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COMPARATIVE SURVEY OF THE MOST USED SELF ADHESIVE DENTAL CEMENTS BASED ON RESIN COMPOSITES

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The present study is dedicated to the investigation of self-adhesive cements, based on resin composites (RBC). Reported cases of dental restorations decays, are influenced by interface/surface quality and marginal adaptation to dentin and enamel. The influence is given by organic and inorganic (filler) phase as well. Regarding the organic phase, this is involved in bonding with dentin remains and enamel. Differences were noticed between the investigated materials; results from EDX patterns reveal major differences between inorganic phase (filler) in specimens and a non homogenous state for all samples. Results are confirmed by the mapping patterns. Low discontinuity areas for samples specimen were remarked for Biscem and RelyXU100 samples, then for MaxcemElite dental cement. Regarding mechanical properties, those are dramatically influenced by the filler. The major determination is given by the particles size and state of homogeneity for a given specimens composition. SEM results revealed a textured structure with a small filler particles size for RelyX U100 than other samples (less than, $d = 1\mu m$). A stirring method is recommended for all samples before application for an improved homogeneity.

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1. Introduction

After a tooth has been damaged or destroyed, restoration of the missing structure can be achieved with a variety of treatments. Various dental materials are used in dentistry to restore damaged dental tissues. A large interest today is focused on indirect dental restorations (manufactured by a technician in laboratory). These are made by various materials as metal ceramic or high strength dental ceramics like alumina or zirconia.

Dental resin cements are used today to lute indirect ceramic restorations. Classic dental cement will fill the microscopic space between tooth and restoration, but resin cement is able to bond at the substrate: enamel, dentin or ceramic. New products are developed in order to improve and simplify luting procedures.

Self-adhesive cements are the latest subgroup of resin cement introduced in the clinical practice. They were firstly launched to satisfy clinician`s demands for simplification of luting procedures and to reduce post-operatories sensitivity of total etch resin cements [1]. The self–adhesive resin cements are directly applied on the restoration that is seated in place without any previous treatment.

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Recent studies, in vitro, have evaluated the bonding performance of the self-adhesive resin cements and have appreciated them to be inferior comparative with total-etch resin cements [2-6].

The bonding mechanism of these cements is based on a chemical interaction and micromechanical retention with the adhesive substrate [2,5]. A chemical reaction is established between multifunctional monomers with the phosphoric acid groups of the cement and the hydroxiapatita from teeth. On the other hand, the latest studies are focused to develop new monomers to improved this chemical bonding [7-11] and to find the best procedure of conditioning the adhesives substrates: enamel, dentin [12, 13] or ceramic [6, 7, 14,15].

Regarding clinical behaviors of self-adhesive resin cements the clinical studies on short term validate these materials [16, 17], but they are not yet evaluated on long term.

The purpose of this study is a deep investigation of the chemical composition and the micro structure as well of the three most used self-adhesive resin cements: MaxCemElite (from Kerr), Biscem(from Bisco), and RelyXU100 (from 3M Espe). The evaluation will establish an explanation to the reported cases of incomplete adhesive diffusion throughout the demineralized dentin for conventional dentin-bonding or dental restoration fracture [7, 18].

Like resin composite materials used for direct restorations, those materials are structured as an organic matrix and a filler of inorganic particles silanised for chemical bonding [1]. Bonding performance is related with the organic matrix and the mechanical/physical properties are associated with the inorganic filler used as reinforcement.

In some cases the manufactures provide details about the composition of the cement but in other cases they are not. This is the high motivation of the present study.

The organic component is comprised of conventional mono-, di -, or multi-methacrylate monomers and acid functional monomers currently used to achieved demineralization and bonding to the tooth surface. These are the most critical elements in self – adhesive resin cements, influenced by curing procedure and clinical conditions.

The fillers used are represented by a combination selected from barium fluoric alumino silicate glass, quartz, colloidal silica, ytterbium fluoride and other glass fillers [7].

The ions released from the acid –soluble filler neutralize the remaining acidic groups of monomers to create a chelate reinforced methacrylate network [7, 18]. Some materials include calcium hydroxide, likely to contribute to a more rapid neutralization process rather than simply being present for its antimicrobial action [7]. Rely XUnicem contents 2% calcium hydroxide [19].

