Characterization of the Resin Luting Materials: Percentage, Morphology and Mechanical Properties

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Abstract

Aim: The purpose of this study was: 1) to determine the percentage of fillers by weight of the investigated materials by thermogravimetric analysis (TGA), to examine their fillers morphology using scanning electron microscopy (SEM), 2) and to evaluate the mechanical properties of these materials.

Methods: Seven luting materials (Rely X Unicem, Maxcem, Monocem, G-Cem, Panavia F2, Variolink II and Clearfil Esthetic Cement) and the micro-hybrid resin composite Clearfil AP-X (control) were evaluated. Thermogravimetric analysis (TGA) was used to determine the percentage of fillers by weigh and the fillers morphology was determined using scanning electron microscopty (SEM). Regarding mechanical properties, five specimens of each material were used to measure dynamic and static moduli of elasticity and Vickers microhardness.

Results: The percentage of fillers by weight ranged between 60% (Monocem) and 73% (Variolink II). For the micro-hybrid resin composite Clearfil AP-X used as control, the weight percentage of fillers was 83.5%.

Some values in this study were different from those given by the manufacturers. SEM photographs showed various shapes and sizes of inorganic fillers. Irregular shaped particles were found in Maxcem, Monocem and Variolink II. Rely X Unicem showed large irregular shaped filler aggregates. Irregular and spheroidal particles associated with aggregates were found in Panavia F2, Clearfil Esthetic Cement, G-Cem and Clearfil AP-X.

Variations in mechanical properties were observed within the tested materials.

Conclusion: Wide variations in morphology and percentage of fillers were observed between our TGA's data and those given by the manufacturers and will probably affect the mechanical properties of luting materials.

Keywords: Characterization; Fillers; Luting cements; Morphology; Percentage

Introduction

As an esthetic alternative to amalgam for the restoration of posterior teeth, resin-composites are being increasingly employed. Limitations regarding these materials concern limited strength, toughness and durability, although more recent formulations have better survival [1]. Despite these improvements, the effects of polymerization shrinkage remain a cause for concern. Thus, the use of indirect ceramic or resin composite restorations has increased thanks to their higher aesthetic properties and wears resistance [2]. Such restorations need to be cemented adhesively and various commercial luting materials are available for that purpose.

The behaviour of these luting cements partially depends on percentages, composition, dimensions and shape of their fillers. Several authors have demonstrated that mechanical properties are better correlated to the filler fraction of the resin composite [3-6]. Other authors studied the effect of fillers size and shape on mechanical properties [7,8].

The aim of this study was to characterize the inorganic fraction of luting materials regarding percentage and morphology of filler particles and to evaluate the mechanical properties of these materials. The null hypothesis is that there is no difference in fillers percentage between manufacturers and TGA's data among cements.

Materials and Methods

Seven commercial are listed respectively: Rely X Unicem, Maxcem, Monocem, G-Cem, Panavia F2, Variolink II and Clearfil Esthetic Cement. As control, the micro-hybrid resin composite Clearfil AP-X (Kuraray) was used.

The composite cements tested in this study are described in Table 1.

