Effect of Zinc Oxide-Eugenol Materials on Resin-Based Restorative Materials Hardness

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The effect of zinc oxide-eugenol material (Cariosan, Spofa Dental) on resin-based restorative materials (a composite resin - Premise, Kerr Company, a compomer - Dyract Extra, Dentsply, a giomer - Beautifil, Shofu) hardness was investigated. Surface hardness was evaluated using a digital microhardness tester (Micro-Vickers Hardness System CV- 400DMTM, CV Instruments Namicon). In contact with eugenol-based cement the hardness values of all tested materials significantly decreased. After cement storage in artificial saliva for 1 and 7 days, the hardness values of all three resin-based materials registered a significantly increase when compared to the samples where the materials were placed in contact with eugenol-based cement immediately after setting, but still significantly lower when compare to the samples having no contact with eugenol-based cement.

Keywords: Zinc oxid eugenol material, composite resin, giomer, compomer, surface hardness

In dentistry the indications for use of zinc oxide-eugenol (ZOE) materials include pulp protection and temporary restoration. The major goal of eugenol-based temporary materials for filling is to protect the pulp from physical and chemical injuries from the oral cavity [1] and to sterilize the remaining affected dentine in acute caries lesions. Provisional restorations have some advantages related to good sealing property and easy handling [2-6].

Most of the time these cements are completely or partially replaced by resin-based restorative materials. More than thirty years ago some studies that investigated the effect of ZOE bases on composite resins concluded that ZOE has the capacity to inhibit the polymerization of this kind of materials [7, 8]. The results of these studies were, however, assumed by further studies, without taking in account the fact that composite resins studied were mainly chemically activated and they were no longer available on the market. For the light activated composite resins, the use of bonding agent decreased the effect of eugenol on resin polymerization [8]. Except the effect on resin polymerization, eugenol also affect their mechanical properties [9], increase the microleakage [10, 11] and change the dentine wettability [12].

Regarding the effects of eugenol on resins materials for filling, the results of different studies are not in consensus. The decrease of bond strength to dental hard tissues was demonstrated in previous studies [13-17]. On a contrary, newer researches reported minimal or no effect of ZOE bases on bond strength of adhesive systems and composites polymerization [18-22]. Some studies demonstrated that IRM ZOE base even increase the hardness of some composite resin [23].

New materials for filling appeared in the latest years to improve some properties of composite resins. Hybrid materials as compomers and giomers have been developed to associate the advantages of composite resins (surface hardness, physical strength, low shrinkage and resistance to wear, good esthetic aspect) and the advantages of glass ionomer cements (fluoride release and chemical bonding to tooth structure). Lack of scientific reports regarding the effect of eugenol on polymerization and hardness of these materials are present.

The aim of this study was to assess the effect of ZOE base on resin-based restorative materials polymerization by hardness evaluation.

Experimental part

Samples preparation

Three different resin-based materials: a composite resin (Premise, Kerr Company), a compomer (Dyract Extra, Dentsply), a giomer (Beautifil, Shofu) (table 1) and a zinc oxide eugenol base material (Cariosan, Spofa Dental) were chosen for this study. Ten samples of each resin-based materials having having 15 mm in length, 7 mm in width and 4 mm in height were obtained by placing the composite resin in contact with a transparent matrix between two glass slabs in order to flatten the surface (group 1, control). The samples were built-up in two increments of 2mm. Each layer was light cured for 40 s using a LED curing light unit (LED B, Guilin Woodpecker Medical Instrument Co., Ltd, China), having the light source intensity of 850-1000mW/cm^2 and the wavelenght of 420-480 nm. Thirty samples of Cariosan having the same dimensions were obtained by placing the amount of the cement in contact with a transparent matrix between two glass slabs. The cement resulted by mixing the powder and the liquid according to producer instruction for use. The samples were randomly split in three groups (groups 2-4). In group 2 resin-based materials were placed in direct contact with Cariosan cement immediately after the setting time of the cement (12 minutes), in group 3 the cement samples were immersed in artificial saliva for 1 day and

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Material	Type	Resin	Filler	Wt%	Vol%	Size (μm)
Premise	Nanofilled hybrid composite resin	Bis-GMA TEGDMA	Barium silicate glass, silica, prepolymerized Fillers	84	71	0.02-50
Beautifil	Giomer	Bis-GMA TEGDMA	Inorganic glass, aluminuoxide, silica, pre-reacted glass ionomer	83.3	68.6	0.01-4
Dyract Extra	Compomer	UDMA TEGDMA TCB resin	Strontium fluoride glass	73	47	0.8
BisGMA- Bis-glycidyl ether dimethacrylate; TEGDMA - Triethylene glycol dimethacrylate; TCB-Tetracarboxylic acid-hydroxyethylmethacrylate-ester; UDMA-Urethane dimethacrylate						