Some manufactures include fluor in the composition of these cements to confer them a carioprofilactic character [18, 20]. *Gerth and colab.* finds 10% fluoride in RelyXUnicem [19].

Different fillers are responsible by aesthetic characteristics of the cements, very important for ceramic restorations. The cement must be radiopac to a different appearance from dental tissues and restoration materials and so their composition include radiopac fillers like barium, lanthanum, strontium [19 - 21].

There are a few studies that have investigated the mechanical properties of self-adhesive resin cements, comparing them to other types of cements [21-25]. The flexure and compressive strength, the hardness, the elastic modulus increase with the amount of inorganic fraction while the polymerization shrinkage and the solubility decrease. The decay of ceramic dental restoration is caused by the stresses introduced during sintering, pressing, machining, post-processing annealing heat treatments, or following pre-cementation surface modifications [26 – 28].

Also the viscosity and the film thickness of the cements increase with the quantity and the size of the inorganic fillers. Some studies developed a thicker film then 25µm for MaxCem and Rely X Unicem [21, 22]. Also the film thickness depends by the seating forces [23].

2. Materials and method

General speaking, the current self-adhesive resin cements are two parts materials that require either hand mixing or are delivered with an auto mixing dispenser. Preserving the commercial name, the following dental cement samples there were investigated:

a) Maxcem Elite, auto mixing. Manufacture: Kerr, Orange, CA and USA;

b) BisCem, auto mixing. Manufacture: Bisco Inc. IL, USA;

c) RelyX U100, hand mixing. Manufacture: 3M ESPE, MN, USA.

Samples were prepared as disc shape with diameter *d = 6mm* and thickness *h = 3mm,* light cured polymerization according manual manufacturer protocol. It was used a light cured lamp (from Kerr Company) with peak light wave for λ = *460 nm,* power P = 1,200 mW for a time unit 15 seconds each sample. The investigated materials are representative for the categories of dental cements used for indirect dental rest orations.

As the investigated materials are RBC, a dental composite typically consists of a resin-based oligomer matrix and inorganic filler. Compositions vary widely, with proprietary mixes of resins forming the matrix, as well as engineered filler glasses, glass ceramics or metals.

According samples composition, different investigation methods were used. Regarding the organic matrix investigation, FTIR (Fourier Transform Infrared) spectrometry method was used. The equipment used for our study was Jasco FTIR 6200. The specimen elements for the inorganic filler part were identified by EDX (Energy-dispersive X-ray) spectroscopy method. Regarding samples homogeneity was performed a mapping investigation for the same sectors as EDX protocol. The equipment used was from Brucker Company, Model S200.

As samples surface quality, compactness of material in fracture and particle sizes are quite important in materials evaluation, a SEM (Scanning Electron Microscopy) investigation was performed. A Zeiss S50 electron microscope was employed in our studies.

3. Results and discussions

3.1 IR investigation

IR investigation highlights for all samples that the organic part is consisted of a conventional mono-, di- and / or multi-methacrylate monomers and a acid-functionalized monomers currently used to achieve demineralization and bonding to the tooth surface. IR spectra for all samples are presented almost for the same wave length peaks, in order to be compared easily. Results from IR evaluation are depicted in Fig. 1.

