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Physical and chemical properties of model composites containing quaternary ammonium methacrylates

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ABSTRACT

Objective. Investigate physical and chemical properties of model composites formulated with quaternary ammonium salt monomers (QAS) at different concentrations and alkyl chains lengths

Methods. QAS with 12 dimethylaminododecyl methacrylate (DMADDM) and 16 dimethylaminohexadecyl methacrylate (DMAHDM) chains lengths were synthesized and incorporated at 5 and 10% in model composites, resulting in four groups: G12.5 (DMADDM 5%), G12.10 (DMADDM 10%), G16.5 (DMAHDM 5%), G16.10 (DMAHDM 10%). One group was used as control group (CG 0%). Degree of conversion (DC); water sorption (WS) and solubility (SL); hygroscopic expansion (HE); degradation temperature (DT); glass transition temperature (T_g) and polymerization shrinkage (PS) were determined. Knoop hardness (KNH), flexural strength (FS) and elastic modulus (EM) were measured before and after storage Data were submitted to ANOVA and Tukey's test ($p \leq 0.05$).

Results. DC ranged between 76.1 (G12.10) and 70.7 (G16.5) %; CG had the lowest WS, SL and HE. There was no statistical difference for PS and FS. KHN values ranged between 30.2 (GC) and 25 (G16.10) and after storage the performance was depended on QAS concentration and chain length. For EM, CG had the highest values before and after storage and no difference was observed in the QAS groups before storage. After storage, the results were dependent on QAS concentration (3.5-4.3 GPa).

Significance. In general, the addition of QAS increased composite's degradation compared with the CG. In the tested QAS, the addition of DMADDM at 5% concentration resulted in a less degradable material.

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1. Introduction

Due to their versatility, composites are widely used in Dentistry for direct restoration [1,2]. Although mechanical properties have been significantly improved in the last decades [1], restorative composites still present a series of shortcomings. Basically, these materials tend to accumulate more plaque than other restoratives materials due to the degradation process of the organic content and in the interface with reinforcing fillers [3]. Therefore, control of bacterial growth could be a strategy to increase their clinical lifetime [4]. Several compounds have been added to composites resin with this aim [5–8] but, in general, these combinations are not copolymerized with the resin matrix and over time could weaken the polymer matrix [9].

The use of polymerizable quaternary ammonium salts monomers (QAS) could be an interesting approach to improve materials' ability to control bacterial growth. QAS do not lose its antibacterial properties over time because it might be copolymerized with the monomers commonly used in the formulation of commercially available materials [9]. The antibacterial activity is provided by contact and would cause bacteriolysis by binding the cell membrane, resulting in cytoplasmic leakage [10,11]. Previous studies have shown excellent antibacterial properties of this antibacterial monomers [11–18], even after 6 months of storage [19]. Regarding to cytotoxicity, previous studies reported that quaternary ammonium monomers were similar to a commercially available adhesive system [20] and less toxic than BIS-GMA [13,16].

Alkyl chain length is one factor that influences the QAS antibacterial ability. In previous studies [12–14,17,18] an increase in antibacterial efficiency was observed by increasing chain length from 3 to 16, but it decreased when reached 18. Among QAS, previous studies have demonstrated elevated bactericidal efficiency of methacrylates compounds DMADDM (dimethylaminododecyl methacrylate) and DMAHDM (dimethylaminohexadecyl methacrylate) [13,14,17] with alkyl chain length of 12 and 16 respectively. Besides the chains lengths, by increasing QAS concentration the antibacterial ability of composites is elevated [12,14,15].

Until now, experimental studies have focused on the antibacterial properties of DMADDM and DMAHDM [14,16,17] and it is necessary to determine if the addition of these monomers would influence composite's overall physical and chemical properties. It was previously reported that QAS might possess hydrophilic characteristics [21], which can increase degradation. Despite scarce, there are studies available on mechanical properties [17,18], but other compounds were added to act in synergism with the QAS, thus, making it impossible to determine the real influence of DMADDM and DMAHDM on these properties.

