Original Research
Dental materials

Physicomechanical and thermal analysis of bulk-fill and conventional composites

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Abstract: The aim of this study was to evaluate the degree of conversion (DC) and the thermal stability of bulk-fill and conventional composite resins. Eleven composite resin samples were prepared to evaluate the DC, Vickers microhardness (VMH), mass and residue/particle loss, glass transition temperature (Tg), enthalpy, and linear coefficient of thermal expansion (CTE) using infrared spectroscopy (FTIR), microdurometer analyses, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and dilatometry (DIL). The data were subjected to statistical analysis, with a significance level of 95%. DC and VMH were not influenced by the polymerized side of the sample, and statistical differences were recorded only among the materials. Decomposition temperature, melting, and mass and residue loss were dependent on the material and on the evaluation condition (polymerized and non-polymerized). Tg values were similar between the composites, without statistically significant difference, and CTE ranged from 10.5 to 37.1 (10^{-6}/°C), with no statistical difference between the materials. There was a moderate negative correlation between CTE and the % of load particles, by weight. Most resins had a DC above that which is reported in the literature. TGA, Tg, and CTE analyses showed the thermal behavior of the evaluated composites, providing data for future research, assisting with the choice of material for direct or semidirect restorations, and helping choose the appropriate temperature for increasing the DC of such materials.

Keywords: Dental Materials; Composite Resins; Transition Temperature; *In Vitro* Techniques.

Introduction

Composite resins have been widely used in the restoration of anterior and posterior teeth. Conventional techniques use increments of up to 2 mm to allow for adequate polymerization and to avoid adverse reactions in the postoperative period. Nevertheless, the incremental insertion technique can cause inconveniences such as polymerization shrinkage inherent in the curing process of methacrylate-based composites, eventually leading to dental cracks, marginal leakage, and postoperative sensitivity.[1] In order to optimize restorative procedures in posterior teeth, bulk-fill resins emerged with the single-step incremental insertion proposal, ranging from 4 to 6 mm^2 in thickness, or two-step insertion, considering a bulk-fill flow for the base, covered with a restorative resin.[2] Thus, the use of these materials in clinical practice considerably decreases chair time in direct restorations of posterior teeth.[3]

Bulk-fill resins been used in clinical applications worldwide, especially because of favorable scientific have evidence concerning their effectiveness. The literature points out numerous studies showing that bulk-fill resins offer better usage conditions,[4] and this is associated with the use of new fillers or possibly photoinitiators, which contribute to increasing translucency, allowing greater penetration of light;[5] with the use of rheological modulators, which minimize polymerization shrinkage stress;[6] with the insertion of a high viscosity material aided by the emission of sonic waves, which increases fluidity and improves marginal adaptation;[7] with the modification of the inorganic phase using reinforcement fibers, applied to some bulk-fill material, which provides restorations with greater resistance.[8]

Regarding physicochemical and thermal properties, there is much to study and research, so that we can have scientific evidence about the most suitable composite to be chosen for direct or semidirect restorative procedures. Application of heat is an additional method used to increase the physicomechanical properties of composites. The heat assists in the final degree of conversion (DC), reduces polymerization shrinkage stress, acts as a homogenizer, and improves the mobility of monomers.[9] On the other hand, when resins are heated until they reach Tg and undergo a slow cooling process, the polymer chains have more time to settle in an orderly and more compact way, favoring hardness properties. However, in the mouth, resins must have low thermal conductivity in order to prevent damage to the pulp tissues and a coefficient of thermal expansion (CTE) similar to that of the dental structure to prevent loss of adhesion, crevice formation, marginal infiltration and, consequently, secondary caries.

Given the innovative nature of bulk-fill composites, the short length of time they have been available in the market, and the paucity of long-term clinical studies,[10] the objective of this study was (a) to evaluate DC using FTIR and Vickers microhardness (VMH); (b) to evaluate degradation and thermal stability considering the extrapolated onset temperature, mass loss, and the weight percent of load particles using thermogravimetric analysis (TGA); (c) to determine glass transition, melting, and degradation temperatures, and enthalpy using differential scanning calorimetry (DSC); and (d) to evaluate the linear coefficient of thermal expansion (dilatometry).

The null hypotheses tested were as follows: a) the DC and VMH would not be influenced by the polymerized side of the sample and between the materials; v) degradation and thermal stability would not depend on the material and on the evaluation condition; c) there would be no significant differences in the CTE between the evaluated materials.

Methodology

Materials and sample preparation

Eleven resins (Table 1) were evaluated in this study: nine bulk-fill composites –Aura Bulk Fill (SDI, Australia), Filtek Bulk Fill Flow (3MESPE, Germany), Filtek Bulk Fill Sculptable (3MESPE, Germany), Surefil SDR + (Dentsply, Germany), Tetric EvoFlow Bulk Fill (Ivoclar-Vivadent, Liechtenstein), Admira Fusion (Voco, Germany), X-tra Fil (Voco, Germany), X-tra Base (Voco, Germany), Opus (FGM, Brazil), and two conventional resins – Filtek Z350XT (3MESPE, Germany) and Filtek Z350 Flow (3MESPE, Germany).