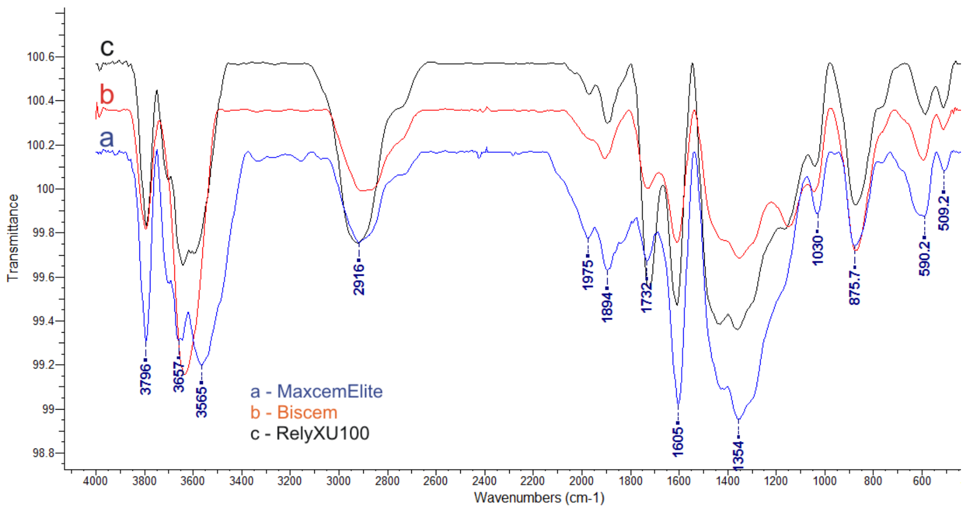


Fig. 1. IR Spectra. Samples: (a) MaxcemElite, (b) Biscem, (c) RelyXU100.

An important peak was noticed for all samples, around λ=*1,730 cm*$^{-1}$, corresponding absorption bands of carbonyl groups from methacrylic acid. Also an important peak was for the value λ=*2,920 cm*$^{-1}$ corresponding to C - H stretching mode. The value is closer for RelyXU100 to be identified with a possible elastomer (polyvinylidene, based on fluorine). Additional investigation is requested, by Raman method. For peak corresponding to λ=*1,354 cm*$^{-1}$ is evidenced symmetric COO^- stretch of calcium polyacrylate for all investigated samples. Extra, just for RelyXU100, is noticed the symmetric COO^- stretch of aluminum polyacrylate corresponding to $\lambda=1,431\ cm^{-1}$. A better behavior to alumina dental ceramic core is suggested. A confirmation in the same direction just for RelyXU100 is given by the presence of the peak for $\lambda = 586.38\ cm^{-1}$ corresponding to Si-O-Al linkages.

Results are more complex, chemical groups belonging to chemical compounds not mentioned by the manufacturer being identified. Interesting to mention, for all samples is the presence of the large interval $\lambda = 3500 \div 3800\ cm^{-1}$ bands corresponding to OH groups or polyvinylidene fluoride.

For all samples was remarked the peak for $\lambda = 505.37\ cm^{-1}$ assigned to P-O bending, corresponding to acid functional monomers currently used to achieved demineralization and bonding to the tooth surface.

3.2 EDX Investigation

The inorganic part of dental cements samples was investigated by EDX method. Investigation was performed for five points on each sample surface. Because samples were covered with a short layer of gold (10 nm) for performing SEM evaluation in the mean time, carbon (C) and gold (Au) must be neglected. All results were normalized to the unit. Regarding EDX results, we noticed that for all investigated samples there were a lot of chemical specimens in common (with small differences) such as: oxygen, aluminum, silica, phosphorus or calcium. All samples have a higher percentage of oxygen (highest percentage value is for MaxcemElite sample, 46.08%), indicating large amounts of oxides such as: glass silica (SiO_2), alumina (Al_2O_3) or barium oxide (BaO). Most of the oxides mentioned before are forming different types of glasses with different heavy metals (titanium for Biscem and RelyXU100 or lanthanum for Biscem) added for improved optical properties. No heavy metals were noticed for MaxcemElite sample, except barium (BaO) in a higher percentage (10.48 %). An important specimen presence is strontium (Sr), with higher percentage for Biscem (17.82%) and RelyXU100 (15.71%). The specimen element is very similar to calcium (Ca), forming strontium oxide (SrO). Strontium is in row II a of the periodic table, just below calcium. Like calcium, strontium has two positive charges in its ionic form. To the right side, in the periodic table, rows III and IV there are yttrium (Y) and zirconium (Zr) – representative specimen elements for zirconia dental ceramic.

Results regarding EDX investigation are depicted in Table 1.

Table 1. EDX results for RBC cements, inorganic part (average values for five points, wt%).