Due to the lack of data, the aim of this study was to determine the influence of the addition of antibacterial monomer QAS (DMADDM or DMAHDM) on the physical and chemical properties of model composites at different concentrations. It was determined specifically (1) degree of conversion; (2) sorption and solubility; (3) hygroscopic expansion; (4) polymerization shrinkage; (5) thermal properties (6) Knoop hardness before and after storage in ethanol; (7) flexural properties before and after storage in water. The research hypothesis was that the addition of QAS in model composites, regardless of concentration, does not influence the variables tested.

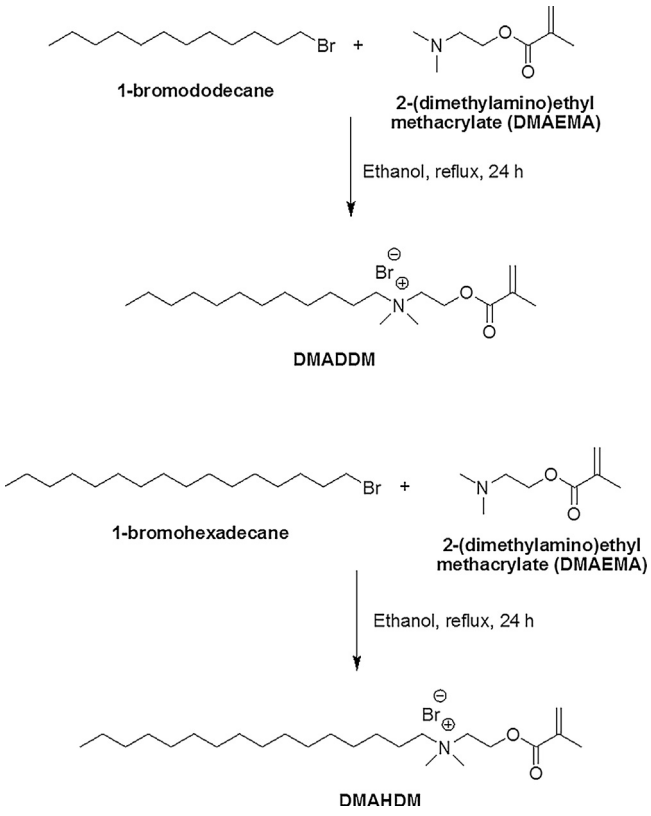

Fig. 1 – Synthesis of antimicrobial monomers DMADDM and DMAHDM.

2. Materials and methods

2.1. *Synthesis of antimicrobial monomers*

The antimicrobial monomers were synthesized using the Menschutkin reaction, as previously reported [14]. In this addition reaction, a tertiary amine and an organo-halide were added, in equal amounts (60 mmol), into a round bottom flask coupled to a condenser with 20 mL of ethanol and were refluxed for 24 h. After that, the solvent was evaporated to dryness (rotary evaporator) to afford the pure monomer, which did not require any purification. For each monomer, a different organo-halide was used (Fig. 1), and the tertiary amine was always 2-(dimethylamino)ethyl methacrylate (DMAEMA).

To characterize the reaction products, Nuclear Magnetic Resonance (NMR) Spectroscopy and High-Resolution Mass Spectrometry (HRMS) were used. ^{1}H and ^{13}C NMR spectra were recorded on an Avance 200 MHz spectrometer (Bruker, Billerica, MA, USA), using $CDCl_3$ as the solvent. Standard Bruker software was used throughout and chemical shifts were given in ppm (δ scale) and coupling constants (J) were given in hertz (Hz). High-resolution mass spectra were obtained on a Bruker microTOF II mass spectrometer using ESI.

2.1.1. *Dimethylaminododecyl methacrylate (DMADDM)*
Yield 24.07 g (98.8%); ^{1}H NMR ($CDCl_3$) δ 6.11 (s, 1H), 5.64 (s, 1H), 4.64 (br s, 2H), 4.11 (br s, 2H), 3.72–3.50 (m, 2H), 3.47 (s, 6H), 1.92 (s, 3H), 1.81–1.63 (m, 2H), 1.30–1.17 (m, 18H), 0.84 (t, J = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 166.4, 135.3, 127.4, 65.6, 62.4, 58.3, 52.0, 32.0, 29.6, 29.5, 29.5, 29.4, 29.3, 26.4, 23.0, 22.7, 18.3, 14.2; HRMS-ESI: m/z $[M-Br]^+$ calculated for $C_{20}H_{40}NO_2Br$: 326.3059; found: 326.3062.