Luting cements, Manufacturer and batch number	Composition
RELYX UNICEM (Aplicap) 3M Espe, Seefeld, Germany *Lot 256677*	Powder: Glass fillers, silica, calcium hydroxide, self-curing initiators, pigments, light-curing initiators Liquid: methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing and light –curing initiators
MAXCEM Kerr, Orange, USA Lot 32857	Glycerol dimethacrylate dihydrogen phosphate (GPDM), co-monomers (mono-, di- and tri functional methacrylate monomers), self-curing redox activator, photoinitiator (camphorquinone), stabilizer, barium glass fillers, fluoroaluminosilicate glass filler, fumed silica
MONOCEM Shofu, Kyoto, Japan *Lot 060605*	Mono-, di and multifunctional acrylate resins, dual-initiators and fillers.
G-CEM GC, Japan *Lot 0608220*	Liquid: 4-MET, phosphoric acid ester monomer, water, UDMA, dimethacrylate, silica powder, initiator, stabilizer Powder: Fluoro-alumino-silicate glass, initiator, pigment
PANAVIA F2.0 Kuraray, Japan *Lot 41196*	Base: hydrophobic aromatic and aliphatic dimethacrylate, sodium aromatic sulphinate, N,N-diethanol-p-toluidine, sodium fluoride, silanized barium glass Catalyst: MDP, hydrophobic aromatic and aliphatic photoinitiator, dibenzoyl peroxide dimethacrylate, hydrophilic dimethacrylate, silanized silica
Clearfil Esthetic Cement Kuraray, Tokyo, Japan *Lot 41111*	Paste A: Bis-GMA, TEG-DMA, others methacrylate monomers, silanated glass filler, colloidal silica Paste B: Bis-GMA, TEG-DMA, others methacrylate monomers, silanated glass filler, silanated silica, colloidal silica, benzoyle peroxide, di-camphorquinone, pigments
VARIOLINK II Ivoclar-Vivadent, Schaan, Liechtenstein *Lot J22596*	BisGMA, UDMA, TEGDMA, barium glass fillers, ytterbium trifluoride, boroaluminofluorosilicate glass, spheroidal mixed oxide, catalysts, stabilizers, pigments
CLEARFIL AP-X *[Lot 000125]* (Shade A3)	

Abbreviations: Bis-GMA: bisphenol A glycidyl methacrylate; GPDM: Glycerol dimethacrylate dihydrogen phosphate; HEMA: Hydroxy ethyl methacrylate; 4-MET: 4-methacryloyloxyethyl trimellitic acid; 5-NMSA: N-methacryloyl 5-aminosalicylic acid; 10-MDP: 10-methacryloyloxy decyl dihydrogenphosphate acid; PENTA: dipentaerythritol penta acrylate monophosphate; TEGDMA: triethylene glycol dimethacrylate; UDMA: urethane dimethacrylate.
Table 1: Composition of the composite cements tested (technical information provided by the respective manufacturers)

Weight percentage of fillers

Thermogravimetric analysis (TGA) was used to determine the percentage of fillers by weight using a thermogravimetric Analyser (Perkin-Elmer TGA-7, USA). Weight changes were evaluated as a function of time and temperature during a thermal program ranging from 30 °C to 900 °C at the rate of 10 °C/min in normal atmosphere followed by air cooling to room temperature. The calculated ratio between the final weight of the sample and its nominal weight is assigned to the inorganic fraction. Three samples of each material were analyzed.

Fillers morphology

The fillers morphology was determined using scanning-electron microscopy (SEM). Unpolymerized monomers were removed by a washing technique [9]. A sample of 0.5 g of each material was dissolved in 4 ml of acetone and centrifuged for 5 seconds at 2000 rpm. This process was repeated three times using acetone and three others with chloroform for a further washing and elimination of the unpolymerized resin. The remaining filler particles including the prepolymerized fillers were placed in 3 ml of absolute ethanol and the suspension of filler particles was smeared on glass slide (7.5 x 2.5 cm) and dried at 37 °C during 6 hours. After gold-coating of the specimens (Leica EM ACE600, Germany), fillers were observed by SEM (Leica Stereoscan S-260, Cambridge, UK) at 5000x magnifications.

Mechanical properties

Five specimens of each material were prepared in moulds of 25 mm × 2 mm × 2 mm as specified in the ISO specification 4049 [10]. Samples were light-cured using two conventional curing devices (XL 3000, 3M-ESPE, St. Paul, MN, USA, 650mW/cm2) by overlapping irradiations for a total of 60 s on both sides. The same specimen was used to measure the following properties: dynamic and static moduli of elasticity and Vickers microhardness. Specimens were stored for 7 days in water at 37 °C before measurement.

