EUROPEAN ENDODONTIC JOURNAL

ORIGINAL ARTICLE

Effect of Polydopamine on Bonding Characteristics of Mineral Trioxide Aggregate to Resin Composite

Arumugam KEERTHIVASAN, Kothandaraman RAJKUMAR, Sampath VIDHYA, Sekar MAHALAXMI

Department of Conservative Dentistry and Endodontics, SRM Institute of Science and Technology, SRM Dental College, Chennai, India

ABSTRACT

Objective: The success of vital pulp therapy is crucial to preserve the integrity of the teeth and to enable an uninterrupted root formation in a young permanent tooth. This warrants placement of an intact permanent seal immediately in contact with the pulp capping material. Mineral trioxide aggregate (MTA) sets by hydration and deters placement of an immediate permanent resin composite restoration over it. The aim of this *in vitro* study is to evaluate the wettability, surface morphology and shear bond strength (SBS) of polydopamine (PDA)-pretreated MTA to resin composite (RC).

Methods: The contact angle (CA) and morphological changes caused by self-etch (SE) adhesive on untreated and PDA-pretreated MTA was analyzed using contact angle meter and scanning electron microscope (SEM) respectively. To evaluate SBS, 144 MTA samples were prepared using a custom-made mold of 5 mm diameter and 3 mm height. The samples were randomly divided into two groups of 72 samples each based on whether their surface was pretreated with PDA or not. Under each group, nano-hybrid RC restoration was done either immediately or after a delay of 3 h, 24 h and 96 h. SBS of the MTA/resin composite assembly was tested in a universal testing machine. CA values were analyzed using One-way analysis of variance and Games-Howell Post Hoc test. Mann-Whitney test and Friedman post-hoc Dunn test were used to analyze SBS values.

Results: SE adhesive made a significantly lesser mean CA with PDA-pretreated MTA (27.20°±2.28) compared to untreated MTA (34.22°±1.45, $p<0.05$). SEM micrographs showed that while etching with SE primer eroded the surface characteristics, PDA coating minimized the erosive effect of the acidic primer and preserved the original crystalline plate-like structure of MTA. At all tested time intervals, PDA pretreatment significantly increased the SBS of MTA to RC, compared to untreated control. Immediate bond strength of PDA pretreated MTA (26.30±7.60 MPa) was equivalent to the SBS value achieved at 96 h with untreated MTA (27.82±2.96 MPa).

Conclusion: Within the limitations of this *in vitro* study, it can be concluded that PDA pretreatment of MTA surface improved its wettability, prevented loss of surface integrity following etching and increased the SBS of RC to MTA.

Keywords: Composite resins, dentine bonding agents, dopamine hydrochloride, mineral trioxide aggregate, shear strength

HIGHLIGHTS

- Performing bonding procedure on freshly mixed MTA compromises its bond strength to resin composite.
- This is the first study to evaluate the effect of wettability, surface morphology and shear bond strength of polydopamine-pretreated MTA to resin composite.
- The wettability of self-etch adhesive was improved following polydopamine pretreatment of MTA surface.
- Polydopamine pretreatment of MTA surface prevented loss of surface integrity following etching and increased its shear bond strength to resin composite.

Please cite this article as:
Keerthivasan A, Rajkumar K, Vidhya S, Mahalaxmi S. Effect of Polydopamine on Bonding Characteristics of Mineral Trioxide Aggregate to Resin Composite. Eur Endod J 2023; 8: 207-14

Address for correspondence:
Sampath Vidhya
Department of Conservative Dentistry and Endodontics, SRM Institute of Science and Technology, SRM Dental College, Chennai, India
E-mail: drvidhyas@yahoo.co.in

Received November 21, 2022,
Revised January 14, 2023,
Accepted March 15, 2023

Published online: April 28, 2023
DOI 10.14744/eej.2023.73745

INTRODUCTION

A tooth requiring vital pulp therapy (VPT) in the form of indirect/direct pulp capping or pulpotomy procedures requires an immediate capping material over the pulp to protect it from further bacterial insults or other noxious stimuli. Placement of a durable pulp capping agent (PCA) at the required site is crucial as the outcome of the procedure not only determines the vitality of the pulp, but also ensures continual root development in young permanent teeth (1, 2). A definitive bonding between the pulp capping material and the overlying restoration is imminent to seal the PCA in place, enabling it to withstand dislodging forces and facilitate better stress distribution at the interface (3). Calcium hydroxide, calcium silicate (CS) cements, calcium-enriched mixture (CEM), triple antibiotic paste (TAP), platelet-rich fibrin (PRF) and recently nano-hydroxyapatite are some of the materials used successfully as PCAs (2–4). CS–based materials are hydraulic cements predominantly composed of dicalcium and tricalcium silicates. They are hydrophilic in nature and self-set forming a sticky calcium-silicate-hydrate gel that hardens over time (5). They are widely used in VPT, regenerative endodontic procedures and perforation repair owing to their biocompatibility, bioactivity and biomineralization potential (5). Among these, CS-based mineral trioxide aggregate (MTA) is widely used as an endodontic repair material and as a PCA (6).

MTA sets by means of hydration (6). In order to allow an uninterrupted setting reaction of MTA, a moist cotton pellet is placed immediately after its placement. The prolonged setting time of MTA requires a temporary restorative material to be placed over the cotton pellet, which might prevent the completion of permanent restorative procedure at the same appointment (7, 8). Literature reveals reports on the time of placement of the final restoration over MTA, which ranges from 24 to 96 hrs (9, 10). The two-visit procedure is a concern as it increases the number of appointments, which could result in distortion or disintegration of the MTA and could make the tooth vulnerable to microleakage through the temporary restorative material (11).

