Acta Odontologica Scandinavica. 2014; 72: 831–838

informa
healthcare

ORIGINAL ARTICLE

Addition of benzalkonium chloride to self-adhesive resin-cements: some clinically relevant properties

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Abstract

Objective. The clinical survival rates of the adhesive restorations are limited due to the deterioration of resin-dentin bonds over time, partly due to the endogenous enzymatic activity of dentin. Recently, benzalkonium chloride (BAC) has been shown to effectively inhibit endogenous protease activity of dentin. This study evaluated the effect of different concentrations of benzalkonium chloride (BAC) on the degree of conversion (DC), vickers hardness (VH), setting time (ST) and biaxial flexural strength (FS) of two self-adhesive resin luting cements (RC). ***Methods.*** Two RC SpeedCEM (Ivoclar-Vivadent) and BisCem (Bisco) were modified by addition of 0.1, 0.5, 1, 1.5, 2 wt% BAC. The luting cements without the addition of BAC served as control. The DC (FT-IR/ATR from the bottom of the resin disc), vickers hardness (from top and bottom of the light-cured specimen), setting time (ISO 4049) and biaxial flexural strength (0.6 × 6 mm discs) of the specimens were tested. Data were analyzed using ANOVA and Tukeys HSD. ***Results.*** DC results were in the range of 70–80%, with some significant changes in BisCem ($p < 0.05$). VH values of both materials increased significantly compared to control, with no significant change as the BAC percentage increases. BAC addition influenced the ST differently for both materials. For BisCem, a gradual decrease ($p < 0.05$) was observed whereas, for SpeedCEM, a gradual increase was observed until 1% BAC ($p < 0.05$). For FS values, a gradual decrease was observed for both materials with increased amounts of BAC ($p < 0.05$), compared to the control group. ***Conclusions.*** BAC addition of up to 1% seems to be acceptable considering the properties tested. ***Clinical significance.*** Incorporation of benzalkonium chloride to self-adhesive resin luting cements during the mixing procedure does not significantly affect the degree of conversion or flexural strength of the luting agent and may be a good option to improve the durability of adhesive interface.

Key Words: *self-adhesive cements, benzalkonium chloride, monomer conversion, vickers hardness, setting time*

Introduction

With the development of the adhesive technology, adhesively bonded minimal invasive restorations became the standard of care for restoring the missing tooth structure [1–3]. Adhesively bonded dental restorations depend on the strong and durable bonding created by the luting cements to dentin [4]. Debonding of the restoration will usually result in failure of the restoration which, when unrecognized, could lead to secondary caries and harm the abutment teeth [5].

Both hydrolytic degradation of resin layer by water sorption and endogenous enzymatic degradation of dentin are known to impair adhesive bonding and result in lost integrity of the adhesive restoration [6–8]. Matrix metalloproteinases (MMP) and cysteine cathepsines (CC) were identified in the dentin matrix [6], providing two different paths for the collagen degradation. Both MMPs and cysteine cathepsines

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(Received 9 October 2013; accepted 24 March 2014)

ISSN 0001-6357 print/ISSN 1502-3850 online
DOI: 10.3109/00016357.2014.913307

are capable of degrading nearly all extracellular matrix molecules when activated by acid-etching procedures [6,7]. Even mildly acidic self-etch adhesives were reported to be sufficiently acidic to activate dentin proteases, which impair the resin-dentin bond stability over time [9].

Attempts have been focused on inhibition of the protease activity to increase the durability of resin dentin bonds [10]. Recently, quaternary ammonium compounds (QACs), well recognized antibacterial agents, have been reported to be effective on inhibiting endogenous dentin proteases [11,12]. Benzalkonium chloride (BAC), which is a QAC, was previously shown to bind strongly to demineralized dentin and inhibit soluble and matrix-bound MMPs [12]. Hence, BAC seems to be a good candidate for directly being incorporated into the adhesive systems.