For energy-dispersive X-ray spectroscopy (EDS), DC, and VMH analyses, specimens obtained from each material, measuring 5 mm in diameter and 4 mm in thickness, were prepared. In order to prevent oxygen inhibition, a transparent polyester strip was placed on the top and bottom of the mold, and resins were inserted and photopolymerized with a LED device (KaVo Poly Wireless, KaVo - Brazil) in compliance with the manufacturer's instructions (Table 1). The light-curing unit was calibrated at 1,200 nW/cm^2 and irradiance was measured using a radiometer. All specimens were stored in distilled water at 37°C for 24 h prior to testing. For the linear CTE, the samples measured 10 mm in diameter and 4 mm in thickness.

Table 1. Test materials and manufacturer's information.

Code	Material and manufactured batch no	Monomers	Fillers	Photoinitiators/ Coinitiators	Shade	Thickness (mm)/Curing time and light intensity
ABF	Aura bulk fill (SDI, São Paulo, Brazil) – 150931	n.i	n.i	n.i	U	4 mm/20s ≥ 1,000 mW/cm^2 (LED) or 2x20s (halogen light).
FBFF	Filtek Bulk Fill Flow™ (3M/ESPE St. Paul, MN, USA) – N735392	Bis-GMA, UDMA Bis-EMA Procrylat	Ytterbium trifluoride Zirconia/silica - 64wt %, 42.5 vol	n.i	A2	4 mm/20s ≥ 1,000 mW/cm^2 or 40s 550–1,000 mW/cm^2 (halogen or LED)
FBFS	Filtek Bulk™ Fill Sculptable (3M/ESPE St. Paul, MN, USA) – N686825	Bis-GMA, AUDMA UDMA DDDMA	Silica, zirconia, ytterbium trifluoride, zirconia/silica – 76.5wt%, 58.4 vol	n.i	A2	4 mm/20s ≥ 1,000 mW/cm^2 (LED) or 40s 550–1000 mW/cm^2 (halogen light).
SDR$^+$	SureFil® SDR$^+$ Flow ™ (DENTSPLY Petropolis, Brazil) – 160613	Modified UDMA EBPADMA TEGDMA	Barium and strontium fluoro-alumino silicate glasses - 68 wt%, 44 vol%	Camphoroquinone (CQ), BHT, UV Stabilizer, Titanium dioxide, iron oxide pigments, Fluorescing agent	U	4 mm/20s 500–1,000 mW/cm^2 (LED and halogen) or 10s (high-power lights).
AF	Admira Fusion x-tra (VOCO Cuxhaven, Germany) – 1619518	n.i	Inorganic fillers - 84wt%	n.i	U	4 mm/20s ≥ 800 mW/cm^2 or 40s 500–800 mW/cm^2
TEF	Tetric EvoFlow Bulk Fill® (IVOCLAR VIVADENT Amherst, NY, USA) – U41169	Bis-GMA Bis-EMA UDMA	Prepolymer fillers, barium glass filler, ytterbium fluoride and spherical mixed oxide fillers - 62.5 wt%, 60 vol%	Camphorquinone / amine Highly reactive, patented Ivocerin light initiator	U	4 mm/20s ≥ 600 mW/cm^2 10s ≥ 1,000 mW/cm^2
XTB	X-tra Base (VOCO Cuxhaven, Germany) – 1621410	n.i	Inorganic fillers - 75wt%, 58 vol%	n.i	U	4 mm/ 10s ≥ 800 mW/cm^2 or 20s 500–800 mW/cm^2
XTF	X-tra Fill (VOCO Cuxhaven, Germany) – 1547611	Bis-GMA, UDMA, TEGDMA	Inorganic fillers - 86wt%, 70,1 vol%	n.i	U	4 mm/ 10s ≥ 800 mW/cm^2 or 20s 500–800 mW/cm^2
Opus	OPUS Bulk Fill Flow (FGM Joinville - SC - Brazil) – 010816	Monomers Urethane dimethacrylate	Silicon dioxide (silica) silanized	Camphorquinone	A1	4 mm/ 20s ≥ 450 mW/cm^2

Continue

Continuation

Z350F	Filtek Z350 XT Flow™ universal restorative (3M ESPE, St Paul, MN, USA) – 1605300512	BisEMA, TEGDMA, Procrylat K	Terbium and silica fluoride Silica / zirconia - 65wt%, 46vol%	n.i	A2	2 mm/ 20s 500–1,000 mW/cm^2 (LED and halogen) or 10s (high-power lights).
Z350	Filtek™ Z350 XT universal restorative (3M ESPE, St Paul, MN, USA) – 236236	UDMA, BisEMA, BisGMA, TEGDMA, PEGDMA	Silica, zirconia, silica/ zirconia – 72.5wt%, 55.6 vol%	n.i	A2	2 mm/ 20s ≥ 400 mW/cm^2 (LED or halogen).

UDMA: urethane dimethacrylate, Bis-GMA: bisphenol A glycidyl methacrylate, Bis-EMA: ethoxylated bisphenol A glycol dimethacrylate, EBADMA: ethoxylated bisphenol A dimethacrylate, EDMAB: ethyl-4-dimethylaminobenzoate, DDDMA: 1,12-dodecane-DMA, TEGDMA: Tetraethyleneglycol Dimethacrylate, PEGDMA: Poly(ethylene glycol) diacrylate. n.i: without manufacturer's information.

Physicomechanical analysis

Identification of chemical elements in EDS

The specimens were cleaned in an ultrasonic tank at 50ºC for 5 min and then washed with distilled water and dried at room temperature (30 min). Afterwards, the samples (n = 3) were subjected to EDS (PHENOM pro X, Scientific ANACOM) to determine the chemical elements present at the point of the beam incidence. Three areas of each sample were selected for reading. The samples received no surface treatment for preview.