Dynamic modulus

The dynamic modulus of elasticity was measured non-destructively by the impulse excitation technique [2]. Each sample was set in flexural vibration by a light mechanical impulse. The signal produced was captured via a microphone placed underneath the sample by a special signal analyzer, the Grindosonic (Lemmens Elektronics, Haasrode, Belgium). Modulus of elasticity (GPa) was calculated from the fundamental frequency (Hz), the mass (g), the width (mm), the length (mm), and the thickness of the bar (mm), as follows: [11]

$$E_d = 0.9465 \frac{m f_t^2}{b} \frac{L^3}{t^3} T_1$$

where m is the mass of the bar, b is the width of the bar, L is the length of the bar, t is the thickness of the bar, f_t is the fundamental frequency of the bar in flexion, which appears on the screen of the machine, and T_1 is a correction factor for fundamental flexural mode to account for finite thickness of the bar, Poisson's ratio and other constants. Poisson's ratio is the ratio of transverse strain (contraction) to axial strain (elongation) in a uniaxial tensile test [12]. When applied to dental resin composites, its value lies around 0.30, which has been taken as the mean value for all the materials tested in this study.

Static modulus

The static modulus was measured using a three-point bending setup according to the ISO-4049 specification [10]. Samples were loaded in an Instron machine (Instron 5566, High Wycombe, UK) at a speed rate of 0.75 mm/min until fracture occurred.

The load and the corresponding deflection were recorded and used to calculate the modulus (GPa) and the strength (MPa):

$E_s = Fl^3/4bh^3d$ [11].

where F is the load, l is the distance between the supports (mm), b is the width of the bar (mm), h is the thickness of the bar (mm), and d is the deflection corresponding to the load F.

Vickers microhardness

Microhardness measurements were carried out on the fractured samples issued from the previous test with a Durimet microhardness tester (Leitz, Wetzlar, Germany). A load of 200 g was applied during 30 s on their surface. The length of the diagonal of each indentation was measured directly using a graduated eye-lens. The Vickers Hardness Number is obtained using the following equation: $H = 1854.4 \times P/d^2$ where H is Vickers hardness in kg/mm^2, P is the load in grams and d is the length of the diagonals in μm [13].

Statistical analysis

Statistical analysis for all the mechanical properties was made using a one-way ANOVA and post hoc Scheffe's tests at $p < 0.05$ level. This was performed separately for each of the different mechanical properties.

Results

Percentage and morphology of inorganic fraction

The mean values and standard deviations of the size and percentage of fillers by weight are shown in Table 2 and Figure 1. They ranged from 43.0% for Monocem to 71.5% for Panavia F2.0. For the micro-hybrid resin composite Clearfil AP-X used as control, the weight percentage of fillers was 83.5%.

The SEM microphotographs are shown in Figure 2. Irregular shaped particles were found in Maxcem, Monocem and Variolink II. Rely X Unicem showed large irregular shaped filler aggregates. Irregular and spheroidal particles associated with aggregates were found in Panavia F2, Clearfil Esthetic Cement, G-Cem and Clearfil AP-X.

Mechanical properties

Mean values and standard deviations of the dynamic and static moduli of elasticity of the materials tested are shown in Table 3. Values of the dynamic moduli of elasticity for the luting materials varied between 6.62 GPa for Monocem to 9.79 GPa for G-Cem. The highest value (11.22 GPa) was obtained with the restorative resin composite (Clearfil AP-X).