Samples / Chemical Elements	MaxcemElite	Biscem	RelyXU100	Error* (%)
C	9.69	9.42	9.96	1.2
O	46.08	36.14	27.83	12.8
F	10.34	-	7.94	1.4
Al	3.16	7.96	7.20	0.3
Si	10.11	15.48	15.03	0.6
P	0.16	1.56	1.85	0.0
Ca	0.07	0.76	0.19	0.0
Ni	1.51	-	-	0.1
Cu	2.40	2.58	3.48	0.1
Ba	10.48	-	-	0.3
Ti	-	0.39	0.60	0.0
Sr	-	17.82	15.71	0.7
La	-	1.81	-	0.1
Zn	-	-	3.68	0.1
Au	6.01	4.76	6.46	0.2

*Errors were calculated by the soft of the equipment employed to our studies.

Regarding the position of strontium (Sr) in the periodic table, the action to oxygen is opposite than that for elements as yttrium and zirconium. A long lasting bonding to zirconia ceramic core is just a desired success. Many cases of zirconia dental restorations failure were reported [15]. An important role is playing by strontium in dentin surface adhesion because of its chemical similarity to calcium; it can replace calcium to some extent in various biochemical processes in the body, including replacing a small proportion of the calcium in hydroxyapatite crystals of calcified tissues as dentin. Those properties are improved for Biscem and RelyX U100 because of strontium content.

Because of alumina and silicates content, bonding to alumina ceramic core is more improved and with better results for Biscem and RelyX U100 because of higher percentage content (Table 1).

3.2 Mapping Investigation

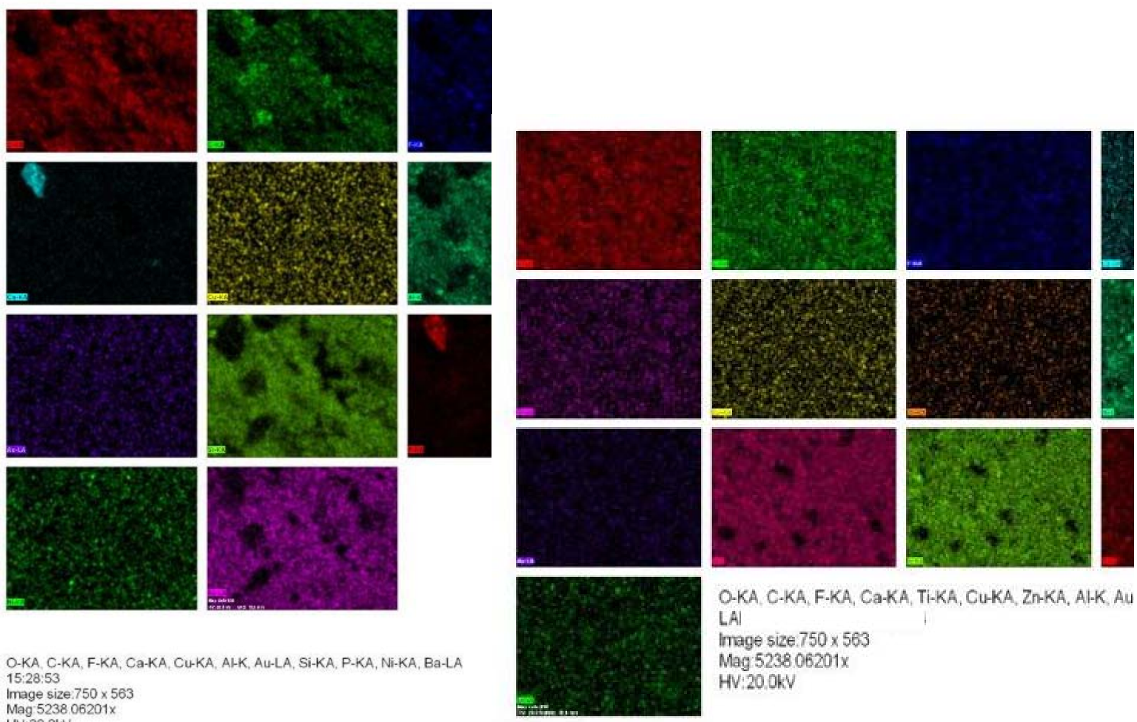
EDX investigation was completed by samples mapping investigation regarding each specimen element predicted by the previous investigation. Results obtained are highlighted major differences between investigated samples. Differences were noted regarding distribution area for each chemical specimen element to each investigated sample. For all samples was noticed a high non homogeneity.