Degree of conversion

The non-polymerized material and the top and bottom surfaces of the photopolymerized samples (n = 3) were analyzed after 24h by an FTIR spectrophotometer (Perkin Elmer, Norwalk, CT, USA) equipped with attenuated total reflection (ATR) wavelength between 4,000 and 650 nm. Thirty-two scans were performed on each sample (n = 3) with a resolution of 2.0 cm^{-1}. Peak heights of 1,637 cm^{-1} (double bonds of aliphatic carbon) and 1,608 cm^{-1} (double bonds of aromatic carbon) were measured using the normalized baseline method on the same equipment and the % DC values of the monomers were determined by the following equation:

$$\%DC = \left[1 - \left(\frac{\frac{1637\ \text{cm}^{-1}}{1608\ \text{cm}^{-1}}\ \text{Peak height cure}}{\frac{1637\ \text{cm}^{-1}}{1608\ \text{cm}^{-1}}\ \text{Peak height uncure}}\right)\right] \times 100$$

Vickers microhardness

Although some studies indicate Knoop microhardness as the most suitable method for testing composite resins, others advocate the use of VMH. The Knoop indenter penetrates less deeply. Especially in composite resins with irregular surfaces, because of the presence of charge particles, VMH allows obtaining more reliable results, despite possible interference from elastic deformation. The VMH test was performed using a digital microdurometer (FM 700, Future Tech Corp., Equilam, Tokyo, Japan) with a load of 50 kgf applied for 15 s. Three readings were performed at the top and bottom (4 mm), obtaining a final mean for each sample (n=5). The length of the diagonals (d1 and d2) left by the indenter was measured digitally under a light microscope coupled to the microdurometer.

Thermal analyses

Thermogravimetric analysis

TGA was performed in a thermogravimetric analyzer (SDT 2960 - TA Instruments). As polymerization parameters, polymerized and non-polymerized samples (10 mg, n = 3) were heated from 25°C to 600°C, considering a heating rate of 10°C/min and a nitrogen flow of 200 mL/min. Proteus software was used to generate TGA curves and calculate the percentage of mass loss, the amount (%) of residues after decomposition, and thermal stability. The extrapolated onset decomposition temperature, according to ASTM E794-06 and E793-06 (American Society for Testing and Materials), was determined for each material.

Differential scanning calorimetry

For the DSC analysis (DSC, Perkin Elmer), the polymerized samples (10 mg, n = 3) were subjected to a heat flow ranging from 25ºC to 45 ºC, at a heating rate of 10ºC/min^{-1}, in a nitrogen atmosphere. An identical and empty aluminum capsule was used as reference. The data provided in graphs were analyzed using the software – (NETZSCH-TA4_5 Proteus Software, Netzsch, D). The glass transition temperature (Tg), the melting and degradation temperatures, and enthalpy (ΔH) were obtained.

Linear thermal expansion analysis

The analyses were performed using a differential horizontal dilatometer (NETZCH DIL 402 C, Selb, Germany) with 3% of accuracy. The CTE and the linear CTE were measured in the temperature range of 27 to 100°C with variation of 4°C/min. The values were obtained by the following equations:

$$\Delta L - L_0 \,.\, \alpha \,.\, \Delta T \qquad \text{CTE}_{\text{Linear}} = \frac{\Delta L}{L_0 \,.\, \Delta T}$$

Where,

ΔL: linear dilation;

L_0: initial length;

α: linear coefficient of expansion;

ΔT: temperature variation.

CTE: coefficient of thermal expansion

Before the experimental test, the equipment was calibrated with silica and an initial scan was performed.

Statistical analysis

Statistical analysis was performed using Statistical Software 2007 (Utah, USA), SPSS version 23. In addition to standard descriptive statistics (mean and standard deviation), the F-test (ANOVA) with post-hoc Tukey's test was used when the variances were equal, or Tamhane test when the hypothesis of variance was rejected. VMH and DC were analyzed by the Wilcoxon test for paired data, Kruskal-Wallis test with paired comparisons between DC and VMH, and by means of the Mann-Whitney test. Regression analysis was performed to investigate the relationship between % DC and VMH according to the evaluated surfaces; % DC and Tg; weight % of residues/load particles after TGA and microhardness, and between these and % DC. Regression analysis was carried out to investigate the relationship between Tg and onset temperature, mass loss, and final residue quantity. The level of statistical significance was set at 0.05.

Results

Physicomechanical analysis

Identification of chemical elements (EDS)

EDS analysis showed that silica (Si) was the predominant compound in all materials. It was possible to identify components such as Ba, Zr, Al, F, Ca, and Sr, among others (Figure 1).

Degree of conversion and Vickers microhardness

The resins showed no significant difference in % DC and VMH. Statistical differences were observed only among materials (Table 2). AF, FBFS, and XTF resins showed the highest DC on the top surface (99%, 98%, and 90%, respectively), while Z350F obtained a lower conversion (57%). On the bottom surface, ABF presented lower conversion (20%). Regarding microhardness, Z350 and XTF presented significantly higher values than the other resins (Table 2). A low positive correlation was found between DC and VMH, according to the evaluated surfaces. Data also show a moderate correlation (r = 0.64) between the weight % of residues/load particles after TGA and microhardness and a low correlation (r = 0.49) between these and DC (Figure 2). The coefficient of correlation between % DC and Tg was low (r = -0.37).