Cements	Fillers percentage (SD)	Fillers percentage/weight	Fillers size
	(TGA)	(manufacturers)	
RelyX Unicem	68.3 (0.4)	72 %	< 9.5 μm
Maxcem	68.8 (1.9)	67 %	3.6 μm
Monocem	43.0 (2.8)	60 %	-
G-Cem	66.9 (0.9)	71.4 %	4 μm
Panavia F2.0	71.5 (1.8)	70.8 %	2 μm
Clearfil Esthetic Cement	69.9 (0.4)	70 %	2.5 μm
Variolink II	69.6 (3.0)	73 %	0.04-3.0 μ

Mean = 0.7 μm

Table 2: Fillers sizes and percentage of the composite cements tested (data obtained after thermogravimetric analysis (TGA) and technical information provided by the respective manufacturers)
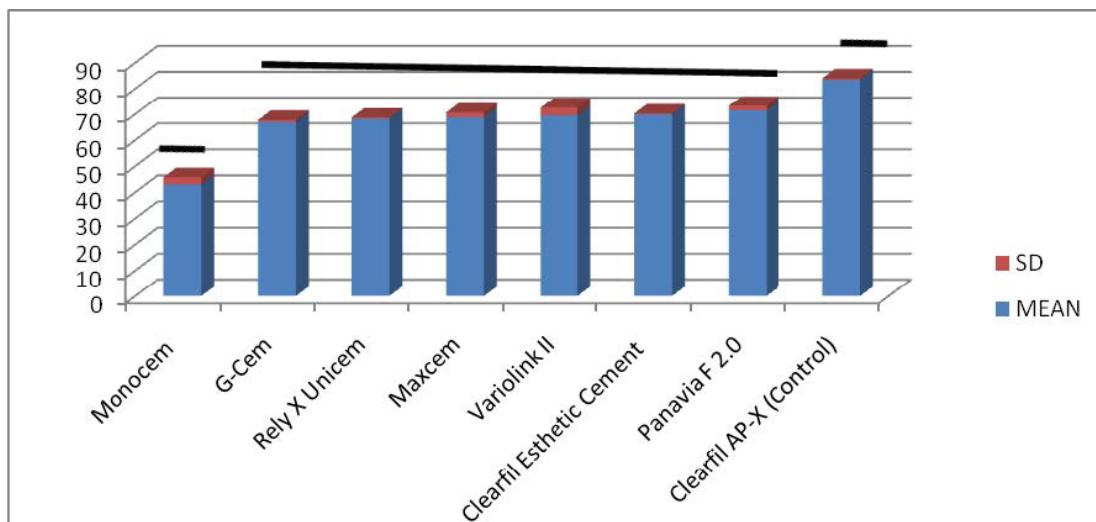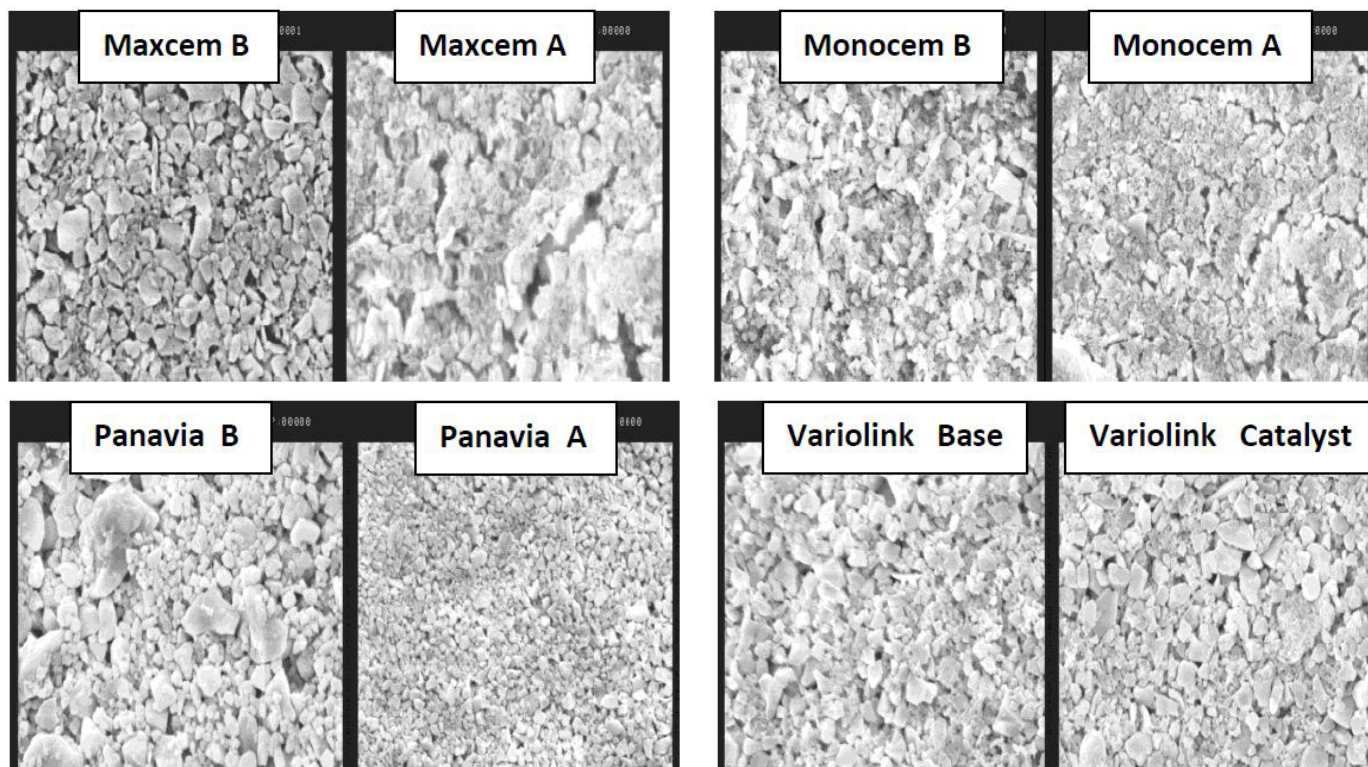