Table 1
RESIN-BASED MATERIALS INCLUDED IN THE STUDY

	Area 1	Area 2	Area 3	Area 4	Area 5
Group 1	59.8 (± 0.2)^{A}	59.6 (± 0.4)^{A}	59.7 (± 0.3)^{A}	59.8 (± 0.2)^{A}	59.6 (± 0.3)
Group 2	40.2 (± 0.3)^{A,a}	47.3 (± 0.5)^{A,a}	48.8 (± 0.4)^{A,a}	56.2 (± 0.3)^{A,a}	59.7 (± 0.2)
Group 3	44.4 (± 0.4)^{A,a}	48.3 (± 0.3)^{A,a}	53.2 (± 0.4)^{A,a}	56.1 (± 0.4)^{A,a}	59.8 (± 0.1)
Group 4	51.6 (± 0.2)^{A,a}	54.4 (± 0.2)^{A,a}	57.0 (± 0.1)^{A,a}	58.2 (± 0.5)^{A,a}	59.9 (± 0.4)
^{A} significantly statistical differences between groups; ^{a} significantly statistical differences between areas					

Table 2
THE MEAN PREMISE VHN VALUES (± STANDARD DEVIATION)

	Area 1	Area 2	Area 3	Area 4	Area 5
Group 1	77.4 (± 0.3)^{A,}	77.2 (± 0.8)^{A}	77.1 (± 0.8)^{A}	77.5 (± 0.4)^{A}	77.3 (± 0.4)
Group 2	58,5 (± 0.8)^{A,a}	62,8 (± 0.9)^{A,a}	67,6 (± 0.9)^{A,a}	72,9 (± 0.9)^{A,a}	77,2 (± 0.4)
Group 3	65.7 (±0.6)^{A,a}	67.4 (± 0.7)^{A,a}	70.9 (± 0.8)^{A,a}	71.1 (± 0.8)^{A,a}	75.0 (± 0.3)
Group 4	67.0 (± 0.7)^{A,a}	71.0 (± 0.5)^{A,a}	75.8 (± 0.7^{A,a}	76.2 (± 0.6)^{A,a}	77.5 (± 0.5)
^{A} significantly statistical differences between groups; ^{a} significantly statistical differences between areas					

Table 3
THE MEAN BEAUTIFIL VHN VALUES (± STANDARD DEVIATION)

then resin-based materials were placed in direct contact with the cement. In group 4 cement samples were immersed in artificial saliva for 7 days and then resin-based materials were placed in direct contact with the cement. The artificial saliva used in this study was AFNOR NF S90-701.

Surface hardness evaluation

The samples included in groups 1-4 were subjected to surface hardness evaluation using digital microhardness tester (Micro-Vickers Hardness System CV- 400DMTM, CV Instruments Namicon). A 50 g load was applied through a Vickers indenter. For each sample of resin-based materials placed in contact with the cement and for the samples in control group, five areas having equal length of 3 mm (numbered 1-5) were established for surface hardness determination starting from the resin-based material-cement junction toward the opposite side of the sample. In each of these five areas five indentations were made and the final value of Vickers hardness was calculated as a mean result of these five recordings. The surface hardness values of the samples in the groups and in the areas were statistically analysed using ANOVA and post hoc Bonferroni tests (significance level of $p < 0.05$).

Results and discussions

The mean VHN values and standard deviation recorded for Premise composite resin in groups 1-5 and in areas 1-5 are presented in table 2. The surface hardness values were highest in control group. The contact of composite resin with the eugenol-based cement significantly decreased the VHN values when compared to control. Immersion of cement samples in artificial saliva for 1 day and 7 days before the contact with composite resins leaded to significantly higher VHN values when compared to the samples where the composite resin was placed in direct contact with the cement immediately after setting. In all groups the lowest VHN values were recorded in the area closest to the junction with the cement (area 1). In areas 2, 3 and 4 the hardness values significantly increased when compared to area 1. In area 5 the values were similar to that recorded in control group.

The mean VHN values and standard deviation recorded for Beautifil giomer in groups 1-5 and in areas 1-5 are presented in table 3. The samples included in control group recorded the highest surface hardness values. In contact with eugenol-based cement the VHN values significantly decreased when compared to control. After cement storage in artificial saliva, the VHN values of giomer samples registered a significantly increase when compared to the samples where the giomer was placed in contact with eugenol-based cement immediately after setting. In all groups the lowest VHN values were recorded in the area closest to the junction with the cement (area 1). In areas 2, 3 and 4 the hardness values significantly increased when compared to area 1, but still significantly lower when