Thermal analysis

TGA and DSC

TGA results are shown in Table 3. The final weight percent of the residues/load particles ranged from 60.1 (Z350F) to 87.1 (AF) in the non-polymerized material and from 33.4 (FBFF) to 87.0 (AF) in the polymerized material. Mass loss (m%) was higher in Z350F and FBFF, without polymerization and with polymerization, respectively, and FBFF showed a greater mass loss (57.7%) before reaching the peak of the initial decomposition temperature. The other materials presented similar mass loss to each other.

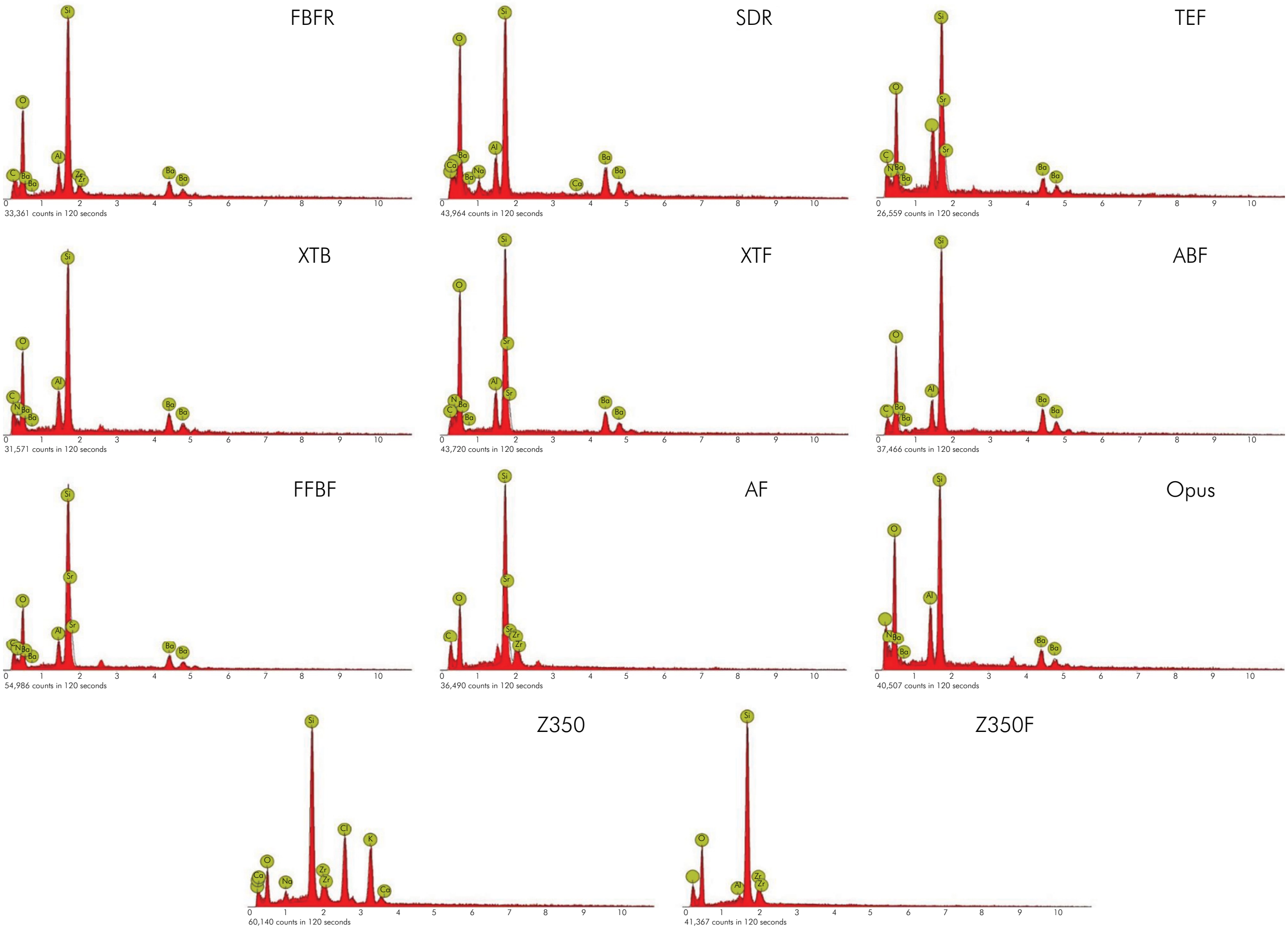

Figure 1. Representative EDS images of bulk-fill dental composites. Chemical elements present in each sample, obtained by EDS analysis.

Table 2. Mean ± standard deviation of the degree of conversion and Vickers microhardness according to the material and to the polymerization side of the specimen.