Self-adhesive resin luting cements (RC) have been introduced with the aim of simplifying the multistep adhesive procedures, eliminating the inexperienced operator factor for restorative applications such as post cementations [1]. Furthermore, the simplified application technique also increased the acceptability of resin cements for the clinician, with more clinicians preferring resin-based cements with self-adhesive capability [3,4]. They are applied to smear layer covered dentin and, by means of acidic monomers included in these luting agents, simultaneous demineralization and infiltration of the dentin layer is accomplished. Despite their mild acidic actions, after the application of the cement, acidic monomers create an acidic interface layer and may facilitate activation of endogenic proteases at the interface layers [9]. Consequently, such a superficial infiltration of acidic monomers may form incomplete hybrid layers containing voids or layers that are not impregnated properly and are permeable to water [13–15]. Thus, such a hybrid layer leaves the collagen fibrils unprotected, accelerating their degradation by host derived MMPs and CCs [6].

Optimal adhesion between resin and tooth structure depends on the degree of conversion (DC) of the bonding agent. Incomplete polymerization of resin specimens for a particular resin system or composite exhibit higher elution of monomers over time [16]. DC also correlates with the materials microhardness during the setting reaction that gives useful information on the monomer conversion for a specific resin [17]. In addition to the mechanical properties of adhesive resin cements, setting time of the cement gives a good idea about the change in polymerization reaction kinetics as a result of added ingredients or mixing conditions [18]. Therefore, the purpose of this study was to assess degree of conversion (DC), Vickers hardness (VH), setting time (t_s) and biaxial flexural strength of self-etch adhesive resin cements after addition of increasing concentrations of BAC and, in this context, to evaluate the effects of BAC on physical properties of adhesive resin cements. The hypothesis tested was that the addition of BAC for improving the durability of resin cements did not have any adverse effect on their physical properties.

Materials and methods

The adhesive resin cements (RC) tested in this study were: SpeedCEM (Ivoclar-Vivadent, Schaan, Liechtenstein) and BisCem (Bisco Inc, Schaumburg, IL) (Table I). Different amounts of BAC were added directly to RC to prepare mixtures containing five different concentrations of BAC: 0.1 wt%, 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%. Materials without BAC addition served as control.

Degree of conversion

The DC of the materials was determined in real time using Fourier transform infrared spectroscopy (FT-IR) (Spectrum One, Perkin Elmer, Beaconsfield, Bucks, UK) with an attenuated total reflectance (ATR) sampling accessory. The unpolimerized adhesive paste was put directly on the diamond ATR crystal in a mold with 0.6 mm thickness and 6 mm diameter. A polyester strip and a glass slide was placed

Table I. Materials used in the study.

Name	Type	Manufacturer	Total filler content	Monomers	Shade	Lot numbers
BisCem	Dual-curing self-adhesive resin cement paste/paste (Automix)	Bisco Inc., Schaumburg, IL	>50% volume	Bis-GMA, TEGDMA, Bis[2-(methacryloyloxy)ethyl] phosphate	Translucent	1100011020
SpeedCEM	Dual-curing self-adhesive resin cement paste/paste (Automix)	Ivoclar Vivadent AG, Schaan, Liechtenstein	~40% volume	UDMA, TEGDMA, PEG dimethacrylate, 12-Methacryloyldodeylphosphate, BPO	Transparent	R56666

Bis-GMA, Bisphenol A-glycidyl methacrylate; TEGDMA, Tetraethylene glycol dimethacrylate; UDMA, Urethane dimethacrylate; PEG dimethacrylate, polyethylenglycol dimethacrylate; BPO, Benzoyl peroxide.

on the paste, respectively, and gently pressed to expel the excess material. A halogen curing-unit tip (XL 3000; 3M, ESPE, St Paul, MN) with an output intensity of 600 mW/cm^2 was positioned 1 mm from the adhesive surface during photopolimerization and the specimen was light cured for 40 s (Figure 1). The infrared spectra were recorded every 5.2 s for 15 min, beginning from the mixing of the resin cement. The DC% was calculated from the aliphatic C=C peak at 1638 cm^{-1} and was normalized against the aromatic C=C peak at 1608 cm^{-1} according to equation:

$$\mathrm{DC\%} = \left(\frac{\mathrm{C}_{aliphatic} / \mathrm{C}_{aromatic}}{\mathrm{U}_{aliphatic} / \mathrm{U}_{aromatic}} \right) \times 100\%$$

where: $C_{\mathrm{aliphatic}}$ = absorption peak at 1638 cm^{-1} of the cured specimen, C_{aromatic} = absorption peak at 1608 cm^{-1} of the cured specimen, $U_{\mathrm{aliphatic}}$ = absorption peak at 1638 cm^{-1} of the uncured specimen and U_{aromatic} = absorption peak at 1608 cm^{-1} of the uncured specimen. The fraction of the remaining double bonds for each spectrum was determined by standard baseline techniques using the comparison of maximum heights of aliphatic and reference peaks for calculations. Light polimerized RC without BAC was used as control. Five specimens with 0.6 mm thickness and 6 mm diameter were prepared for each group.

