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Inorganic characterizations and filler particles morphology of self-adhesive cements

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ABSTRACT

This study evaluated the thermal and morphological filler characteristics of self-adhesive resin cements. The cements (Embrace WetBond, MaxCem Elite, Bifix SE, G-Cem, and RelyX U200) were manipulated according to the manufacturers' instructions. Thermogravimetric analysis and differential thermal analysis were performed to obtain the glass transition temperature (T_g) and weight loss. Specimens were also obtained to characterize the zeta potential, the mean particle size and distribution, and the polydispersity by dynamic light scattering. An elemental analysis of the fillers was also conducted using X-ray spectroscopy analysis and micromorphology under SEM. MaxCem Elite contained the least organic matrix, followed by G-Cem, Bifix SE, RelyX U200, and Embrace WetBond. Bifix SE presented the highest T_g and G-Cem the lowest. Bifix SE presented the broadest filler size distribution, exhibiting lower zeta potentials and mobility. G-Cem was found to be a highly filler loaded cement with the lowest effective diameter, highest zeta potential and mobility. RelyX U200 presented chromium in the composition and G-Cem presented fluorine. Differences in the nature and chemistry of inorganic fractions seemed to dictate the morphology of the filler content and also the thermal behavior of the materials tested and, may consequently influence the clinical performance of self-adhesive resin cements.

1. Introduction

Filler load and consequential mechanical and physical properties of dental composite materials can be partly related to the nature of the particles [1]. The incorporation of filler particles into a resin matrix and filler characteristics (i.e., radiopacity, filler distribution, shape, and size) changes the physical properties, such as elastic modulus, compressive and tensile strength [2,3]. Thus, the size of the inorganic fractions is a valuable indicator of quality and performance of composite materials [4]. Specifically for luting cements, not only is the relative size and shape distribution of the powder particles important for the viscosity of the cement, but also different packing densities can be achieved with an appropriate selection of the particle format and size [5]. Different parameters such as particle size, viscosity, fillers, and polymerization reactions may also affect the film thickness of resin cements [6]. The rheological properties of the material influence its handling characteristics, for example, the cement must flow readily under pressure to form a thin film [7]. In addition, the amount of fillers and their influence in the decrease of the mobility of polymer radicals have been associated with the decrease of the reactivity of monomers, impacting the polymerization process [8]. In this way, it is suggested that a practical limit to the amount of filler particles in resin cement formulations must be far less than the densest pack limit possible [9].

Resin cements are low-viscosity composites, containing reduced filler content and a resin matrix based on different monomers, such as Bis-GMA, TEGDMA, and methacrylates [10]. Other components like glasses and/or ceramic fillers that contain chemical elements such as barium, strontium, and zirconium can be added to provide radiopacity characteristics [11]. Resin cements have shown improved properties with the incorporation of fillers and also because of the bonding established between fillers and the resin matrix, which is provided by

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a silane coupling agent [2]. It has also been claimed that the fillers play an important role in the self-adhesive resin cements, materials that require no technique-sensitive steps such as acid-etching, priming, and bonding [12], as the initial low acidity of the cement is quickly neutralized during the polymerization process in part due to the chemical interaction of the phosphoric acid groups with the basic inorganic fillers [13,14].

The aim of this study was to investigate and compare thermal characteristics of commercial self-adhesive resin cements. Thermogravimetric analysis and differential thermal analysis were performed to obtain the glass transition temperature (T_g) and weight loss. The inorganic fractions were morphologically characterized using scanning electron microscopy at different magnifications with the respective elemental mapping. Filler morphology was also investigated for their effective diameter, volume, number, zeta potential (colloidal stability), mobility, and polydispersity using dynamic light scattering analysis.

2. Materials and methods

2.1. Experimental design

In this in vitro study, thermal and morphological characterizations of five commercial self-adhesive resin cements were performed, including Embrace WetBond, MaxCem Elite, Bifix SE, G-Cem, and RelyX U200. The characteristics of the resin cements selected are described in Table 1.