2.1.2. *Dimethylaminohexadecyl methacrylate (DMAHDM)*
Yield 27.52 g (99.3%); ^{1}H NMR ($CDCl_3$) δ 6.12 (s, 1H), 5.65 (s, 1H), 4.64 (br s, 2H), 4.13 (br s, 2H), 3.70–3.55 (m, 2H), 3.49 (s, 6H), 1.93 (s, 3H), 1.90–1.61 (m, 2H), 1.37–1.20 (m, 26H), 0.85 (t, J = 5.7 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 166.4, 135.3, 127.4, 65.6, 62.3, 58.3, 52.0, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.4, 23.0, 22.7, 18.3, 14.2; HRMS-ESI: m/z $[M-Br]^+$ calculated for $C_{24}H_{48}NO_2Br$: 382.3685; found: 382.3691.

2.2. Model composites formulation

The mixture bisphenol-A-glycidyldimetacrylate (Bis-GMA): triethylene glycol dimethacrylate (TEGDMA) (Esstech Inc., USA, batch 610-43) was used at ratio 50:50% by weight. To this, 1% camphorquinone (Esstech Inc., USA; Lot TSNP004397) and 1% EDMAB amine (Sigma–Aldrich, MO, USA, lot MKBB3614) were added as the photoinitiator/co-initiator system. Inorganic filler particles were added to obtain a composite with 50% mass load, whereas 85% composed by borosilicate barium glass silane-treated particles (0.7 μm average size, Esstech Inc., USA, batch 699-17) and 15% of spherical silica silane-treated particles (7 nm average size; Aerosil R812, Evonik Degussa lot 3523102). QAS obtained by Menshutkin reaction (DMADDM or DMAHDM) were added in concentration of 5% and 10% of the total organic matrix weight. Groups were named according to the alkyl chains lengths and the used concentration, being arranged as follows: G12.5 (DMADDM 5%) G12.10 (DMADDM 10%), G16.5 (DMAHDM 5%) G16.10 (DMAHDM 10%) and control group (CG), which had no QAS.

2.3. Degree of conversion

The degree of conversion was determined by Fourier-transformed infrared spectrometry (32 scans, resolution of 4 cm^{-1}, Alpha-P; Bruker Optics, Ettlingen, Alemanha) with an attenuated total reflectance technique (ATR). Droplets of the model composites unpolymerized (n = 3) were placed on ATR crystal large enough to cover its surface. After baseline measurement, the composites were photoactivated for 40 s (Demi Plus LED Curing Light, Demetron SDS Kerr, Middleton, WI, USA), with an irradiance of 800 mW/cm^2, measured with a radiometer (LED Radiometer, Demetron SDS Kerr, Middleton, WI, USA), standardized at a distance of 0.5 mm between the photopolymerizer's tip and the curing material. The same curing unit, irradiance and radiometer were used for all subsequent methodologies. FTIR analysis was repeated after the photoactivation procedure. Degree of conversion was calculated by determining the FTIR bands area spectra with the software, whereas the area of the 1638 cm^{-1} signal was used as a standard, and 1608 cm^{-1} was used for the aromatic vinyl bonds of bisphenol A. The degree of conversion was calculated using the following formula:

$$DC = 1 - \left[\frac{(Abs_{1638cm^{-1}}cured / Abs_{1608cm^{-1}}cured)}{(Abs_{1638cm^{-1}}uncured / Abs_{1608cm^{-1}}uncured)} \right] \quad (1)$$

2.4. Sorption and Solubility

Five samples were prepared for each model composite (Ø 6 mm × 1 mm h). The material was inserted in a single increment in a metal mold between Mylar strips, with a glass coverslip on top of which a weight of 500 g was placed. Photo activation was performed for 40 s as previously reported. Both surfaces were mechanically polished with 2000 and 4000-grit SiC papers. The same procedure was used for all subsequent methodologies.