Resin composite (RC) is the ideal material of choice for coronal placement over MTA because of its esthetic, insulating and strength properties (12). RC secures its adhesion to the tooth structure micromechanically through the porosities created by acid etching. One study showed that etching freshly placed MTA with 37% phosphoric acid results in undesirable porosities on its surface (13). This surface disintegration of MTA has been reported to adversely affect its compressive strength (14). In addition, its mechanical properties upon setting are influenced by the pH and humidity of the environment (14, 15). The microhardness values of CS-based materials are known to decrease in acidic conditions, as encountered in total-etch (TE) technique (13). Alternative to 37% phosphoric acid is the use of milder self-etch (SE) adhesives, which do not require an additional rinsing step. However, it was observed that bonding with SE adhesive resulted in the loss of the crystalline structure of MTA (13). Hence, there is a quest for a material, which when applied over the MTA surface would both preserve its surface integrity as well as allow an immediate permanent sealing.

Polydopamine (PDA) is a synthetic analogue of mussel foot proteins, which are secreted by the mussel byssus that enables it to tenaciously adhere to aquatic bodies (16). Its unique adhesive nature could be traced to the presence of catechol and amine functional groups, which makes it bind tenaciously to and functionalize any material surface, including wet and hydrophobic ones (16). PDA can be synthesized from dopamine by three methods namely, enzymatic catalytic oxidation, electrochemical polymerization and oxidative polymerization (16). The well documented, alkaline-potentiated, self-oxidative polymerization is used to prepare PDA, as this is a facile process that can be conveniently conducted at room temperature in basic aqueous solutions (17). Studies have shown that coating implant surface with PDA improves cell adhesion and osseointegration (18). Chen et al. (17) inferred that the glass fibre posts (GFP) functionalized with PDA showed improved adhesion to dentine. Tu et al. (19) observed that coating PDA onto MTA powder did not jeopardize the physicochemical and biological properties of MTA.

A thorough review of literature showed that the bond strength of RC to MTA, after immediate pretreatment of the MTA surface with PDA, has not yet been evaluated. Hence the aim of this *in vitro* study was to pretreat white MTA surface with PDA and to evaluate the wettability, surface morphology and SBS of PDA-pretreated MTA to RC. The null hypothesis was that PDA pretreatment of MTA surface will not have any influence on the tested parameters.

MATERIALS AND METHODS

The study protocol was submitted to the Institutional Review Board and its approval was obtained (SRMDC/IRB/2018/MDS/NO.302). The study was conducted in conformation with the principles of Declaration of Helsinki. The materials used in the study, their composition and instructions of use are given in Table 1.

Preparation of Polydopamine (PDA)

20 mg of dopamine hydrochloride (Sigma Aldrich, St. Louis, Missouri, USA) and 12.11 mg of Tris buffer powder (Loba Chemie Pvt. Ltd., Mumbai, India) were weighed using an electronic weighing balance (BSA224S-CW, Sartorius AG, Goettingen, Germany). The powders were dispensed into a beaker containing 10 mL of distilled water and the solution was stirred mechanically using a magnetic stirrer for 1 minute to obtain a homogenous mixture. Then the solution was kept open for oxidative polymerization of dopamine hydrochloride.

Contact Angle Measurement

White MTA powder (MTA Angelus, Londrina, PR, Brazil) was mixed with distilled water according to manufacturer's instructions using a glass slab and cement spatula. 1 mm thick layer of MTA was coated on a glass microscope slide to obtain a flat surface. The coated slides were stored for 96 h in 100% relative humidity at 37°C. The wettability of a drop each of distilled water (group 1), SE adhesive (group 2, AdheSE One, Ivoclar Vivadent, Schaan, Liechtenstein) and PDA (group 3) on untreated MTA surface and SE adhesive on PDA-pretreated MTA surface (group 4) was analyzed. A drop of the respective

TABLE 1. Materials used in the study, their composition and instructions of use

Materials	Composition	Instructions of use
Mineral trioxide aggregate (MTA Angelus, Londrina, PR, Brazil)	Tricalcium silicate, dicalcium silicate, tricalcium aluminate, calcium oxide, bismuth oxide	The contents of one sachet is mixed with one drop of distilled water for 30 seconds to a homogeneous wet sand consistency
Dopamine hydrochloride (Sigma Aldrich, St. Louis, Missouri, USA)	Dopamine hydrochloride (≤100%)	Used as polydopamine (PDA) solution. 0.10 µml of PDA was dispensed over MTA surface using a micropipette, brushed with a micro applicator tip for 15 sec and left in place for 1 min
AdheSE One, One-step self-etch (Ivoclar Vivadent, Schaan, Liechtenstein)	Derivatives of bis-acrylamide, water, bis-methacrylamide dihydrogen phosphate, amino acid acrylamide, hydroxy alkyl methacrylamide, silicon dioxide	Apply a single layer, brush for 30 sec, dry with a strong stream of air and light cure for 10 sec
AdheSE, Two-step self-etch (Ivoclar Vivadent, Schaan, Liechtenstein)	Primer: Acrylic ether phosphonic acid, bisacrylamide, water, camphoroquinone, stabilizers. Bond: bisphenol A-glycidyl methacrylate, glycerol dimethacrylate, hydroxyethyl methacrylate, fumed silica, camphoroquinone, tertiary amine, stabilizers	Apply primer, brush for 15 sec and dry with mild air. Apply bond, dry with mild air and light cure for 10 sec
Tetric N-Ceram (Ivoclar Vivadent, Schaan, Liechtenstein) Lot No. X29208	Dimethacrylates, barium glass, ytterbium trifluoride, mixed oxide and copolymers, additives, initiators, stabilizers and pigments	Apply in layers of not more than 2mm thickness, contour and light cure for 15 sec

liquid was dispensed on the MTA surface and the advancing contact angle (CA) was measured via standard sessile drop technique with a measurement range of 0–180° in a contact angle meter (HO-IAD-CAM-01, Holmarc's Opto-Mechatronics Pvt. Ltd., Kochi, India). The angle formed was analyzed by automatic curve fit analysis using drop snake method. The experiment was repeated thrice and the mean CA value obtained was used for statistical analysis.

