been ongoing on Portland cement as a potential substitute for WMTA for many years (15, 29–31). Portland cement is cheaper compared to WMTA and it showed favourable cytotoxic activity on both human dental pulp and periodontal ligament cells (15, 18). PC has an almost similar composition to WMTA except for the lack of a radiopacifier, where WMTA is composed of 80% PC and 20% BO (17, 32). Still, Portland cement has problems such as long setting time (145 min on average) (33), and it does not meet the ISO 6876:2001 requirements for radiopacity (29).

It was reported that the addition of ZrO into PC at a ratio of 1 to 4 provides adequate radiopacity recommended by ISO 6876 specifications, besides enhancing the physicochemical and biological profile of PC (33–36). Moreover, the addition of ZrO of small particle size was found to enhance the mechanical properties of the cement; this was attributed to the finer structure of the particle which could fit in and result in superior packing of the nanoparticles in the interstitial spaces between the larger cement grains (37). For these reasons, nano-ZrO was used as the radiopacifying agent in this study.

Studies evaluated the effectiveness of fast-set formulations of both WMTA and PC by adding calcium chloride as a setting accelerator (14, 15, 31, 38). From the previous study by Abdullah, et al. (38), the accelerated formulations of the cements with the addition of 10–15% calcium chloride was proven to be non-toxic and showed good evidence of biocompatibility. Likewise, another study showed evidence of improvement in the physicochemical properties such as reduced setting time and solubility along with maintaining the high pH of the cements (14). Another study reported a favourable response of

fast formulation of RMPC on stem cells from human exfoliated deciduous teeth (SHED) (31). Accordingly, $CaCl_2.2H_2O$ was selected in this study. The addition of $CaCl_2.2H_2O$ to MWPC and WMTA decreased the setting time significantly from 91.67 mins to 24 mins and from 123.75 min to 8.50 min, respectively, thus rejecting the null hypothesis.

The pH profile of WMTA has been widely studied, and it is always alkaline (6, 39), which is consistent with findings of this study. Although some significant differences were detected within some groups at different times, these small differences recorded are not expected to affect the clinical outcome of materials as all were in the alkaline range. This alkalinity is beneficial for material biocompatibility, neutralizing the acidic pH that is usually present in an inflammatory environment and thus, inhibiting the osteoclastic activity and enhancing tissue repair (40). Similarly, MWPC was reported to have a significantly different high (alkaline) pH compared to the control group; this agreed with previous studies that investigated PC (21, 29). On the other hand, the addition of $CaCl_2.2H_2O$ to WMTA and RMPC did not seem to have a significant effect on the alkalinity of both materials. Therefore, for this objective, the null hypothesis was accepted.

One of the aims of this study was to compare the degree of discolouration caused by the studied cements within 17 weeks of storage after application in human teeth. Central and lateral incisors were chosen in this study because they are in the aesthetic zone.

WMTA contains BO as a radiopacifying agent, however, tooth discolouration has been reported (20, 24). This might be attributed to the presence of oxidation products and interaction with collagen in dentinal tubules (41). Destabilization of BO occurs when it comes in contact with a strong oxidizing agent leading to the formation of bismuth carbonate that causes discolouration via the reaction with carbon dioxide in the air. Adding to this point, the oxidation of iron contained in the cement material results in the formation of calcium aluminoferrite in the cement (42). When exposed to light in an oxygen-free environment, which happens when the overlying restoration is placed, BO dissociates into dark-coloured crystals of metallic bismuth and oxygen causing tooth discolouration (43). This discolouration makes WMTA challenging to use in aesthetic areas, accordingly, the experimental cement used in this study (RMPC) contained nano-ZrO instead of BO mainly to avoid discolouration.

The present study revealed that RMPC showed the least colour change amongst the other groups at all time intervals but there was only a statistically significant difference in week 17 ($p<0.05$). Therefore, the null hypothesis was partially rejected. One study showed that nano-ZrO did not show significant tooth discolouration (43), in agreement with the current study in which the FS-WMTA exhibited the highest mean value of ΔE among all experimental groups after 17 weeks of material placement. Superior colour stability was also achieved by RMPC where nano-ZrO was the radiopacifier incorporated into PC; this agreed with one study that found that the incorporation of nano-ZrO did not cause discolouration, either when in contact with dentine or collagen (41). It was noted that discolouration seemed to be more obvious in lateral incisors compared to central incisors, this might be due to thinner labial dentine thickness in the lateral incisors with mean of 2.07 mm compared to 2.4 mm for central incisors.

The of nano-ZrO enhances the compressive and flexural strengths of PC (36). The use of nanomaterials gives a uniform particle distribution, which results in a higher filler load, and lowers viscosity, offering easier handling of the material clinically (44, 45).

In addition to decreasing the initial setting time, $CaCl_2.2H_2O$ also increased the push-out bond strength of both materials, especially with WMTA, which is in agreement with one study (14). Thus, the null hypothesis was rejected. This could be attributed to the filling of $CaCl_2.2H_2O$ into the cement pores, thus accelerating the hydration process resulting in the quicker formation of hydration products and reduction in setting time, thus gaining the initial strength earlier (14).

This study has limitations. The relevance for the ability of a given cement to resist indentation testing does not simulate the clinical situation. Material properties and thickness, preparation of the substrate and dentine surface characteristics play important roles in the accuracy and relevance of the push-out testing (46, 47). Further research is needed to investigate the biological effect of the new formulations on human cell lines.

CONCLUSION

Addition of calcium chloride dihydrate decreases setting time and increases push-out bond strength of both RMPC and WMTA while preserving the alkaline effect of the materials. Discolouration effect was more obvious in specimens restored by WMTA compared to all other groups. Radiopaque Malaysian white Portland cement could be a cheaper potential substitute for WMTA which can solve the discolouration problem reported with WMTA in an accelerated or non-accelerated form.

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