Vickers hardness

Each of the samples prepared for DC testing were also used for Vickers hardness testing after 15 min of light polymerization. The Vickers indenter was applied to self-adhesive resin cement disc surfaces at a load of 490.6 mN and with a dwell time of 15 s. Six randomized indentations were made on both the top and bottom surfaces of each resin disc 15 min after light polymerization, with each indentation seperated by ~0.5 mm. Microhardness was measured using a Struers Duramin hardness microscope (Struers, Copenhagen, Denmark) with a 40× objective lens. The diagonal length impressions were measured and

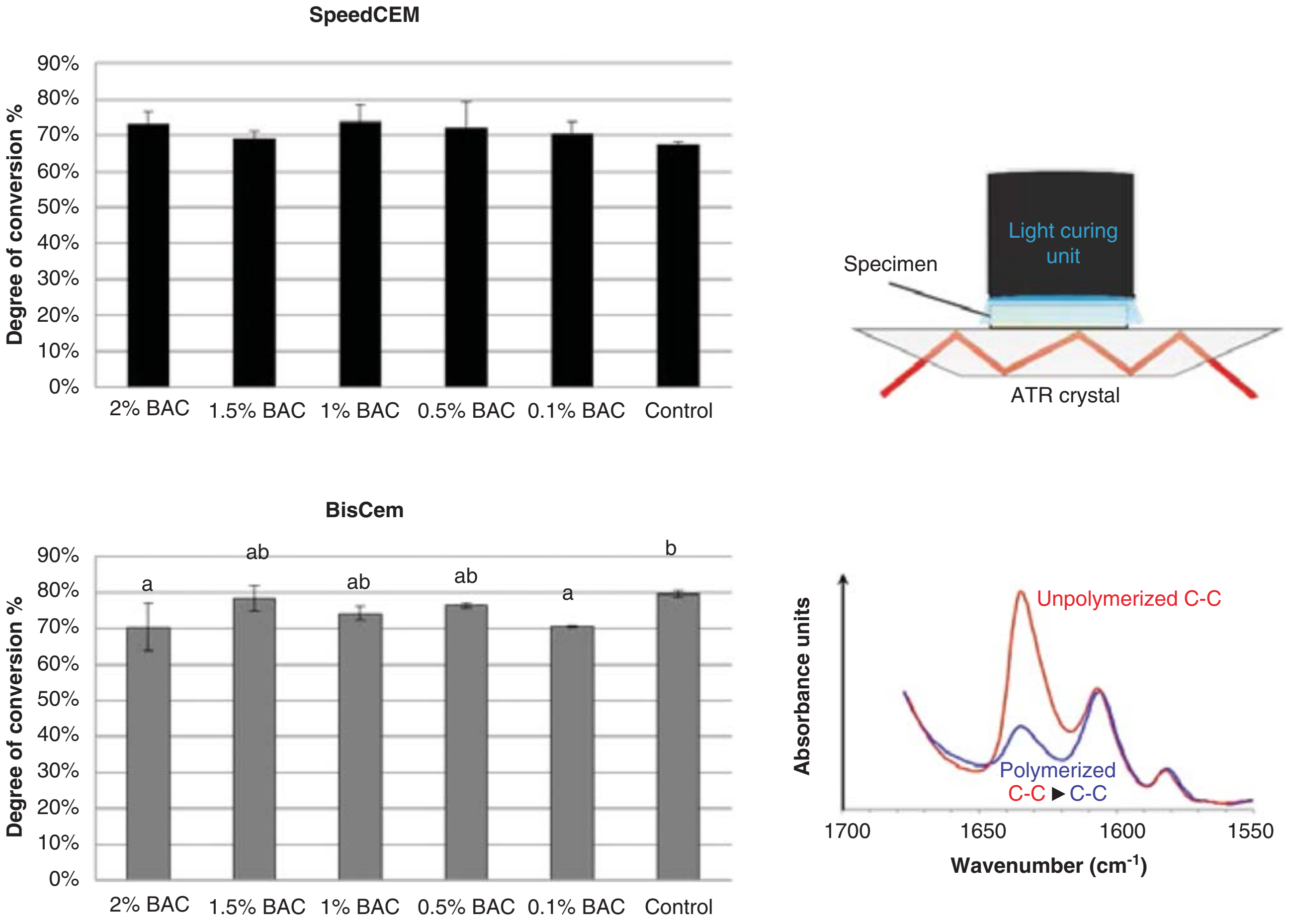

Figure 1. Degree of conversion (%) of resin cements. Letters show the statistically similar groups ($p > 0.05$) illustrations show the test set-up (above) and the calculation method where the change in monomer conversion was calculated using the aliphatic-aliphatic C=C peak and normalized against the aromatic C=C peak (below).

Vickers values were converted into microhardness values by the machine.

Microhardness was obtained using the following equation:

$$H = \frac{1854 \times P}{d^2}$$

where H is Vickers hardness in N/mm^2, P is the load in N and d is the length of the diagonals in mm.

Setting time measurements

Setting time of the materials tested was assessed by using the thermocouple apparatus described in the ISO 4049 test. The apparatus consisted of a 6 mm diameter polyamide block with a 4 mm diameter and 2 mm high locating part. A 6 mm long and 1 mm