Scanning Electron Microscopic Analysis

A total of 12 acrylic molds were prepared with an inner diameter of 5 mm and height of 3 mm. MTA was mixed, placed into the mold and packed tightly using a condenser. A moist cotton pellet was placed over it and MTA was allowed to set for 96 h by storing the samples in 100% relative humidity at 37°C. They were randomly divided into four groups of three samples each based on the surface treatment done. Samples in group 1 did not receive any further treatment, while those in group 2 were etched with SE primer (SEP, AdheSE, Ivoclar Vivadent, Schaan, Liechtenstein) for 15 seconds and the excess primer was blot dried with tissue paper. Samples in group 3 received a coating of 0.10 mL of PDA over the MTA surface, whereas samples in group 4, were etched with self-etch primer following PDA coating of the MTA surface. The samples were mounted on aluminium stubs, vacuum dried and sputter coated with gold following which the microstructure of the MTA surface was observed under SEM (Phenom Pro X, Thermo Fischer Scientific, USA) with secondary electron mode of 10kV using 1000x and 2500x magnification.

Shear Bond Strength Evaluation

Preparation and grouping of MTA samples

A total of 144 acrylic molds were prepared and filled with MTA as mentioned above. The samples were divided into two groups of 72 each, based on the surface pretreatment of MTA with PDA. Samples in group 1 (PDA pretreatment), were coated with a layer of PDA prior to bonding with RC. 0.10 mL of PDA was dispensed on the surface of MTA using a micropipette and brushed with a micro applicator tip for 15 seconds and left in place for 1 minute. In the remaining half of the samples, RC was directly bonded to the MTA surface without an intermediate layer of PDA (group 2). Each group was further divided into 4 subgroups of 18 samples each, based on the time the final restoration with RC was done, either immediately (A) or after a delay of 3 h (B), 24 h (C) and 96 h (D). In subgroups B, C and D, the MTA samples were stored in 100% relative humidity at 37°C until the time of permanent restoration.

Bonding and resin composite build up

All the MTA samples were bonded using a one-step self-etch (SE) adhesive system (AdheSE One, Ivoclar Vivadent, Schaan, Liechtenstein). The adhesive was applied over the MTA surface using an applicator tip. A cylindrical plastic matrix with an inner diameter of 3 mm and height of 2 mm was secured in place, prior to curing the adhesive with a light emitting diode (LED) light curing unit (Bluephase N, Ivoclar Vivadent, Schaan, Liechtenstein) having an intensity of 1,200 mW/cm^2 and the adhesive was cured for 10 sec. Nano-hybrid RC (Tetric N Ceram, Ivoclar Vivadent, Schaan, Liechtenstein) was then placed over the MTA surface in two increments of 1 mm each, with each increment being light cured for 15 seconds. The bonded samples were stored in 100% relative humidity at 37°C for 24 h.

Shear bond strength testing

The SBS test was performed in a universal testing machine (TECSOL INDIA, Chennai, India) using a 50 kN load cell. A knife edge blade set at a crosshead speed of 0.5 mm/min was directed at the MTA-composite interface. SBS was calculated by dividing the peak load at failure with the sample surface area.

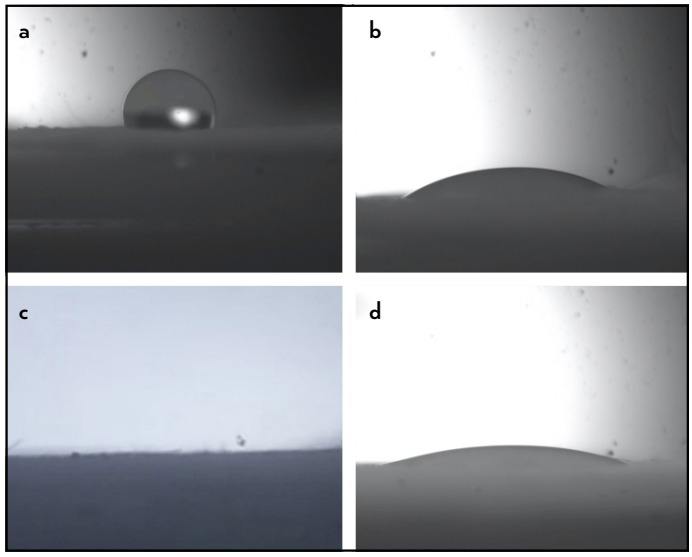

Figure 1. The images of contact angle formed by a drop each of (a) distilled water, (b) SE adhesive and (c) PDA on untreated MTA surface and (d) SE adhesive on PDA-pretreated MTA surface

SE: Self-etch, PDA: Polydopamine, MTA: Mineral trioxide aggregate

The fractured samples were mounted on aluminium stubs, vacuum dried, sputter coated with platinum and observed under SEM (JSM-IT800, JEOL, Massachusetts, USA) with secondary electron mode of 2.20kV. The mode of fracture was classified as cohesive, adhesive and mixed failures (20).

Statistical Analysis

Statistical analysis was done using IBM SPSS Statistics for Windows V22.0 (IBM Corporation, Armonk, New York). Shapiro-Wilk test was used to assess whether the CA and SBS data were normally distributed. Since significant differences were elicited, it was inferred that the data was not normally distributed. CA values were analyzed using One-way analysis of variance (ANOVA) and nonparametric Games-Howell Post Hoc test. For SBS, nonparametric Mann-Whitney test was used to study the intergroup comparison. Intragroup comparison was done using Friedman post-hoc Dunn test. The significance level was set at 0.05.

RESULTS

Contact Angle Measurement

The images of contact angle formed are presented in Figure 1. The mean (±S.D) contact angle of water, self-etch adhesive and PDA on untreated MTA was 123.47°±1.19, 34.22°±1.45 and 0.0 respectively. Compared to untreated MTA, self-etch adhesive recorded a significantly reduced contact angle of 27.20°±2.28 on PDA-pretreated MTA ($p<0.05$).