For MaxcemElite sample representative is the non homogeneity for phosphorus (P) and calcium (Ca). Other specimen elements like silica (Si) and fluorine (F) have large areas of discontinuity (dark areas, Fig. 2 a). The best chemical element distribution is noticed for nickel (Ni).

For Biscem sample was noticed a better homogeneity. For each specimen elements were noticed just discontinuity areas (dark areas, Fig. 2 b), but smaller then for the MaxcemElite sample.

The best results were obtained for RelyXU100. Best specimen elements distribution was presented for titanium (Ti), alumina (Al), strontium (Sr) and silica (Si). Significant discontinuity areas were remarked for fluorine (F) as presented in Fig. 2 c.

Even sample syringe is fitted with auto mixing dispenser or not, a good stirring of material is recommended before application to obtain a good homogeneity.



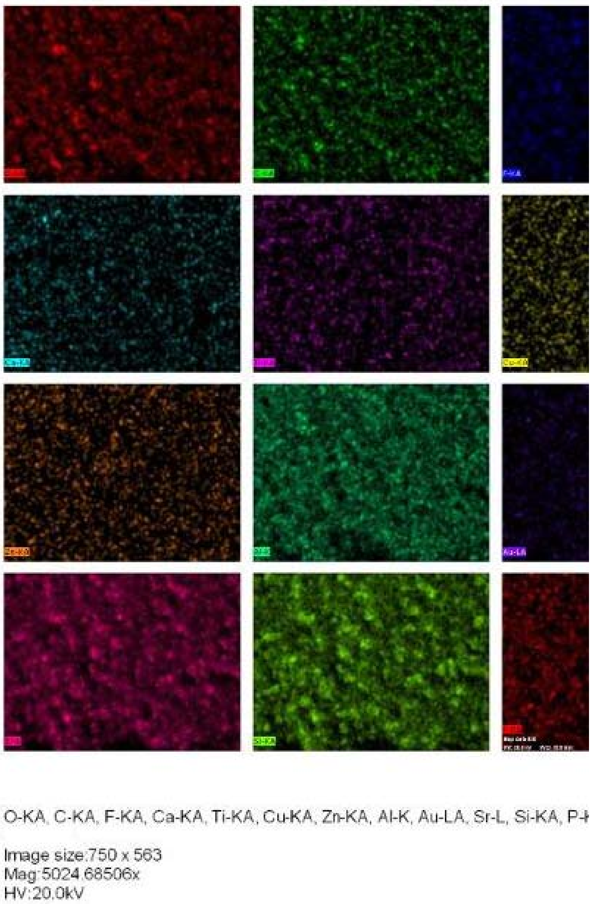


Fig. 2. Mapping results. Samples: (a) MaxcemElite, (b) Biscem, (c) RelyXU100.

3.3 SEM Investigation

As was mentioned before, a major determination of mechanical properties and interface adhesion (dentin/cement/ceramic core) is given by the inorganic particles size and polymer ‘grains’. A SEM investigation was performed for all cement samples, respecting the same magnification in order for the results to be compared.

For MaxcemElite sample, the surface is not smooth and presents a large distribution for inorganic particles or grains size with a non compact aspect. Large grains (G) are observed with diameter $d = 12\ \mu m$ and inorganic particles (filler, F) with diameter $d = 2 \div 6\ \mu m$ (Fig. 3 a).

Regarding Biscem sample, the surface quality is smoother and presents a hard compact aspect. Is very hard to distinguish ‘grains’ (G), but if so, the diameter is $d = 6\ \mu m$, much smaller than for MaxcemElite. For inorganic particles (filler, F) was noticed diameter $d = 0.5 \div 1\ \mu m$ (Fig. 3 b) and maybe smaller.

Dental cement RelyXU100 presents a textured and high compact structure. The mass of material is disposed almost layered. It is difficult to evidence ‘grains’, the diameter is $d = 4 \div 5\ \mu m$, maybe smaller. Regarding inorganic particles (filler, F), the diameter measured was $d = 1\ \mu m$ (Fig. 3 c) and even smaller than Biscem.