The samples were stored in a desiccator with silica gel blue for 22 h, at 37 °C. Then samples were transferred to a desiccator at room temperature, for 2 h. They were weighed in a 24 h cycle with an analytical balance, accuracy 0.01 mg, (XS105 DU, Metler-Toledo, Leicester, UK) until obtaining a constant weight (range smaller than ± 0.1 mg for three consecutive weighing — m1). The thickness and diameter of the samples were measured with a digital calliper (ABS digital calliper, Mitutoyo, Tokyo, Japan) at four equidistant points, and the volume (V) was calculated in mm^3. Afterwards, the samples were placed individually in glass phials, immersed in 10 mL of distilled water, and weighed in a 24 h cycle until reaching the equilibrium (m2). After equilibrium was reached, they were taken back to the desiccator and weighed every 24 h, repeating the same cycles required to obtain m1, until the mass equilibrium (m3) was reached. Using the following equation sorption (Eq. (2)) and the solubility (Eq. (3)) during the course of water immersion and drying were obtained in mg/mm^3:

$$Sp = (m2 - m3)/V \quad (2)$$

$$Sl = (m1 - m3)/V \quad (3)$$

2.5. Hygroscopic expansion

Five discs (Ø 15 mm × 2 mm h) of each material were prepared, as previously descripted. Due to the difference between the size of unit curing tip (11 mm) and sample, light curing was performed in 5 overlapping portions, 40 s each, in both sides [22]. Samples were stored individually in glass phials in a light-proof desiccator at 37 °C with silica gel. After, samples were weighed on an analytical balance (Ohaus Analytical Plus, Ohaus Corporation, USA) with an accuracy of 0.01 mg until mass change of specimens was less than 0.2 mg in a period of 24 h. Changes in the size of samples were measured with a laser micrometre (Measuring Unit LSM-503 sand Display Unit LSM-6200, Mitutoyo Corporation, Japan) customised to the test with a resolution of 200 nm. The instrument has been described previously [22,23]. After samples have reached equilibrium, their diameters were measured (d1). Then, individually immersed in 10 mL water at 37 °C their diameters were measured at specific times (d2 — 1 and 3 h, 1–7 days) until reached equilibrium. After 7 days of immersion, the sam-

ples reached the diametrical balance. The percentage of the diametric change was calculated according to the formula:

$$\Delta d\,(\%) = 100d1\,(t) - \frac{d2}{d1} \quad (4)$$

The percentage of volume change of hygroscopic expansion was calculated with the following formula, which accepts that there is an isotropic expansion behavior:

$$V\,(\%) = \left[100\left(1 + \frac{\Delta d\,(\%)}{100}\right)^3 - 1\right] \quad (5)$$

2.6. Volumetric shrinkage evaluation

The volumetric shrinkage evaluation was performed through the bonded-disc method [24]. Approximately 0.15 g of the resin composite was dripped between a rigid glass plate and a coverslip to form a disc-shape uncured specimen. A peripheral brass ring with 0.8 mm thickness was used between the glass plate and the coverslip to standardise the sample thickness. The set was then fixed into a rigid platform holding a linear variable differential transformer (LVDT) (RDP Electronics, Wolverhampton, UK) and the light-curing unit. The irradiation procedure (40 s) was performed through the rigid plate. The LVDT, which was positioned in contact with the coverslip, was able to detect continuously sample's deformation during the following 60 min (n = 3).

2.7. Thermal analyses

2.7.1. Thermogravimetric analysis (TGA)

For each group, a sample of 18 ± 5 mg of the milled composite was inserted into an alumina crucible and submitted to a heat of 10 °C per minute to 500 °C in the device (TGA 209F3 NETZSCH, Germany) under atmospheric dynamics of nitrogen (50 mL min^{-1}). In the TGA, the decomposition temperature of the organic matrix and the percentage by weight of inorganic filler were determined. At the moment there was a stabilisation of the sample weight, the amount of inorganic residue was recorded.

2.7.2. Differential scanning calorimetry (DSC)

To complement these results, the differential scanning calorimetry technique was used. In this analysis, grounded specimens (15 ± 5 mg of each model composite) were weighed on an analytical balance. The differential scanning calorimetry measurements were used to monitor the weight change and energy involved during the process of the material heating under an atmospheric dynamics of nitrogen (50 mL min^{-1}) in a 50-DSC apparatus (DSC Nietzsch 200F, Germany) coupled on a computer. The DSC curves were obtained using a hermetic aluminium pan with a heating rate of 10 °C per minute with a temperature range from 0 to 450 ° C.