Material	Degree of conversion (% DC)			VMH (Kg/f)		
	Top	Bottom		Top	Bottom	
AF	99.0 (0.51) $^{(A)}$	58.97 (15.3) $^{(ACGH)}$		92.92 (14.5) $^{(A)}$	87.67 (12.0) $^{(AD)}$	
ABF	77.1 (1.08) $^{(B)}$	20.70 (7.19) $^{(B)}$		76.33 (8.26) $^{(AD)}$	63.41 (9.26) $^{(EFHI)}$	
FBFS	98.0 (0.20) $^{(AC)}$	56.17 (2.01) $^{(AB)}$		80.73 (3.28) $^{(A)}$	74.81 (3.97) $^{(AB)}$	
SDR^{+}	85.9 (1.74) $^{(BD)}$	66.70 (1.84) $^{(CEIJ)}$		74.21 (10.3) $^{(BD)}$	69.07 (11.5) $^{(BE)}$	
TEF	74.3 (1.22) $^{(E)}$	64.33 (2.14) $^{(ACI)}$	$p^{(1)} > 0.05$	59.49 (11.0) $^{(C)}$	52.63 (9.52) $^{(C)}$	$p^{(1)} > 0.05$
Opus	72.2 (4.33) $^{(E)}$	67.13 (2.60) $^{(CDEIL)}$		62.27 (6.42) $^{(C)}$	55.15 (9.04) $^{(CH)}$	
XTB	75.0 (0.40) $^{(E)}$	68.77 (1.83) $^{(FI)}$		87.32 (7.88) $^{(C)}$	70.05 (11.4) $^{(BI)}$	
XTF	90.5 (3.31) $^{(CD)}$	75.37 (2.75) $^{(FL)}$		152.87 (14.0) $^{(E)}$	145.69 (8.70) $^{(G)}$	
Z350	64.6 (1.35) $^{(F)}$	58.73 (2.96) $^{(AJM)}$		112.02 (4.60) $^{(E)}$	104.00 (6.02) $^{(DG)}$	
Z350F	57.3 (0.91) $^{(F)}$	54.77 (0.50) $^{(BGM)}$		60.37 (4.15) $^{(BD)}$	50.76 (6.29) $^{(C)}$	
FBFF	72.3 (4.22) $^{(E)}$	67.53 (1.80) $^{(HIL)}$		59.49 (11.0) $^{(C)}$	52.63 (9.52) $^{(C)}$	
	$p^{(2)} = 0.001$*	$p^{(2)} = 0.008$*		$p^{(2)} < 0.001$*	$p^{(2)} < 0.001$*	

(*) Significant difference at 5%. (1) By the Wilcoxon test for paired data. (2) By the Kruskal-Wallis test with paired comparisons. (3) By the Mann-Whitney test. P.s. Different letters in parentheses indicate a significant difference between the corresponding materials.

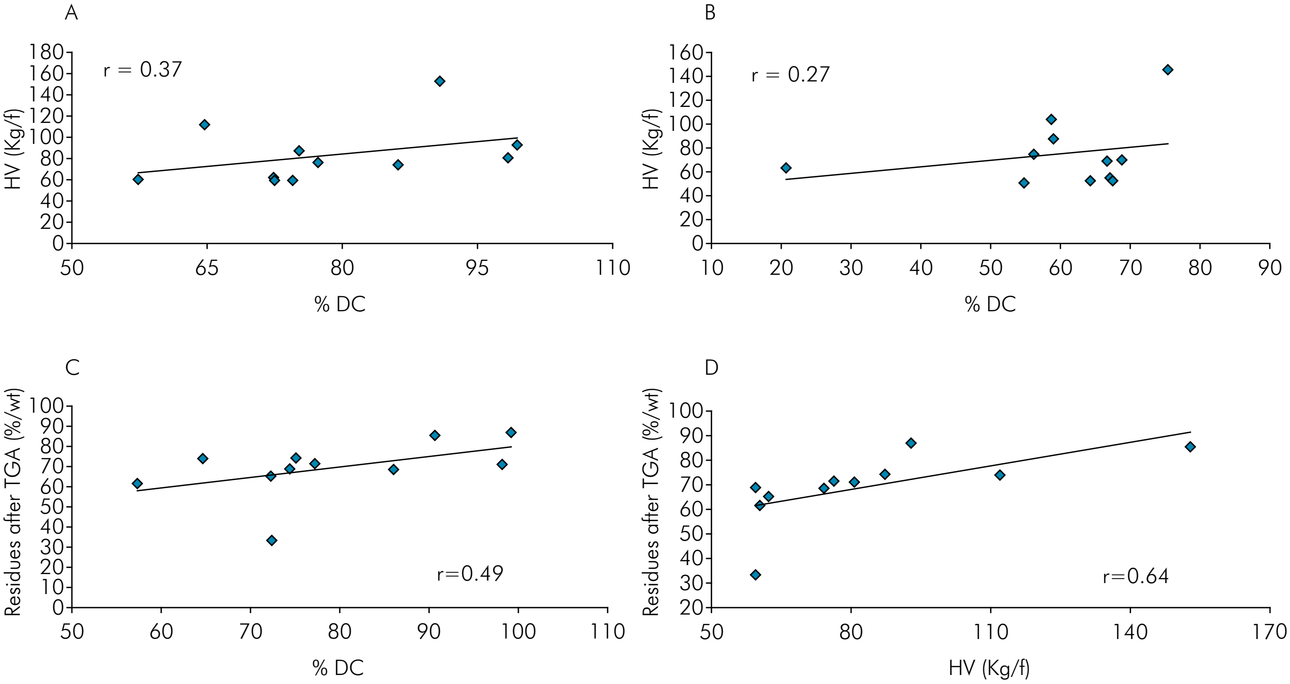

Figure 2. Correlation between degree of conversion and Vickers microhardness, considering the polymerized side: top (A) and bottom (B); between the % of residues, in weight, of the polymerized sample after TGA, and the degree of conversion (C) and microhardness (D).

Table 3. Mean values of mass loss (%), residues (%), and onset decomposition temperature of each resin – TGA.