thick high density polyethylene tubing to fit on the locating part was used to form the specimen well. A T-type thermocouple wire surrounded by steel tubing was located inside the polyamide block [ISO 4049:2009 (E)]. In order to facilitate removal of the samples after testing, the thermocouple junction had a conical solder tip which protruded 1 mm into the base of the sample well (Figure 2). Five samples for SpeedCEM and BisCem including 0.1 wt%, 0.5 wt%, 1 wt %, 1.5 wt%,and 2 wt% of BAC and no-BAC as the control were mixed and put into the specimen well. The elapsed time between the begining of the mixing of the adhesive resin cements was recorded. Before and during the test, the apparatus was kept in an 37°C incubator. The temperature rise was recorded with a sampling rate of 10 Hz using a thermocouple data logger with a built-in cold junction compensation (TC-08, Pico Technologies Ltd, Cambridgeshire, UK). Measurement was continued until a plateau at maximum temperature was reached. The plateau was extended backwards to meet an extension of the straight line of temperature increase. Time at the intersection of the both lines were recorded as the setting time, t_s.

Biaxial flexural strenght measurements

Disc shaped specimens (0.5 mm thick and 6.0 mm in diameter) were fabricated in a polyethylene mold after 40-s light exposure on both sides with a halogen light curing unit. Before the mechanical tests were applied, adhesive discs were stored at 37°C for 24 h in a dark container. Ten discs for both materials for five