SEM Analysis

The SEM micrographs of the surface morphology of untreated and PDA-pretreated MTA are shown in Figure 2. Untreated MTA surface (group 1) showed irregular crystalline plate-like structures and superficial gel matrix with clusters of globular aggregate particles. MTA etched with self-etch primer (group 2), showed evidence of selectively eroded superficial gel matrix with absence of the crystalline plate-like structures, while these

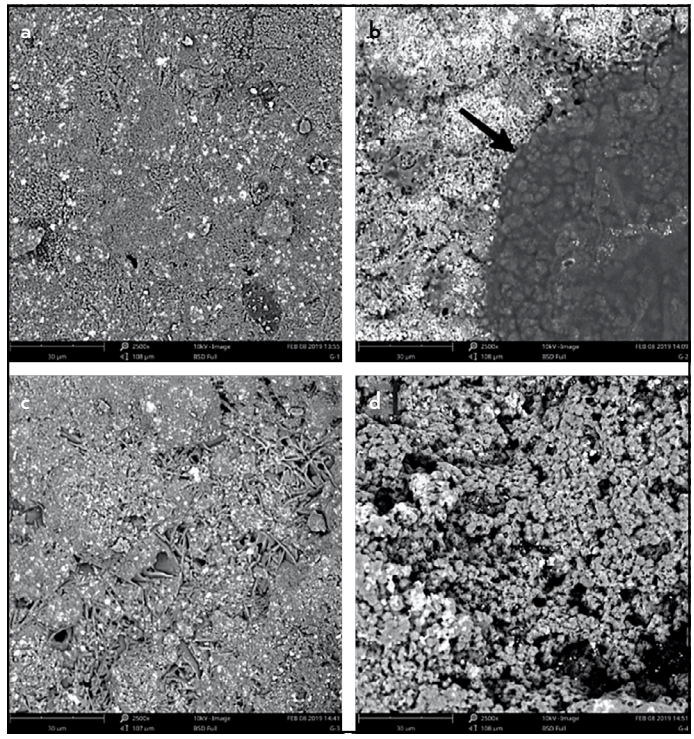

Figure 2. SEM micrographs of the surface morphology of (a) untreated MTA, (b) MTA etched with self-etch primer showing eroded areas (arrow), (c) PDA-pretreated MTA and (d) PDA-pretreated MTA surface etched with self-etch primer

SEM: Scanning electron microscope, MTA: Mineral trioxide aggregate, PDA: Polydopamine

structures were still present in the PDA-pretreated MTA (group 3). Multiple areas of erosion were observed in MTA etched with self-etch primer at a lower magnification (Fig. 3). Etching the PDA-pretreated MTA surface (group 4) showed aggregation of microspherical particles and clusters of globular aggregate particles on the MTA surface, suggestive of a layer of PDA.

Shear Bond Strength Evaluation

Mean (±S.D) shear bond strength (in MPa) of resin composite to MTA with and without PDA pretreatment at various time intervals is given in Table 2 and the graphical representation of the same is given in Figure 4. Intergroup comparisons showed that at all time intervals, MTA pretreated with PDA showed significantly higher mean SBS to RC than their untreated counterparts [1A (26.30±7.60 MPa) > 2A (12.26±3.82 MPa), 1B (29.14±6.50 MPa) > 2B (17.26±6.15 MPa), 1C (40.66±8.60 MPa) > 2C (25.92±6.67 MPa), 1D (43.79±4.40 MPa) > 2D (27.82±2.96 MPa), $p<0.05$]. Intragroup comparison of both untreated and PDA pretreated groups showed no significant difference between immediate and 3 h subgroups. Similarly, no significant difference was noticed between 24 h and 96 h subgroups (1A ≤ 1B, 1C ≤ 1D, 2A ≤ 2B, 2C ≤ 2D, $p>0.05$). Fractographic analysis revealed that cohesive failure in MTA was the predominant mode of failure in group 2A, the percentage of which decreased with time as observed in the other subgroups under group 1 and PDA-pretreated subgroups under group 2. There were no cohesive failures in composite. Table 3 summarizes the failure mode analysis of all the groups at various time intervals. Representative images of fractographic analysis are shown in Figure 5.

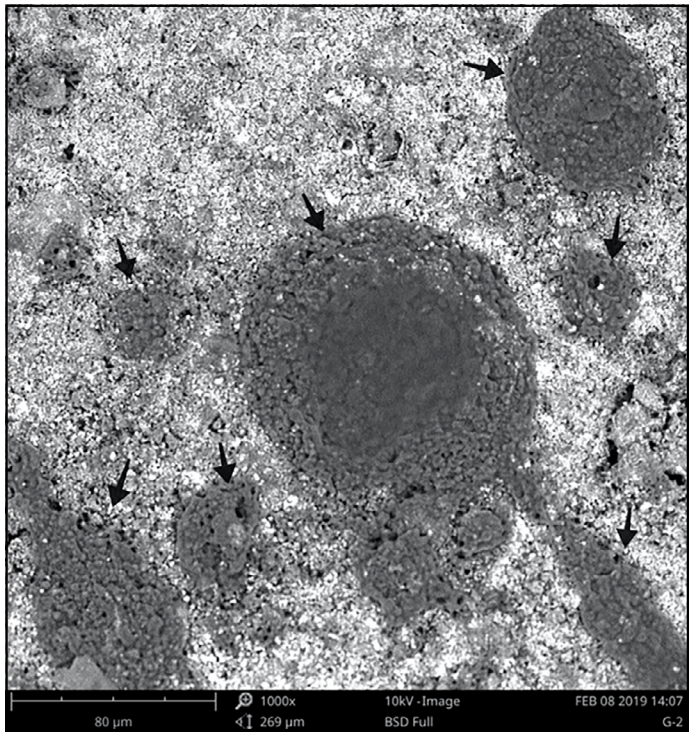

Figure 3. SEM micrograph of the surface morphology of MTA etched with self-etch primer at 1000x magnification showing multiple eroded areas (arrows)