TGA	Composite resins										
	ABF	Z350	AF	TEF	SDR$^+$	FBFS	XTB	XTF	Opus	Z350F	FBFF
Non-Polymerized											
Mass loss (%)	27.5	25.6	13.0	29.3	31.5	25.6	25.0	15.3	35.7	40.0	39.2
Residues (%)	72.4	74.2	87.1	70.7	68.5	76.2	75.0	84.2	64.3	60.1	62.7
Onset decomposition temperature (°C)	172.8	361.2	396.0	303.6	263.8	300.1	196.9	201.6	336.7	300.9	341.7
Polymerized											
Mass loss (%)	28.6	26.0	12.8	31.2	31.5	28.9	25.8	14.5	34.7	38.5	66.7
Residues (%)	71.5	74.0	87.0	68.9	68.6	71.1	74.3	85.5	65.3	61.6	33.4
Onset decomposition temperature (°C)	346.6	368.3	418.9	344.6	413.6	358.5	344.7	416.6	405.8	355.1	475.7

Table 4 shows the mean Tg, enthalpy, and melting and degradation temperatures for the polymerized resins. The composites had similar Tg, with no statistically significant difference. There was a low correlation between Tg and onset temperature (r = -0.35), mass loss (r = 0.1), and final residue quantity (r = -0.1).

Linear thermal expansion

Figure 3 (A) shows the relative variation of ΔL/L for each resin. The XTF resin exhibited lower dimensional variation and lower linear CTE. From 27°C, the CTE (10^{-6} /°C^{-1}) of the resins was as follows, in decreasing order (mean ± SD):

Table 4. Mean glass transition temperature (Tg), ΔH, melting and degradation temperatures.

DSC	Composite resins										
	ABF	Z350	AF	TEF	SDR⁺	FBFS	XTB	XTF	Opus	Z350F	FBFF
Polymerized											
Tg	54.64	55.52	50.71	56.57	54.54	54.78	58.17	57.07	54.46	55.05	55.05
Melting temperature	237.0	196.0	252.4	184.2	296.3	197.6	267.1	-	-	189.5	-
ΔH (J/g)	0.33	0.79	0.56	0.76	2.74	1.34	1.25	1.69	0.66	0.15	1.50
Degradation temperature	424.5	-	383.3	-	-	394.0	392.7	420.2	395.4	416.8	431.0

(-) it was not possible to determine it.

Z350F (37.1 ± 21.4), ABF (22.5 ± 11.4), FBFF (22.2 ± 3.9), TEF (20.2 ± 5.8), AF (19.5 ± 4.1), Opus (19.0 ± 6.2), Z350 (17.5 ± 5.0), FBFS (16.5 ± 3.0), XTB (15.8 ± 2.2), SDR+ (15.0 ± 3.2), and XTF (10.3 ± 2.8), without statistically significant difference ($p > 0.05$) (Figure 3B). The linear regression analysis showed a moderate negative correlation ($r = -0.56$) between the amount of load particles and CTE (Figure 3C).

Discussion

This study evaluated the thermal and physicomechanical behaviors of some commercial resins to identify chemical elements and to determine the % DC and VMH, thermal stability, degradation behavior, glass transition temperature, and enthalpy, in addition to the linear CTE. Some manufacturers did not provide information on the composition of the inorganic part of the composites used in this study (Table 1), so it was necessary to carry out the EDS analysis, for understanding that the type of load particle influences the thermal behavior of composites before, during, and after polymerization. Composites filled with quartz or silicon nitride/silica exhibit higher thermal diffusivity, while composites containing radiopaque fillers, such as barium or strontium, exhibit lower thermal diffusivity.[11] In this study, silica (Si) was the component with the highest percentage among all materials. This may be justified by the fact that the inorganic components were not evaluated separately from the organic ones, and silica is present in the silane binding agent. Other components such as Ba, Zr, Al, Y, Ca, and Sr have also been identified. Zirconia and silica peaks correspond to zirconia-silica clusters or to silicate particles present in the composition of these composites and have the potential to transfer more heat during polymerization. Ba and Y are related to radiopacity properties.[12] Some of the composites used (Table 1) also contain agglomerated particles of 100 nm of ytterbium trifluoride ($YbF3$) to increase their radiopacity.[13] Additionally, the amount of load particles is related to the improvement in the physicomechanical properties of the composites.[14]

The first null hypothesis related to DC and VMH was rejected, since a significant difference was found between the materials. The DC of all analyzed materials did not show significant differences between the evaluated surfaces (top and bottom), but the conversion values on the lower surface were smaller, indicating incomplete conversion of double carbon bonds. This is due to the chemical nature of the monomers which, upon initiating the polymerization process, promote the formation of a cross-linked solid polymer within a few seconds, increasing viscosity throughout the organic matrix, thereby preventing complete polymerization. Unreacted molecules may be present as residual monomers or as pending groups of the polymer network. When present as residual monomers, they act as plasticizers, reducing mechanical strength and increasing water uptake.[15]