2.2. Characterization of the self-adhesive resin cements by thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were simultaneously used for thermal characterization of the selected cements. Approximately 60 mg of each SARC, photoactivated according to the manufacturers' instructions, was placed in standard NETZSCH alumina 85 μL crucibles attached to the thermoanalytical unit (TGA-50 Netszch-Thermische Analyse, Selb, Germany) with a TA System Controller (TASC 414/2), a temperature range of 50–800 °C, at a heating rate of 10 °C/min, and under dynamic nitrogen atmosphere (50 mL/min). TGA measured the change in mass of the cements as a function of temperature. In DTA, the cement and the inert reference underwent identical thermal cycles, while recording any temperature differences between the specimens and the reference. This differential temperature of the cements was plotted against the heating. Changes in the temperature of the specimens, either exothermic or endothermic, were detected relative to the reference. The baseline to correct the thermo-analytical curves of the specimens was also performed for both analyses using empty alumina crucibles under the same experimental conditions.

The glass temperature (T_g), defined as the temperature at half the height of the step (midpoint temperature, $T_{g\ midpoint}$) according to the German norm DIN 53765, was also determined by means of extending straight lines along the left-hand and right-hand branches of the heat flow curves. T_g was then obtained from the point of intersection of the bisecting lines with the measured curves [15,16].

2.3. Particle size and polydispersity index measurement by phase laser light scattering

10 mg of uncured resin cements was diluted in 1.5 mL of absolute ethanol (G.R.). The diluted sample was centrifuged at 3.000 rpm (*g* force of 1.000*g*) for 5 min and the resulting pellet was suspended in absolute ethanol using the same volume of ethanol and centrifuged again. This process was repeated twice. The ethanol was then discarded and the pellet containing the filler particles was suspended in 1.5 mL of a 0.001 mol% KCl solution [17,18]. A fraction of 10 μL of the liquid suspension was deposited in a 3.00 mL KCl solution in a 3 cm^3 polystyrene cuvette with a path length of 10 mm and analyzed by dynamic light scattering (DLS, 90 Plus, Brookhaven Instruments Corporation, Holtsville, New York, USA). The filler particles' size distribution (number and volume in nm), the effective diameter (in nm), and the polydispersity index of each resin cement were then obtained. Ten replications for each resin cement were evaluated ($n=10$).

Table 1
Self-adhesive resin cements characterized in the present study.[a]

Material	Lot no./Expiration date	Composition	Working time (min)	Setting time (min)	Curing time (s)	Filler content W(%)V (%)
Embrace WetBond	130711	Co-monomers (mono-, di-, and tri-functional methacrylate	2	3	40	36.6
Pulpdent Corporation, Watertown, MA, USA	2015-07	monomers, Barim, glass, ytterbium trifluoride, inert minerals.) Automix system.				39.0
MaxCem Elite	5011290	GPDM, co-monomers (mono-, di-, and tri-functional	1	4	10–20	69.9
Kerr Corporation, Orange, CA, USA	2015-03	methacrylate monomers, water, acetone, and ethanol. Inert minerals and ytterbium fluoride.) Automix system.				46.0
Bifix SE	1322421	Bis-GMA, UDMA, Gly-DMA, phosphate monomers, initia-	2	4	10–20	70.0
Voco GmbH, Cuxhaven. Germany	2014-12	tors, stabilizers. Glass. Automix system.				45.0
G-Cem	1308051	Dimethacrylates, 4-META, UDMA, Phosphoric ester mono-	2′ 30	4	10	71.0
GC Corporation, Tokyo, Japan	2015-08	mer, water; silica powder; Fluoro-alumino-silicate glass (amorphous), camphorquinone. Capsule.				56.6
RelyX U200	1329500659	Base: Methacrylate monomers containing phosphoric acid	2	6	20	
		groups, methacrylate monomers, initiators, stabilizers, rheological additives.				
3M ESPE,	2014-12	Catalyst: Methacrylate monomers, alkaline fillers, silanated				72.0
St. Paul, MN, USA		fillers, initiator components, stabilizers, pigments, rheological additives. Zirconia/silica fillers. Clicker delivery system.				43.0

Abbreviations: Bis-GMA: bisphenol A diglycidyl ether dimethacrylate; UDMA: Urethane dimethacrylate; Gly-DMA: glycerol dimethacrylate; GPDM: glycero-phosphate dimethacrylate.

[a] Manufacturers's information.