SEM: Scanning electron microscope, MTA: Mineral trioxide aggregate

DISCUSSION

An increased wettability of the substrate and a decreased contact angle between the adhesive and the adherend are desirable requisites in adhesive bonding (21). PDA is known to increase the surface energy of the substrate through the presence of hydrogen-containing functional groups such as -OH and -NH- and is capable of forming an adhesive polymer film on the surface of the substrate (21). In addition, the catechol groups of PDA exert a chelating effect on the calcium ions of MTA, enabling a rapid and uniform coating on the surface of MTA (19). It was observed that, this unique property of PDA enables the attachment of the organic resin layer onto the surface of an inorganic, bioceramic material like MTA. This may be the reason behind SE adhesive forming a significantly lesser contact angle on PDA-pretreated MTA compared to untreated MTA.

Having known that the biological properties of MTA are influenced by its alkalinity, etching the surface of this material raises concerns of its surface integrity and functionality (22). SEM observations of the present study showed the ability of SEP to erode the surface of MTA. Yavari et al. (22) showed that the solubility of MTA was increased in an acidic environment. This decreases the crystal forming ability of MTA leading to porosities in the set structure. Shin et al. (13) observed micromorphologic changes in MTA following surface treatment with phosphoric acid and SEP. While loss of crystalline structure was seen with both, exposure to phosphoric acid also resulted in surface cracks and internal porosities, whereas SEP, with a higher pH, showed no evidence of surface cracks (13). As an increase in porosities is evident on the surface of MTA in low pH conditions, there is a need to protect its vulnerable surface prior to etching and bonding procedures associated with RC restoration. In the present study, PDA application not only preserved the crystalline structure of MTA, but also protected the morphologic structure of the latter by minimizing erosive loss following etching.

Tu et al. (19) studied the effect of physicochemical properties of PDA coated MTA particles. The authors observed that catechol group of PDA formed aggregates with calcium ions and silicate species of MTA, which served as space fillers thereby eliminating porosities and leading to a dense surface packing of MTA (19). Dopamine also forms complexes with metal species containing calcium, ferric, nickel, zinc and titanium ions (17). It could be hypothesized that such an adhesive complex could have been formed between calcium-rich MTA and PDA in the current study, thereby improving the erosion resistance of MTA in an acidic environment.

Shin et al. (23) stated that benefits of PDA coating were observed even with a shorter coating time (5 min). A more clinically feasible application time of 1 minute was adopted in this study. In order to ensure standardization in the application of PDA, a micropipette was used that enabled uniform delivery of the same amount of solution over the surface of MTA. Improved SBS of RC to MTA was seen with the use of SE adhesive system compared to TE systems. Neelakantan et al. (24) evaluated the SBS of RC to MTA using different adhesive systems (TE, 2-step SE, 1-step SE), and showed that 1-step SE adhesive exhibited significantly higher SBS than the other adhesive systems. Hence, a 1-step SE adhesive system was chosen for this study.

TABLE 2. Mean shear bond strength (in MPa) of resin composite to MTA with and without PDA pretreatment at various time intervals

Statistical parameters	Groups							
	Group 1 (with PDA)				Group 2 (No PDA)			
	Immediate	3 h	24 h	96 h	Immediate	3 h	24 h	96 h
Mean±SD (in MPa)	26.30±7.60[a]	29.14±6.50[a]	40.66±8.60[b,c]	43.79±4.40[c]	12.26±3.82[a]	17.26±6.15[a,b]	25.92±6.67[b,c]	27.82±2.96[c]
Median	24.40	28.50	38.28	44.17	10.84	16.66	24.29	28.23
IQR	4.47	4.10	10.46	7.87	6.63	12.58	4.08	3.22

Under each group, different lower case alphabets denote significant difference between the time intervals ($p<0.05$). MTA: Mineral trioxide aggregate, PDA: Polydopamine, SD: Standard deviation, IQR: Interquartile range

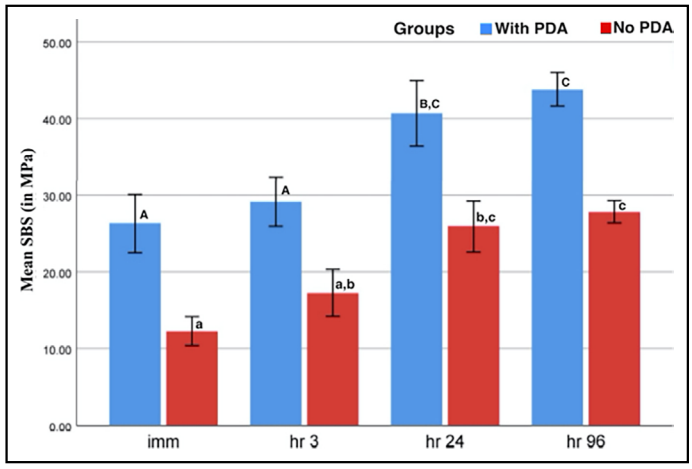

Figure 4. Graphical representation of the mean shear bond strength (SBS) of resin composite to MTA with and without PDA pretreatment at various time intervals. Error bars indicate 95% confidence interval. *Different upper-case alphabets denote significant difference between PDA-pretreated samples at various time intervals. Different lower-case alphabets denote significant difference between the untreated samples at various time intervals ($p<0.05$)