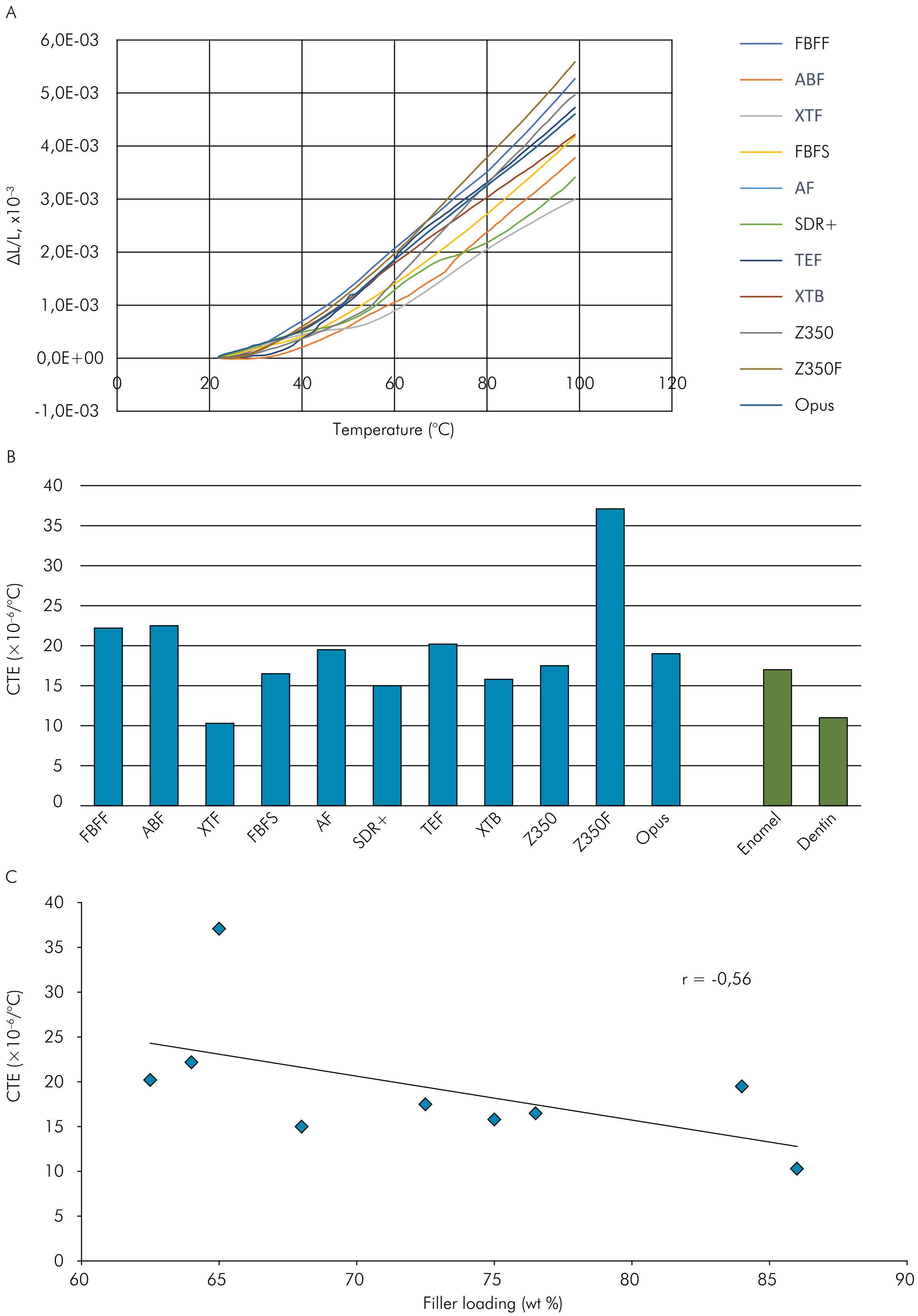

Figure 3. (A) Relative dimensional variation (ΔL/L) of composite resin, (B) thermal expansion, (C) linear correlation between CTE and filler loading of the dental composites.

In addition, the structural arrangement and spatial distribution of the polymer chains, oligomers and monomers, is directly related to the physicomechanical properties of these materials.[16] On the other hand, Czasch and Ilie[17] report that the evaluation of the DC of monomers to polymers in bulk-fill resins would not be a relevant factor for the evaluation of their mechanical properties, because a higher DC in a composite resin with several components does not necessarily mean that better mechanical properties will be obtained. In this study, it should be highlighted that all resins obtained DC values, at the top and bottom, above what is clinically recommended (> 55%) ,according to Alshali et al.,[18] except for AFB, which presented a 56.4% reduction at the bottom. Other studies[19,20] also obtained good results for the DC of bulk-fill resins with a thickness of 4 mm. The higher translucency, the modifications in the photoinitiator system, and the incorporation of load particles, which function as "microscopic springs" in bulk-fill resins, compared to the conventional ones used in these studies (Z350 and Z350F), may explain the higher DC values.

In this study, the bulk-fill resins presented lower microhardness in relation to restorative resins, in agreement with the findings of Czasch et al.,[17] Flury et al.,[21] and Tekin et al.[22] The low percentage of load particles may be related to the obtained data. Among flow resins, XTB presented better VMH than did the other materials, which leads us to believe that the obtained data are related to the loading content of each material, corroborating the findings of Leprince et al.,[14] Zorzin et al.,[19] and AlShaafi et al.[23] Our data showed no significant reduction in microhardness in relation to the polymerized side.