Figure 1: Mean values and SD of the percentage of filler by weight of the composites cements determined by TGA. (Horizontal bars connect values that are not statistically significant ($p < 0.05$))
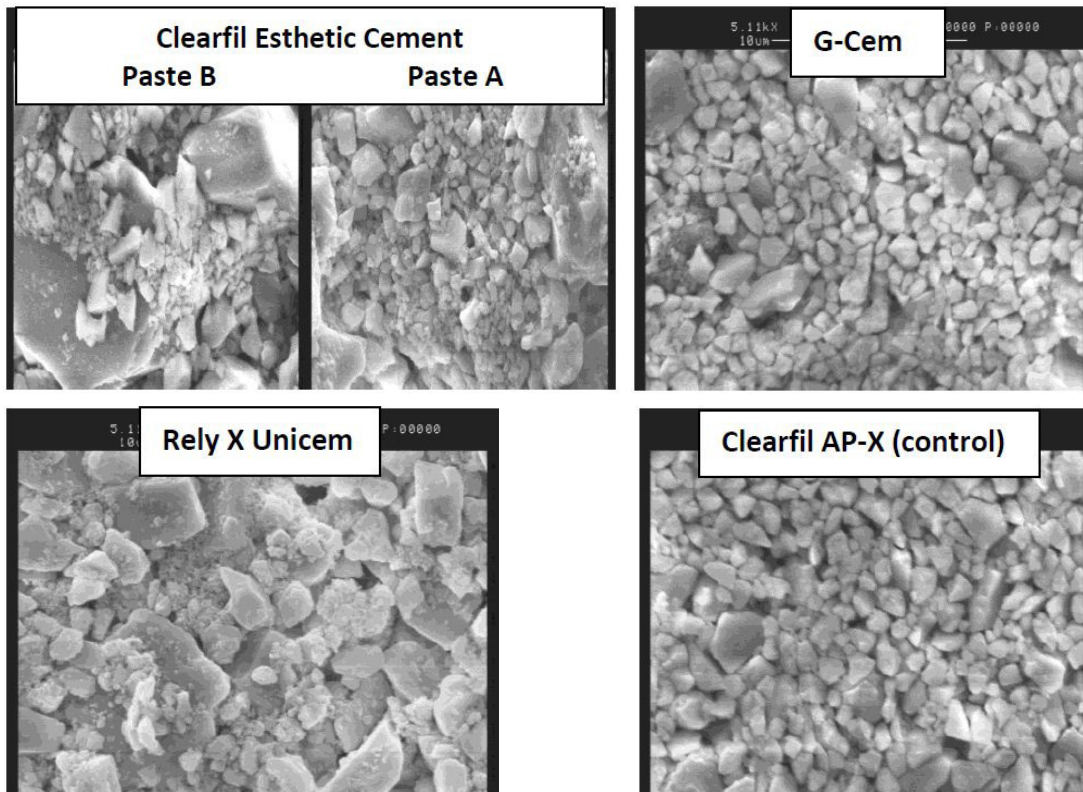
Figure 2: Fillers of studied luting cements by Scanning Electron Microscopy at 5000X magnifications