PDA: Polydopamine, MTA: Mineral trioxide aggregate

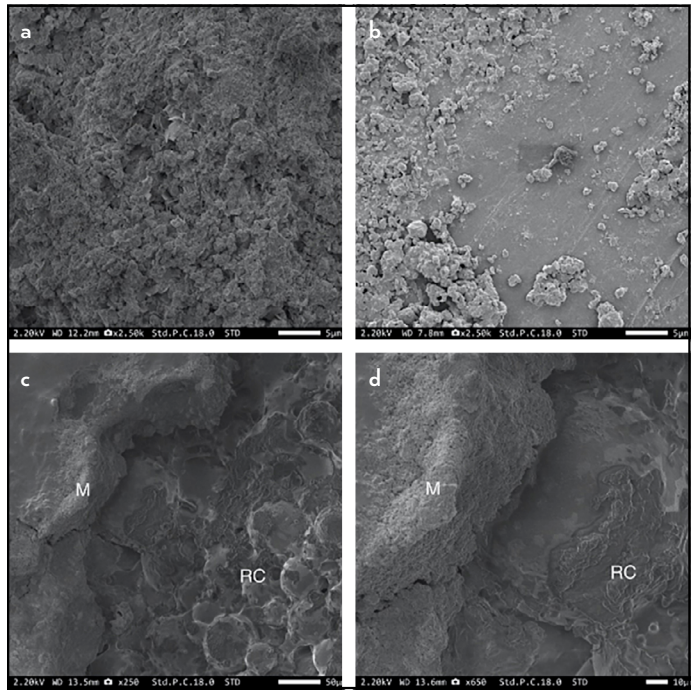

Figure 5. Representative SEM images showing cohesive in MTA (a, 2500x), adhesive (b, 2500x), mixed (c, 250x & d, 650x) failure modes of samples

M: MTA, RC: Resin composite, SEM: Scanning electron microscope, MTA: Mineral trioxide aggregate

MTA requires 120±45 min to complete its initial setting reaction, and an additional appointment is required for the placement of a permanent restorative material (6). A number of studies recommend the placement of both an immediate permanent restoration over freshly mixed MTA as well as delayed restoration after 96 h from the time of mixing, enabling MTA to achieve its optimum physical properties (14, 24). Having given these contradicting literature findings on the time of placement of the final restoration over MTA, four time periods (immediate, 3 h, 24 h and 96 h) were chosen in this study. Owing to the brittle nature of MTA, it was not feasible to evaluate the SBS between MTA and adhesive restorations using micro bond strength test. Hence, a macro SBS test was adopted in this study.

The results of the present study showed that carrying out bonding procedure on freshly mixed MTA results in compromised bond strength to resin composite. The SBS of untreated controls, which were bonded immediately, and after 3 h were significantly lesser than those bonded after 24 h and 96 h. These results are in accordance with previous studies, which have shown that carrying out bonding procedure on freshly mixed MTA results in compromised SBS to RC (9, 14, 25). This could be attributed to the dissolution of ions from the cement leading to poor stability in the interfacial layer between freshly prepared MTA and RC, resulting in cohesive failure of the former (25). The manufacturer of MTA Angelus, used in this study claims a reduced setting time of 15 min. This property was considered an advantage over the white MTA popular at that time, namely the ProRoot MTA by Dentsply Tulsa Dental Specialties, which had a setting time of 165 min. A comprehensive review of bio-inductive materials in direct and indirect pulp capping by Kunert et al. (26) showed that MTA's granular consistency and initial looseness continues beyond their claimed short setting times. They also observed that MTA might take a week to mature and this slow reaction might even continue for a year. The authors emphasized that MTA be left to mature prior to restorative procedure, both to protect it from bacterial insults as well as to preserve its physical and mechanical integrity for bonding (26). Falling in line with these observations, the results of the present study showed that freshly mixed MTA is vulnerable to bond failure and a significant increase in SBS of RC to untreated MTA could be elicited only after a

TABLE 3. Failure mode analysis (in %) of all the groups at various time intervals

Mode of failure	Groups															
	1A		1B		1C		1D		2A		2B		2C		2D	
	n	%	n	%	n	%	n	%	n	%	n	%	n	%	n	%
Cohesive in MTA	7	39	7	39	6	33	6	33	13	72	9	50	5	28	5	28
Adhesive	9	50	10	55	10	56	8	44	5	28	6	33	11	61	10	55
Mixed	2	11	1	6	2	11	4	23	0	0	3	17	2	11	3	17

MTA: Mineral trioxide aggregate

period of 24 h. Bond strength values between 17–20 MPa are considered optimal to produce gap free RC restorations to dentine (27). This optimum value is achieved in the present study when MTA is bonded with the SE adhesive after a period of 3 h. But this finding contradicts with the recent systematic review and meta-analysis by Hardan et al. (3) who analyzed the bond strength of adhesive systems to CS-based materials. The authors observed that the bond strength of RC to MTA was enhanced when a TE adhesive system was used. Various studies were analyzed in the review which showed that the bond strength of RC to MTA is enhanced by using phosphoric acid etching as the porosities formed by the acid promoted interlocking between the two substrates (3).

The results of the current study also revealed that at all the four-time intervals, the SBS of PDA-pretreated subgroups was significantly higher than the corresponding untreated subgroups. Hence the null hypothesis is rejected. In addition, the SBS of samples, which were bonded immediately in the presence of PDA, was equivalent to the SBS of untreated samples at 96 h. Thus, it can be inferred that coating the MTA surface with a layer of PDA reversed the reduction in SBS that could have otherwise occurred due to immediate bonding. It is also evident that application of a layer of PDA allowed bonding procedure to be performed immediately over the freshly mixed MTA surface.

PDA exhibits strong covalent, coordinate or non-covalent interactions with a wide range of inorganic and organic materials, including noble metals, polymers, semiconductors, oxides and ceramics (28). This could have contributed to the increased SBS seen in PDA-pretreated group. Calcium hydroxide, being a product in the setting reaction of MTA increases the surface alkalinity of the cement, which in turn could have catalysed the oxidative polymerization and growth of PDA, ensuring an uninterrupted PDA layer on the MTA surface (15). Ho and Ding (2014) confirmed the presence of silanol groups on MTA, which could have possibly formed hydrogen bonds with the binding sites of PDA (29). Thus, the improved SBS found in the experimental groups could be attributed to the ability of PDA to form a tenacious bond to the particles of MTA through the above-mentioned mechanisms.