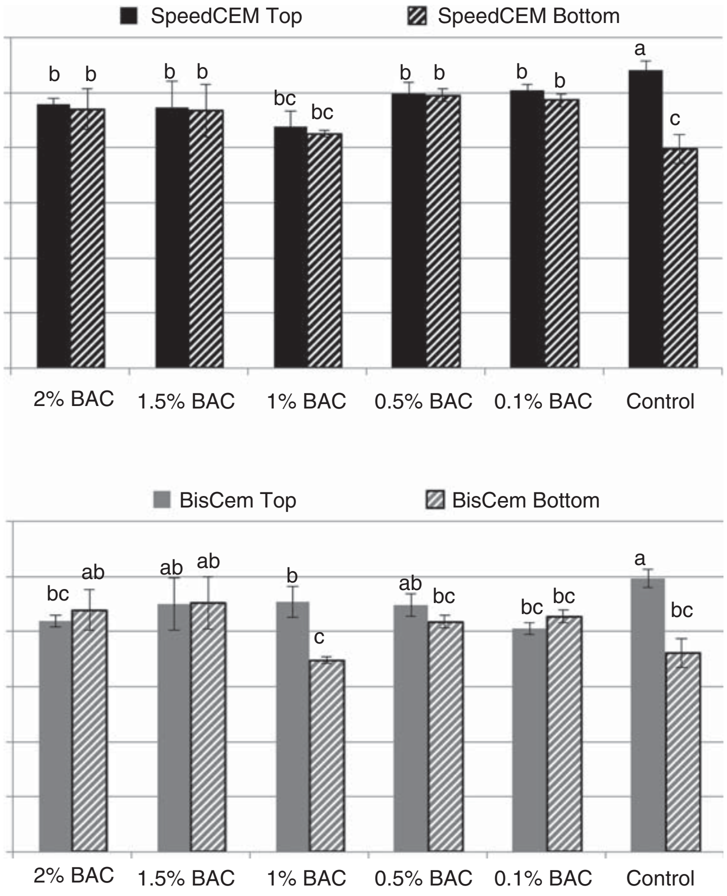

Figure 2. The Vickers Hardness of the materials as the concentration of BAC increases. Letters show the statistically similar groups ($p > 0.05$).

different concentrations (0.1 wt%, 0.5 wt%, 1 wt%, 1.5 wt%, 2 wt%) of BAC were tested ($n = 10$). Therefore, 120 discs were fabricated. Each disc was placed into a custom-made testing jig (Figure 3) and was tested in biaxial flexure on a universal testing machine (Model LR30KPlus; Lloyd Instruments Ltd., Fareham, UK) at 1.27 mm/min until failure. The maximum load was recorded for each specimen, and the following formula for the biaxial flexural strength (σ) was used:

$$\sigma = -0.238 \times \frac{7\mathrm{P}(X - Y)}{b^2}$$

where σ is the maximum center tensile stress (megapascals), p is the total load causing fracture (Newtons),

$$X = (1 + v)\ln(r_2 / r_3)^2 + [(1 - v) / 2](r_2 / r_3)^2$$

$$Y = (1 + v)[1 + \ln(\mathrm{r}_1 / \mathrm{r}_3)^2] + [(1 - v)(r_1 / r_3)^2]$$

and b is the specimen thickness at fracture origin (mm), in which v is Poisson's ratio (used $v = 0.25$), r_1 is the radius of the support circle (mm), r_2 is the radius of the loaded area (mm) and r_3 is the radius of the specimen (mm).

Statistical analysis

Shapiro-Wilk test was applied to test results to confirm normal distribution of the data. One-way ANOVA using Tukey post-hoc analysis was used to detect any statistically significant differences among groups (IBM SPSS Statistics Software version 21, IBM Corporation, Armond, NY).

Results

DC results are plotted in Figure 1. Addition of BAC up to 2% resulted in significant changes on some of the properties tested, with 2% BAC showing the highest change. DC ranged from 67.6–74% for SpeedCEM and 73.5–79.2% for BisCem. The addition of BAC into SpeedCEM caused an increase of ~6%, which was not statistically significant. BAC addition to BisCem caused an ~10% decrease for the 2% BAC group. This change was found to be significant ($p < 0.05$).

Vickers hardness values ranged from 21.94–27.08 for the light activated sides and from 19.88–