Cements	Dynamic moduli of elasticity		Static moduli of elasticity	
	Mean	SD	Mean	SD
Monocem	6.62[a]	0.341	17.99[f]	2.32
Maxcem	8.04[b]	0.325	24.36[g]	5.84
Variolink II	8.17[b]	0.149	26.66[g]	6.66
Panavia F2.0	8.32[b]	0.448	25.18[g]	5.03
Unicem	8.94[b]	0.112	13.47[e]	2.3
Clearfil Esthetic Cement	9.53[b]	0.444	35.09[h]	5.52
G-Cem	9.79[b]	1.016	9.70[d]	0.95
Clearfil AP-X	11.22[c]	0.192	50.49[i]	6.67

[a, b, c, d, e, f, g, h, i] statistical groups (Scheffe's tests at $p < 0.05$ level)

Table 3: Dynamic and static moduli of elasticity of the materials tested

Values for the static moduli of elasticity ranged from 9.70 GPa for G Cem to 35.09 GPa for Clearfil Esthetic Cement. Clearfil AP-X with a value of 50.49 GPa have the highest static moduli of elasticity.

The results for Vickers microhardness ranged from 17.20 for Monocem to 54.58 for Clearfil Esthetic Cement. Mean values and standard deviations are shown in Table 4.

Cements	Mean	SD
Monocem	17.20[a]	0.28
Maxcem	27.12[b]	2.42
Panavia F 2.0	27.56[b]	3.25
GCem	35.68[c]	7.08
Variolink II	45.52[d]	2.05
Unicem	50.44[e]	4.05
Clearfil Esthetic Cement	54.58[e]	5.07
Clearfil AP-X	105.00[b]	1.41

[a, b, c, d, e] statistical groups (Scheffe's tests at $p < 0.05$ level)

Table 4: Vickers microhardness of the materials tested

Discussion

Filler load

The use of thermogravimetric analysis (TGA) is a good method to determine the filler load in weight of dental resin composites, as demonstrated by several authors [12,13]. This method consists on heating the specimens gradually under air flow with a cycle of 20 ± 5 °C.min^{-1} to 725 °C or 800 °C [14,15]. This procedure allows a precise follow-up of the disintegration of each organic component [11].

The TGA technique was used in our study in order to determine the inorganic fraction of tested cements. Different others authors used the ashing in air technique which is based on the elimination of the organic fraction of the composite by heating at a constant temperature [4,16-18]. The stable patterns observed with TGA curves after 750 °C allowed us to validate this technique which can be a good alternative to ashing in air technique.

The percentages of fillers vary widely among the cements. In some cases, differences were found between our TGA's data and those given by the manufacturers. One possible explanation is variable layer thickness and amount of silane. Indeed, manufacturers functionalize the particles' surface according to their own proprietary methods and use different methods to measure the percentage of fillers. Some manufacturers seem to assess the percentage of fillers by weight before the silanization process of the fillers while others include the percentage of silane coating in their calculations [16].