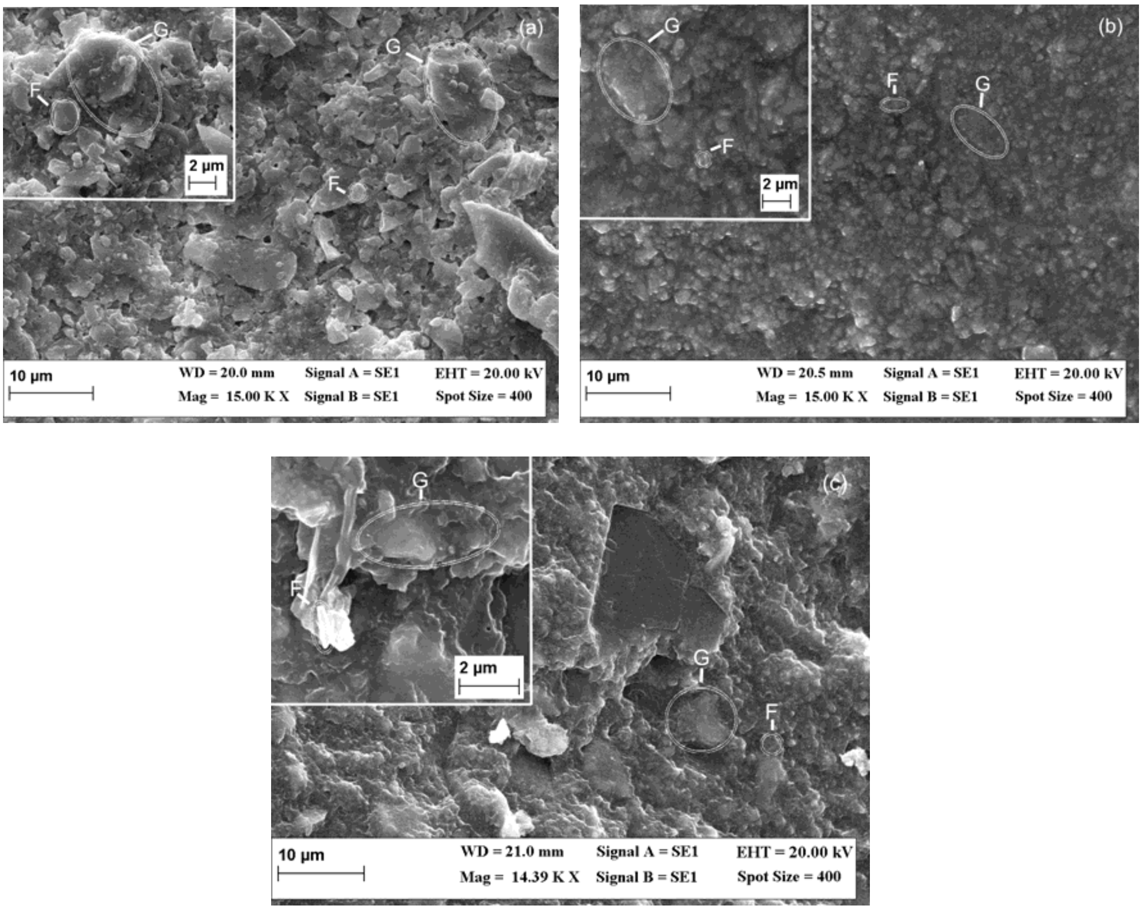


Fig. 3. SEM Micrographs, inset higher magnification. Details: grains (G), filler (F). Samples: (a) MaxcemElite, (b) Biscem, (c) RelyXU100.

4. Conclusions

By bonding a restorative material to tooth structure, the cavity is totally sealed, protecting the pulp, eliminating secondary caries and preventing leakage at the margins. This permits cavity forms to be more conservative and, to some extent, reinforces the remaining tooth by integrating restorative material with the tooth structures. We emphasize through the present study, that materials used as dental cements or RBC dental restorations must be more ‘engineering’ studied according clinical demands: interface adhesion to dentin/enamel and core structure. A model regarding RBC materials is predictable.

The three investigated RBC dental cements were almost similar regarding chemichal composition and sharing to organic respectively inorganic part. More engineering in modeling for more hydrophobic surfaces is requested. A key role is offered by polyvinylidene elastomer, based on fluorine.

Our results underline that a major problem of the studied samples, is homogeneity . A stiring method of RBC materials before application is requested.

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