Since these materials are broadly indicated for posterior tooth restoration both in direct and semidirect techniques, the heating method before and after polymerization has been widely employed to achieve further monomer conversion.[24] The heat supplied to the polymerized material increases the degree of polymerization because of the presence of free radicals, which remain in the material for days or even months, depending on the density of the cross-linked bonds and on the storage temperature.[25] The heat supply before polymerization, on the other hand, assists in the conversion of the monomers in the composites used in direct form, besides increasing fluidity and promoting better adaptation of the cavity walls.[26] However, it is necessary to know how they behave when subjected to high levels of heat. Therefore, the influence of temperature on the stability and on the linear CTE of these composites was evaluated using TGA, DSC, and dilatometry.

The data obtained by TGA showed that the extrapolated onset temperature in the polymerized material ranged from 344.6 (TEF) to 475.7 (FBFF), indicating variations in the thermal stability and degree of cross-linking density established during the formation of the polymer network, demonstrating that the temperature in the non-polymerized material was lower, which led to the rejection of the second hypothesis. According to Teshima et al.,[27] main mass losses occur in the temperature range of 370 to 440 °C, with the release of propionic acid, fernic groups, methacrylic acid, HEMA, and TEGDMA, due to polymer matrix decomposition, which is in line with our results. The highest losses observed in this study occurred in this temperature range. As for the values of the obtained residues, which correspond to the weight percent of the load particles, the information given by the manufacturers was similar for most resins. FBFF, Z350F, and XTF presented lower percentage values than those reported by the manufacturer. This is probably due to the thermal degradation of silane or the evaporation of some inorganic components, or because some manufacturers determine the percentage of the inorganic filler prior to the silanization process, while others include it in their calculations.[28] The polymerized FBFF resin showed a marked discrepancy in the load content when compared to the manufacturers' data and the same was observed without polymerization, which is probably due to the volatilization of unreacted monomers or to other degradation processes. All materials presented more than one stage of thermal decomposition, a phenomenon that occurs because of thermal scission of the polymer matrix during heating, which is characteristic of UDMA-based materials.[29]

The composites showed similar Tg values in DSC, with no statistically significant difference. Studies report that the Tg of direct resin composites is related to monomer composition, type and concentration of load particles, and cross-linking density, the latter of which depends on the DC and is responsible for the determination of the physicomechanical properties of a polymer.[30] The Tg of polymerized samples can be correlated with DC, since materials with a higher DC present greater formation of cross-links between the chains, requiring higher temperatures. However, a low correlation between DC and Tg was found. The DSC results obtained in this study were similar to those obtained in previous studies.[31,32,22]

Linear CTE and dilation were evaluated using a horizontal dilatometer. The resins exhibited linear CTE similar to that of the dental structure, for enamel and dentin: 17 ($\times 10^{-6}$/°C) and 11 ($\times 10^{-6}$/°C), respectively,[33] which is clinically favorable to maintain the integrity of the tooth/restoration interface. However, Raue et al.[34] point out the need to evaluate the CTE of the enamel associated with the material to be used. The highest coefficient was observed in Z350F (37.1) and the lowest one in XTF (10.3), with no statistically significant difference ($p>0.05$), so the third hypothesis was also rejected. Considering that the resin matrix of these composites is similar to the differences found between them, this must be related to the inorganic content, corroborating the literature data when CTE is related to the amount of load particles.[35,36] The percentage of XTF particles (86 wt% and 70.1 vol%) is higher than that of other resins and Z350F (65 wt% and 42% vol), despite having more particles by weight than TEF (62.5 wt% and 60 wt% vol), it had a smaller amount in volume, so it presented a higher CTE. However, a moderate negative correlation ($r=-0.56$) was found between CTE and the load particles. Park et al.[35] and Alnazzawi et al.[37] report a high negative correlation between these two variables. Therefore, the larger the inorganic portion of the resin, the smaller the expansion, then its CTE is about 0.5 ~ 6 ($\times 10^{-6}$/°C) while that of the organic matrix is approximately 110 ~ 190 ($\times 10^{-6}$/°C).[35] Besides, composites with more resin matrix and fewer load particles can generate more heat during polymerization, causing damage to the pulp and to the underlying tissues.[13] The loading percentage should be one of the fundamental criteria for the choice of the restorative material, in order to avoid problems such as microleakage, secondary caries, loss of adhesive material, and staining of restorative resins, because of the expansion and contraction of the resinous material. When analyzing the dilatometry results of $\Delta L/L$ dependencies, a similar size variation was observed for all samples (Figure 3A). At the same time, $\Delta L/L$ variations were in the same range, coinciding with the CTE data, denoting a certain similarity in the composition of the resins.

Conclusion

In this study, composites with conventional and bulk-fill resins were evaluated, presenting some differences in their composition and formulation, which influenced the obtained results. Thus, the conclusions can be summarized as follows:

a. The DC of the evaluated composites was higher than what is expected for commercial composites, except for ABF, on the lower surface. The DC of all resins was higher on the top surface, but with no statistical difference.
b. The restorative bulk-fill resins presented superficial VMH results on the top and bottom surfaces, similarly to those of flow resins, except for XTF, which had higher values. VMH values were lower for all resins on the bottom surface.
c. TGA showed similar mass loss between resins and waste/charge particles, similar to those reported by the manufacturers.
d. The Tg of all resins was within the temperature range of 50 to 60 °C, in agreement with literature data.
e. The linear CTE of the resins was acceptable once it approached the linear CTE of the dental structure, except for Z350F.
f. Silica was the predominant inorganic component in all composites.
g. There was a low positive correlation between DC and VMH, according to the evaluated surface; a moderate correlation between the weight % of residues/load particles after TGA and VMH; and a low correlation between these and DC.

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