Our results showed that our TGA percentages are generally close to those given by manufacturers while differences were noticed for some of the resin cements. This was the case for GCem (-5%) and Monocem (-17%).

Filler shape

Most filler particles are of irregular shape. Irregular shaped particles were found in Maxcem, Monocem and Variolink II. Bayne, *et al.* showed that spherical shape is known to allow an increased filler load in resin composites [19]. According to Suzuki, *et al.* spherical shaped particles contribute to enhance fracture strength of these materials as compared with irregularly shaped ones since mechanical stresses tend to concentrate on the angles and protuberances of the particles [20]. Rely X Unicem contains large filler aggregates while Panavia F2, Clearfil Esthetic Cement, G-Cem and Clearfil AP-X present combinations of irregular and spheroidal particles associated with aggregates. Clinically, the liquid and powder forms prepared by manually mixing the cements were found to cause greater porosity [21]. This situation can be observed for Panavia F2, Clearfil Esthetic Cement and variolink II which are prepared by mixing equal amount of paste A and B while the others are presented in capsule.

Mechanical properties

An ideal dental material should mimic structural, mechanical and physical characteristics of dentin and enamel [6]. Luting cements, as an interface between a tooth and another restorative material, should of course behave as close as possible like tooth tissues. Xu, *et al.* measured the elastic modulus of human enamel and dentin and obtained a mean value of 19 GPa for the dentin [22]. Young's modulus of enamel was 94 GPa while depending significantly on tooth orientation. The mechanical properties of all the cements tested in this study are far from those of enamel and dentin.

Since the cement properties are very close to those of composite, we can hypothesize that, like resin composite, cement with high mechanical properties (i.e. modulus of elasticity, flexural strength, tensile strength and fracture toughness) would better resist to occlusal loads than cement with low mechanical properties.

In our study, Clearfil AP-X shows the higher Vickers microhardness followed by Clearfil Esthetic Cement and Unicem. These findings are in accordance with Sabbagh, *et al.* who showed that hardness may be influenced by degree of set of the organic phase as well as by its filler content [2]. The author found high correlation between the percentage of fillers by weight and the hardness, which explains the low values obtained with lower filled composites. In our study, the same correlation is found with the lower filled cement Monocem (60% of filler by weight, 43% by TGA) which showed lower Vickers Microhardness. In addition, Clearfil Esthetic Cement revealed few and short resin tags formation at TEM and SEM bonding interface analyses [23].

Regarding the dynamic elastic moduli, values ranged from 6.62 GPa to 11.22 GPa. The Clearfil AP-X (control) showed the highest value. No statistically significant differences were found between materials except for Monocem.

For static elastic moduli, considerable differences were found between the materials. The values ranged between 9.70 for G-Cem and 50.49 for Clearfil AP-X. Wide variations in elastic moduli were found for some cements. This is the case for GCem which showed among the best dynamic moduli and worst static moduli. The clinical behavior of this cement may be affected by this fact and this should be taken into account during their use. Peumans, *et al.* reported that the percentage of adhesive failures is higher for CAD/CAM materials with higher flexural strength [24].

The composition and the storage media affected significantly the sorption and solubility behavior of the cements. Thus, as hydrophobic resin cement with higher filler content showed the least sorption and solubility these types of resin-based luting cements are recommended to be used clinically [25].

The null hypothesis stating that there is no difference in fillers percentage between manufacturers and TGA's data among cements must be accepted excepted for G-Cem and Monocem Limitation of this study is the lack of informations regarding manufacturers procedures of silanization.

Conclusion

Within the limitations of this study, the following conclusions could be retained:

a. The percentages of fillers vary widely among the cement and for some cements, differences were found between our TGA's data and those given by the manufacturers.
b. Filler shapes are irregular or spheroidal associated with aggregates.
c. Variations in filler percentage and morphology were found among some of the tested materials and will probably affect the mechanical properties of luting materials.
d. Studies should be conducted between shape and percentage of fillers by weight and the mechanical properties of resin cements.

Acknowledgements

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