Similar results were observed by Chen et al. (30) when glass fibre post (GFP) was treated with PDA. The authors evaluated the push-out bond strength (PBS) of PDA pre-treated GFP bonded to root dentine using two different resin adhesive cements. PDA pretreatment significantly improved the PBS of GFP to root dentine compared to untreated controls (30). Lee et al. (21) showed that PDA coating resulted in a greater number of self-assembled dopamine monomers, which increased the roughness of the PDA-coated surface, thereby increasing the surface area available for adhesion . Drawing inferences from this study, it could be hypothesized that the increased SBS in the PDA pre-treated group in the present study could also be because of the stronger micromechanical interactions between the acidic monomers of SE and the rough surface of PDA coating over the surface of MTA. In addition, He et al. (31) observed that the -OH and -NH- groups of PDA have a strong affinity to poly-methyl methacrylate surface. Hence, it could also be hypothesized that in this study, the methacrylate group of self-etch monomers might have had a strong affinity to the catechol (-OH) and amine (-NH-) groups of PDA coated MTA surface. The effect of PDA if any on the degree of conversion of the adhesive resin can be ruled out as recent studies have shown that PDA improved bond durability of resin composite without affecting the degree of conversion of the adhesive resin (32, 33).

With a variety of bonding agents available commercially, further studies should assess the effect of other bonding strategies and bonding agents in this experimental set up. Similar studies including other commercial formulations of MTA need to be done. Hardan et al. (3) also highlighted the lack of evidence related to the chemical interaction of SE adhesive systems and CS-based materials and recommended pretreatment with phosphoric acid in such conditions . Future studies are warranted in this regard. Long term bond strength of resin composite to MTA also needs to be assessed. One limitation of the study was that the surface morphology of MTA under SEM was observed only at 96 h, unlike the four-time intervals tested under SBS. Lack of assessment of moisture level in MTA, which could possibly influence the outcome of SBS is another limitation of this study. Future studies should assess the effect of PDA coating on the physicochemical properties and microleakage of MTA. The effect of this coating in protecting MTA from any external noxious stimuli, facilitating uninterrupted odontoblast cell differentiation for a successful single visit pulp capping procedure is yet to be analyzed. Further clinical studies should also be done to evaluate the success rate of PDA coated MTA as a PCA.

CONCLUSION

Within the limitations of this *in vitro* study, it can be concluded that compared to untreated control, PDA pretreatment of MTA surface improved its wettability, prevented loss of surface integrity following etching and increased the shear bond strength of direct resin composite to MTA.

Disclosures

Conflict of interest: The authors deny any conflict of interest.

Ethics Committee Approval: This study was approved by The SRM Dental College Ethics Committee (Date: 02/12/2020, Number: SRMDC/IRB/2018/MDS/NO.302).

Peer-review: Externally peer-reviewed.

Financial Disclosure: This study did not receive any financial support.

Authorship contributions: Concept – A.K., K.R., S.V., S.M.; Design – K.R., S.V., S.M.; Supervision – K.R., S.V., S.M.; Funding - A.K.; Materials - A.K.; Data collection and/or processing – A.K., K.R., S.V., S.M.; Analysis and/or interpretation – A.K., K.R., S.V., S.M.; Literature search – A.K., S.V.; Writing – A.K., S.V.; Critical Review – K.R., S.V., S.M.

REFERENCES

1. Didilescu AC, Cristache CM, Andrei M, Voicu G, Perlea P. The effect of dental pulp-capping materials on hard-tissue barrier formation: A systematic review and meta-analysis. J Am Dent Assoc 2018; 149(10):903–17.
2. Eid A, Mancino D, Rekab MS, Haikel Y, Kharouf N. Effectiveness of three agents in pulpotomy treatment of permanent molars with incomplete root development: a randomized controlled trial. Healthcare (Basel) 2022; 10(3):431. [CrossRef]