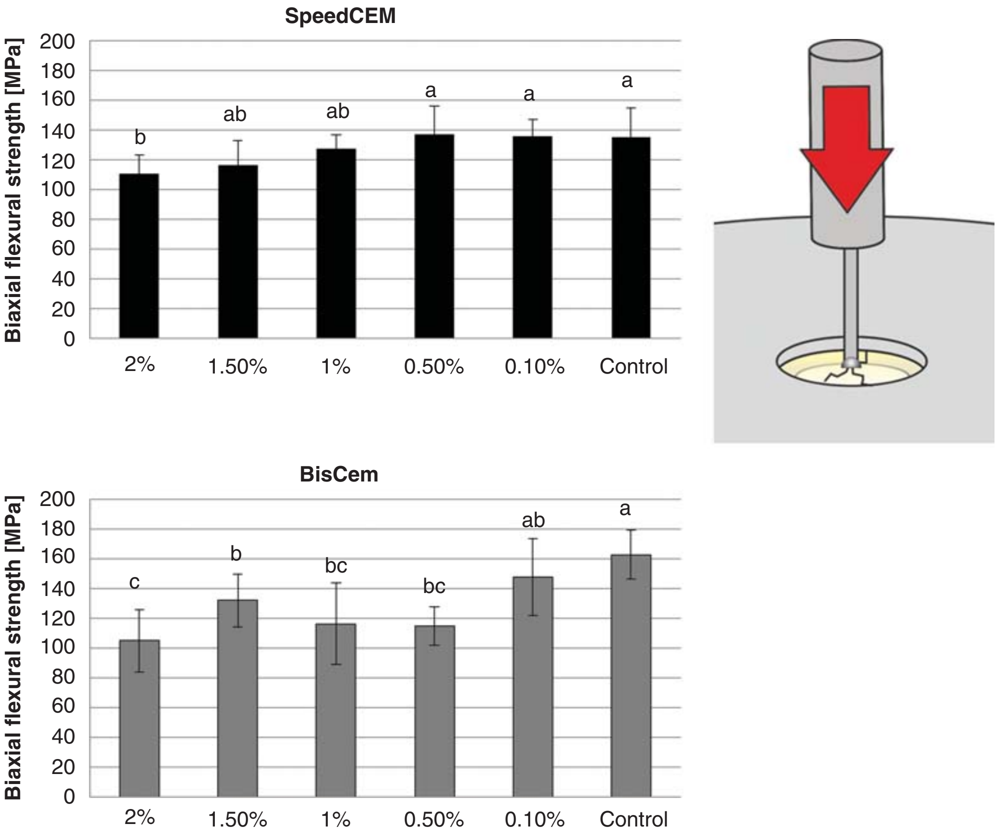

Figure 3. The biaxial flexural strength test results. Letters show the statistically similar groups ($p > 0.05$). The illustration shows the test set-up with a ball plunger and a specimen holder, with the border of the 6 mm holder supporting the edges of the resin disc.

24.80 for the back sides of SpeedCEM samples (Figure 2). For the light activated sides of the SpeedCEM samples, addition of 1%, 1.5% and 2% BAC significantly decreased the hardness values compared to the control groups ($p < 0.05$). For BisCem, hardness values ranged from 20.32–24.84 for the light activated sides and from 17.42–22.60 for the back sides of the samples and for the light activated sides, no significant differences were observed within the groups except for the front side being significantly higher and the 1% BAC group being significantly lower than the others.

Setting time values ranged from 4.7–8.7 min for SpeedCEM and 4.47–12.7 min for BisCem (Figure 4). Addition of 1% and 0.5% BAC significantly increased the setting time compared to the control of SpeedCEM. For BisCem samples, 2% and 1.5% BAC significantly decreased the setting time compared to control, 0.1% and 0.5% BAC added groups ($p < 0.05$).

Biaxial flexural strength values ranged from 110.6–137.4 MPa for SpeedCEM and 105.06–162.8 MPa for BisCem (Figure 3). There was no statistically significant difference between the different concentrations of BAC added SpeedCEM samples and control groups except for the 2% BAC group compared to the 0.5%, 0.1% and control groups where a significant difference was observed ($p < 0.05$). For BisCem, 2%, 1% and 0.5% BAC added groups showed lower flexure strength with statistically significant differences ($p < 0.05$) compared to the control group.

Discussion

Self-adhesive resin cements are a group of luting cements with a relatively complex and filler-dependent polymerization reaction. Therefore, the behavior of these cements can not be predicted using the data accumulated using resin cements. There are two clinical scenarios related to self-adhesive resin cements where a protection from endogenous enzymatic activity may be needed. First, because of the acidic environment at the interface, which may activate the MMPs and CCs [12]. Another vulnerability is created when the self-adhesive resin cements are used after acid etching. Previous studies have shown that the bond strength of self-adhesive resin cements may be improved by acid-etching the enamel surface [19,20]. If this becomes a standard procedure for better durability, hybrid layer degradation will have to be kept in mind, especially when the dentin surface is also intentionally or accidentally etched.