	Area 1	Area 2	Area 3	Area 4	Area 5
Group 1	62.3 (± 0.6)^{A}	62.4 (± 0.5)^{A}	62.5 (± 0.4)^{A}	62.4 (± 0.5)^{A}	62.5 (± 0.3)
Group 2	43.9 (± 0.6)^{A,a}	52.8 (± 0.7)^{A,a}	56.6 (± 0.4)^{A,a}	59.7 (± 0.5)^{A,a}	62.4 (± 0.2)
Group 3	47.9 (± 0.8)^{A,a}	50.4 (± 0.5)^{A,a}	51.7 (± 0.4)^{A,a}	65.2 (± 0.7)^{A,a}	62.3 (± 0.4)
Group 4	48.7 (± 0.6)^{A,a}	53.6 (± 0.4)^{A,a}	58.3 (± 0.7)^{A,a}	59.0 (± 0.5)^{A,a}	62.5 (± 0.5)
^{A} significantly statistical differences between groups; ^{a} significantly statistical differences between areas					

Table 4
THE MEAN DYRACT EXTRA VHN VALUES (± STANDARD DEVIATION)

compared to control. In area 5 no significantly differences were recorded when compared to control group.

For Dyract Extra the mean VHN values and standard deviation obtained in groups 1-5 and in areas 1-5 are presented in table 4. The highest surface hardness values were recorded for the samples included in control group. A significantly decrease of VHN values was obtained for compomer samples that were placed in contact with eugenol-based cement. The VHN values were significantly lower when compomer is placed in the contact with the cement immediately after setting when compared to the samples where the compomer were in contact with the cement after storage 1 and 7 days in artificial saliva. In area nearby the junction between compomer and cement were recorded the lowest values of surface hardness, followed by areas 2, 3 and 4, where the hardness values significantly increased when compared to area 1. In area 5 the values were significantly higher when compared to groups 1-4 and were similar to that recorded in control group.

ZOE materials are probably one of the most common temporary filling materials that can also be used as base due to their biological properties. These materials result by mixing a powder that contains zinc oxide with eugenol. Eugenol (2-methoxi-4-allyphenol) is a radical that, unfortunately, has the disadvantage of inhibiting the adhesive resin [24]. The mechanism of this action is due to the tendency of hydroxyl group of the eugenol molecule to protonize the free radical formed during polymerization, blocking its reactivity, reducing the degree of conversion and the bond strength. In our study the lowest hardness of all resin-based materials were obtained in the area nearby the junction with the eugenol-based material (area 1, having 3 mm) and significantly increased toward the opposite areas. The hardness values were similar to control group at a distance of 12 mm from the junction with eugenol-based material

For all the resin-based tested materials a decrease of surface hardness was recorded after the contact with eugeno-based cement, regardless of the storage in artificial saliva for 1 or 7 days. During the setting, the mixture of eugenol and zinc oxide will lead to a chelation reaction [25]. In this reaction, the remaining eugenol molecules are trapped inside the cement matrix. The presence of moisture will determine the hydrolysis of eugenolate and the release of eugenol [26]. Except that, the trapped, unreacted eugenol molecules, could be released by the degradation of the temporary cement matrix [14, 27]. Same results regarding the significantly hardness decrease were reported in other studies [6].

Previous studies showed that the hydrolysis influences more the diffusion rate of eugenol when compared to the tooth characteristics [28]. As a result, eugenol inhibition of polymerization should be increased near the surface. The maximum eugenol release appear to be in the first 24 h; after that the diffusion rate decreasing slowly [29]. The concentration of eugenol also influences the inhibitory effect on resin polymerization [24]. Some studies showed that after one week the eugenol concentration in dentine does not affect the bond strength of self-etching adhesive systems [30]. In our study, even after 7 days of storage in artificial saliva the hardness of all three resin-based materials was still lower when compared to control.

This study showed that even new hybrid materials, like giomers and compomers, were affected by the contact with eugenol-based materials. Giomer materials are based on the technology where special pre-reactive glass fillers are included in the resin matrix. The giomer tested in the present study contains the surface reaction type of pre-reactive glass fillers (S-PRG) and an adhesive systems (FL-BOND) contained the full reaction type PRG fillers (F-PRG). As a difference from giomer, in compomers variable amount of unhydrated polyacrylic acid is added to the resin matrix and the acid base reaction will not takes place until water comes in contact with compomer. In our study the hardness of compomer were still far from that of composite resin and giomer. Same results when compared to composite resins were reported in previous studies [31, 32].

Conclusions

In the conditions of this study, zinc oxide-eugenol materials used for base significantly decrease the hardeness of composite resin, compomer and giomer material for filling. After eugenol-based cement storage in artificial saliva for 1 and 7 days, the hardness values of all three resin-based materials registered a significantly increase when compared to the hardness of materials placed in contact with eugenol-based cement immediately after setting, but still significantly lower when compare to the samples having no contact with eugenol-based cement. The lowest hardness of all resin-based materials were obtained in the area nearby the junction with the eugeno-based material and significantly increased toward the opposite areas.

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