3. Hardan L, Mancino D, Bourgi R, Alvardo-Orozco A, Rodríguez-Vilchis LE, Flores-Ledesma A, et al. Bond strength of adhesive systems to calcium silicate-based materials: a systematic review and meta-analysis of *in vitro* studies. Gels 2022; 8(5):311. [CrossRef]
4. Chen Y, Chen X, Zhang Y, Zhou F, Deng J, Zou J, et al. Materials for pulpotomy in immature permanent teeth: a systematic review and meta-analysis. BMC Oral Health 2019; 19(1):227. [CrossRef]
5. Gandolfi MG, Van Landuyt K, Taddei P, Modena E, Van Meerbeek B, Prati C. Environmental scanning electron microscopy connected with energy dispersive x-ray analysis and Raman techniques to study ProRoot mineral trioxide aggregate and calcium sislicate cements in wet conditions and in real time. J Endod 2010; 36(5):851–7. [CrossRef]
6. Torabinejad M, Chivian N. Clinical applications of mineral trioxide aggregate. J Endod 1999; 25(3):197–205. [CrossRef]
7. Oskoee SS, Bahari M, Kimyai S, Motahhari P, Eghbal MJ, Asgary S. Shear bond strength of calcium enriched mixture cement and mineral trioxide aggregate to composite resin with two different adhesive systems. J Dent (Tehran) 2014; 11(6):665–71.
8. Awawdeh L, Al-Qudah A, Hamouri H, Chakra RJ. Outcomes of vital pulp therapy using mineral trioxide aggregate or biodentine: a prospective randomized clinical trial. J Endod 2018; 44(11):1603–9. [CrossRef]
9. Atabek D, Sillelioğlu H, Ölmez A. Bond strength of adhesive systems to mineral trioxide aggregate with different time intervals. J Endod 2012; 38(9):1288–92. [CrossRef]
10. Tsujimoto M, Tsujimoto Y, Ookubo A, Shiraishi T, Watanabe I, Yamada S, et al. Timing for composite resin placement on mineral trioxide aggregate. J Endod 2013; 39(9):1167–70. [CrossRef]
11. Banava S, Fazlyab M, Heshmat H, Mojtahedzadeh F, Motahhary P. Histological evaluation of single and double-visit direct pulp capping with different materials on sound human premolars: a randomized controlled clinical trial. Iran Endod J 2015; 10(2):82–8.
12. Tulumbaci F, Almaz ME, Arikan V, Mutluay MS. Shear bond strength of different restorative materials to mineral trioxide aggregate and Biodentine. J Conserv Dent 2017; 20(5):292–6. [CrossRef]
13. Shin JH, Jang JH, Park SH, Kim E. Effect of mineral trioxide aggregate surface treatments on morphology and bond strength to composite resin. J Endod 2014; 40(8):1210–6. [CrossRef]
14. Kayahan MB, Nekoofar MH, Kazandağ M, Canpolat C, Malkondu O, Kaptan F, et al. Effect of acid-etching procedure on selected physical properties of mineral trioxide aggregate. Int Endod J 2009; 42(11):1004–14.
15. Namazikhah MS, Nekoofar MH, Sheykhrezae MS, Salariyeh S, Hayes SJ, Bryant ST, et al. The effect of pH on surface hardness and microstructure of mineral trioxide aggregate. Int Endod J 2008; 41(2):108–16.
16. Ho CC, Ding SJ. Structure, properties and applications of mussel-inspired polydopamine. J Biomed Nanotechnol 2014; 10(10):3063–84. [CrossRef]
17. Chen Q, Wei XY, Yi M, Bai YY, Cai Q, Wang XZ. Effect on the bond strengths of glass fiber posts functionalized with polydopamine after etching with hydrogen peroxide. Dent Mater J 2015; 34(6):740–5. [CrossRef]
18. Lee JJ, Park IS, Shin GS, Lyu SK, Ahn SG, Bae TS, et al. Effect of polydopamine coating on the bioactivity of titanium for dental implants. Int J Precis Eng Manuf 2014; 15(8):1647–55. [CrossRef]
19. Tu MG, Ho CC, Hsu TT, Huang TH, Lin MJ, Shie MY. Mineral trioxide aggregate with mussel-inspired surface nanolayers for stimulating odontogenic differentiation of dental pulp cells. J Endod 2018; 44(6):963–70.
20. Boby A, Pai D, Ginjupalli K, Gaur S. Comparison of shear bond strength of light cure mineral trioxide aggregate and light cure calcium hydroxide with nanofilled composite: a stereomicroscopic and scanning electron microscope analysis. J Indian Soc Pedod Prev Dent 2020; 38:56–63.
21. Lee W, Lee JU, Byun JH. Catecholamine polymers as surface modifiers for enhancing interfacial strength of fiber-reinforced composites. Compos Sci Technol 2015; 110:53–61. [CrossRef]
22. Yavari HR, Borna Z, Rahimi S, Shahi S, Valizadeh H, Ghojazadeh M. Placement in an acidic environment increase the solubility of white mineral trioxide aggregate. J Conserv Dent 2013; 16(3):257–60. [CrossRef]
23. Shin YM, Lee YB, Shin H. Time-dependent mussel-inspired functionalization of poly(L-lactide-co-ε-caprolactone) substrates for tunable cell behaviors. Colloids Surf B 2011: 87(1):79–87. [CrossRef]
24. Neelakantan P, Grotra D, Subbarao CV, Garcia-Godoy F. The shear bond strength of resin-based composite to white mineral trioxide aggregate. J Am Dent Assoc 2012; 143(8):e40–5. [CrossRef]
25. Ajami AA, Bahari M, Hassanpour-Kashani A, Abed-Kahnamoui M, Savadi-Oskoee A, Azadi-Oskoee F. Shear bond strength of composite resin and giomer to mineral trioxide aggregate at different time intervals. J Clin Exp Dent 2017; 9(7):e906–11. [CrossRef]
26. Kunert M, Lukomska-Szymanska M. Bio-inductive materials in direct and indirect pulp capping-a review article. Materials (Basel) 2020; 13(5):1204. [CrossRef]
27. Davidson CL, de Gee AJ, Feilzer A. The competition between the composite-dentin bond strength and the polymerization contraction stress. J Dent Res 1984; 63:1396–9. [CrossRef]
28. Wu C, Han P, Liu X, Xu M, Tian T, Chang J, et al. Mussel-inspired bioceramics with self-assembled Ca-P/polydopamine composite nanolayer: preparation, formation mechanism, improved cellular bioactivity and osteogenic differentiation of bone marrow stromal cells. Acta Biomater 2014; 10(1):428–38. [CrossRef]
29. Ho CC, Ding SJ. Dopamine-induced silica-polydopamine hybrids with controllable morphology. Chem Commun (Camb) 2014; 50(27):3602–5.
30. Chen Q, Cai Q, Li Y, Wei XY, Huang Z, Wang XZ. Effect on push-out bond strength of glass-fiber posts functionalized with polydopamine using different adhesives. J Adhes Dent 2014; 16(2):177–84.
31. He FG, Du B, Sharma G, Stadler FJ. Highly efficient polydopamine-coated poly (methyl methacrylate) nanofiber supported platinum-nickel bimetallic catalyst for formaldehyde oxidation at room temperature. Polymers (Basel) 2019; 11(4):674. [CrossRef]
32. Devarajan SS, Madhubala MM, Rajkumar K, James V, Srinivasan N, Mahalaxmi S, et al. Effect of polydopamine incorporated dentin adhesives on bond durability. J Adhes Sci Technol 2021; 35(2):185–98. [CrossRef]
33. James V, Madhubala MM, Devarajan SS, Mahalaxmi S, Sathyakumar S. Evaluation of degree of conversion, resin-dentin bond strength, and durability of polydopamine incorporated total etch adhesive system. Front Dent 2020; 17:35. [CrossRef]