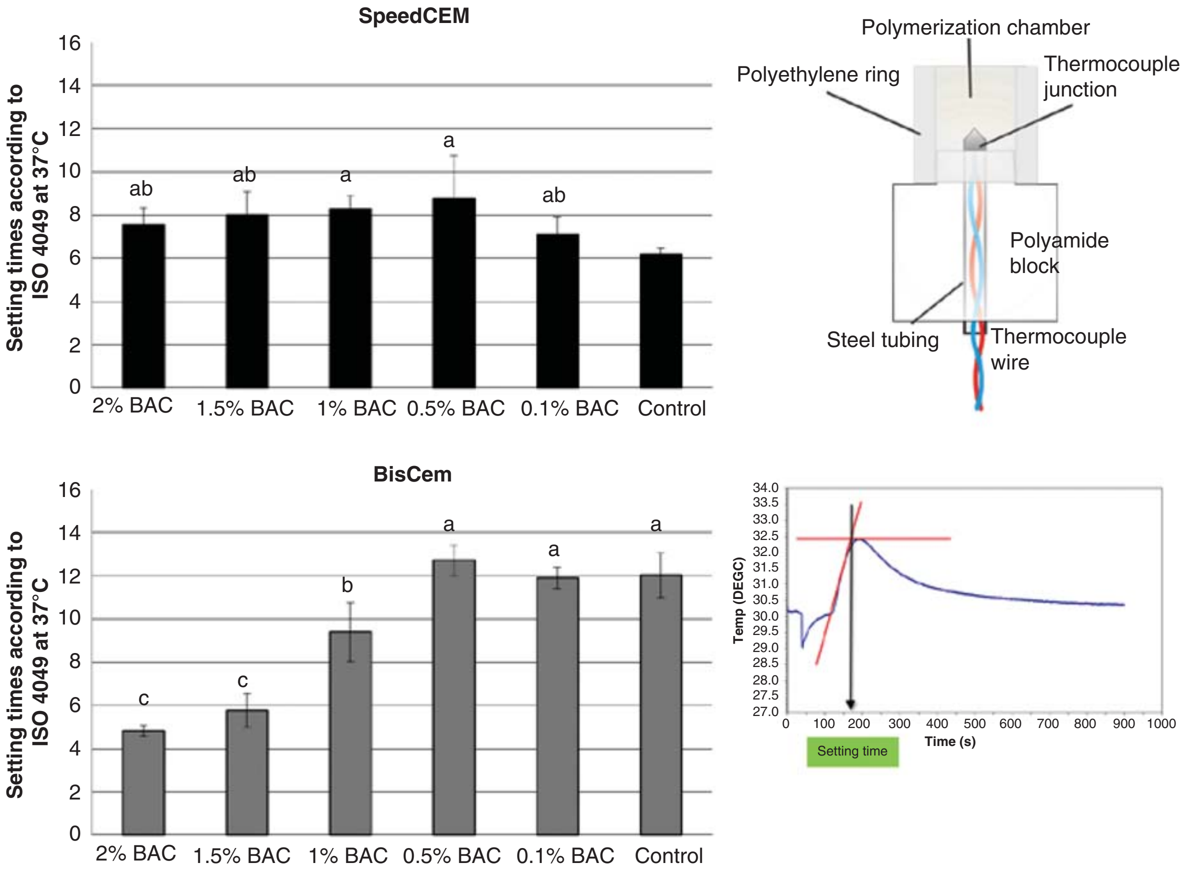

Figure 4. Setting times of SpeedCEM and BisCem as the BAC concentration increase. Letters show the statistically similar groups ($p > 0.05$). The illustrations show the test set-up used (ISO 4049) (above) and the calculation method for t_s, where the intersection point of the plateau of temperature increase and the extension of the temperature increase curve was used for finding the setting time.

The present study evaluated some of the clinically relevant properties of two light-cured self-etch adhesive resin cements after the incorporation of BAC. Results of the present study reject the hypothesis partly as the direct addition of varied amounts of BAC had significant effects on some of the hardness, setting time and biaxial flexural strength results of self-adhesive resin cements tested.

The degree of conversion of dental adhesives is an important parameter which effects nearly every physical property of a resin system [17] and low mechanical properties are related with low percentage of monomer-to-polymer conversion within resin-based materials [21]. Previously, incorporation of quaternary ammonium compounds into methacrylate-based restorative materials were not found to affect the DC and microhardness [21,22]. In the current study, the results showed that the addition of BAC resulted in changes in DC of the tested adhesive resin cements in the order of 6% and 10% for SpeedCEM and BisCem, respectively. The control groups of BisCem showed significantly higher DC than the BAC incorporated groups. The increase in DC is a positive effect. However, addition of 1%, 1.5% and 2% BAC significantly decreased the hardness values of the light activated sides of the SpeedCEM samples compared to the control groups, whereas no significant differences were observed among the light activated sides of the BisCem control group and the BAC added groups except for the 1% BAC groups. Overall, a decrease of hardness values up to 20% at the light-exposed side and an increase of ~25% on the bottom sides of both cements was observed. Previous reports using much higher concentrations of BAC [23] denoted that the addition of ionic dimethacrylate monomers (IDMAs) which contain quaternary ammonium groups slightly increased the viscosity of the mixture and linear correlations were found [24] between viscosity and Knoop hardness values of light-cured dental composites. As is known, BAC is a cationic surfactant with both hydrophilic and hydrophobic ends which might affect the viscosity of the mixtures. The changes in the hardness values in response to different quantities of added BAC shows that the changes observed in DC did not directly correlate with the hardness values.

Benzalkonium chloride, chlorhexidine and triclosan were previously added to orthodontic adhesive resins with no significant effect on the bond strengths of the tested materials [25]. Similar to this study, Othman et al. [26], after testing the tensile bond strength and the diametrial tensile strength, concluded that the incorporation of BAC into a composite adhesive material added antimicrobial properties to the compound without affecting its mechanical properties.

Addition of BAC into SpeedCEM did not significantly increase the setting time compared to the control. For BisCem samples, addition of 1, 1.5 and 2% BAC significantly decreased the setting time compared to added groups. The phosphate acidic monomer gives the advantage of superior adhesion to various materials like metals, dentin and ceramics. The cements used in this study had two different phosphate acidic monomers and SpeedCEM had urethane dimethacrylate as the main polymerizable component compared to Bis-GMA in BisCem. Quaternary ammonium salts were previously shown to act as cationic initiators for N-Benzylpyridinium salts. The difference probably lies in the efficiency and compatibility of BAC as a cationic initiator in these systems [27].

It was previously reported that biaxial flexure strength data provided reliable results since maximum tensile stresses occur within the central loading area of the disc shaped samples, eliminating spurious edge failures associated with three-point flexure testing [28]. According to the results of the biaxial flexure strength tests, the strength of the specimens gradually fall as the amount of BAC increases. Both materials had significantly lower biaxial strength values compared to control at 2% BAC on the order of 20% for SpeedCEM and 35% for BisCem. Similar to the present results, Cadenaro et al. [29] found that addition of 1% or 5% CHX-another cationic agent produced a significant decrease in the modulus of elasticity of the most hydrophilic adhesive resin among five different experimental adhesive blends.

The findings of the present study indicate that the addition of BAC does interfere with the polymerization of self-adhesive resin cements. In the setting time and hardness results from the bottom of hardness specimens, a significant improvement was found for Biscem. These results are indicative of the materials ability to self-cure when there is not enough curing light exposure. On the other hand, conversion, hardness from the top surfaces of the specimens and biaxial fracture strength results, where the specimens are light-cured by direct exposure, were lower compared to controls, especially at higher concentrations. These results indicate that BAC addition especially interferes with the light-curing mechanism negatively and, as a result, lower mechanical properties are obtained. This could be another influence of the cationic activity, which changes the viscosity of the resin effecting the relatively quick polymerization when light activation is preferred.

Incorporation of active ingredients into currently used systems may provide an easy modification method for the clinicians, where an improvement in certain properties is needed. Evaluation of the changes in mechanical and handling properties of materials is essential before such modifications are proposed. The present study gave an overview of the clinically relevant property change for various concentrations of BAC. In conclusion, on account of possessing antibacterial properties and being a potential MMP inhibitor, incorporation of BAC with self-etch adhesive resins could be a good solution in order to improve the bond durability. While improving some of the mechanical properties, BAC could also have some adverse effects on resin systems. However, the effect of BAC on the mechanical properties seems to be material-dependent and dose-dependent. Further studies should be aimed at investigating the effect of lower BAC concentrations on the MMP-inhibiting and anti-bacterial properties to achieve better overall results.

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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