2.8. Knoop hardness

For Knoop hardness test, five discs were prepared (Ø 4 mm × 2 mm h) and non-irradiated surfaces were marked with a surgical scalpel blade. After 24 h, the irradiated surfaces were indented using 25 N of load for 15 s with a Knoop diamond tip (Micromet 5104, Buehler, Lake Bluff, USA) at five different locations. After initial measurements, samples were stored in absolute ethanol [25,26] (Synth, Diadema, SP, Brazil) and Knoop hardness measures were carried out in 14 days. The absolute ethanol was changed every week and readings were randomised.

2.9. Elastic modulus and flexural strength

The elastic modulus and flexural strength were determined by three-point bending test. For each group, 20 bar-shaped samples (1 × 2 × 10 mm) were prepared. The composites were placed in a single increment in a matrix and photoactivated as described above. The surfaces were grounded to remove irregularities with 600-grit SiC paper. Ten samples per group were stored in distilled water at 37 °C for 24 h. Measured with a digital calliper samples were submitted to bending strength test in a universal testing machine (DL2000, EMIC, São José dos Pinhais, PR, Brazil) with 50 kgf load cell and displacement of 0.5 mm/min. The EM and FS were calculated by the following equations:

$$EM = l^3F/4bh^3d \quad (6)$$

$$FS = 3Fl/2bh^2 \quad (7)$$

where l is the distance (mm) between the lower points (6 mm), F is the load applied (N); h is the height (mm) of the sample, b is the width (mm) and d the deflection (mm) on F load during the elastic regime. The ten remaining samples per group were stored in phials containing distilled water (changed weekly) at 37 °C and the test was repeated after one month.

2.10. Statistical analysis

Data of the degree of conversion, sorption and solubility, polymerization shrinkage values were submitted to one-way analysis of variance (ANOVA) and Tukey's test (95%). For Knoop hardness, flexural strength and modulus of elasticity, data were submitted to two-way ANOVA and Tukey test (0.5%), with repeated measures for the factor storage time.

3. Results

Results of degree of conversion, water sorption and solubility, hygroscopic expansion, polymerization shrinkage, decomposition and glass transition temperatures are shown in Table 1. Knoop hardness and flexural properties values are expressed in Table 2.

3.1. Degree of conversion

In general, all groups showed a degree of conversion similar to CG. The only statistical difference was that G12.10 exhibited higher conversion than G16.5.

Table 1 – Mean of degree of conversion (DC, n = 3), sorption (WS, n = 5, μg/mm³), solubility (SL, n = 5 μg/mm³.), hygroscopic expansion (HE, n = 6, %), polymerization shrinkage (PS, n = 3, %) — onset decomposition temperature (DT, °C), glass transition temperature (T_g, °C).

Groups	DC	WS	SL	HE	PS	Thermal properties	
						DT	T_g
G12.5	73.9 (1.8)^{a,b}	41.8 (0.8)^{b}	3.0 (0.4)^{b}	1.7 (0.7)^{a,b}	4.7 (0.3)	402	117
G12.10	76.1 (0.2)^{a}	45.4 (2.1)^{a}	8.7 (2.6)^{a}	1.9 (1.0)^{a,b}	4.7 (0.1)	351	100
G16.5	70.7 (0.9)^{b}	41.3 (0.6)^{b}	4.9 (1.6)^{b}	2.3 (0.4)^{a,b}	4.7 (0.1)	358	89
G16.10	73.6 (1.2)^{a,b}	43.4 (0.9)^{ab}	4.0 (0.9)^{b}	2.6 (0.7)^{a}	4.7 (0.1)	348	81
CG	74.4 (1.8)^{a,b}	32.8 (1.1)^{c}	0.9 (0.6)^{c}	1.3 (0.2)^{b}	4.6 (0.1)	350	65

Different lower case letters indicate statistical differences within a column ($p < 0.05$).
For data of each line, standard deviation value is shown in parenthesis.

Table 2 – Mean of Knoop Hardness (KHN, n = 5, kgf/mm²), % decrease after 14 days on ethanol, Flexural Strength (FS, n = 10, MPa), % decrease after 30 days on water, Elastic modulus (EM, n = 10, GPa) % decrease after 30 days on water.

Groups	Knoop hardness			Flexural strength			Elastic modulus		
	24 h dry	14 days ethanol	% decrease	24 h dry	30 days water	[1]% decrease	24 h dry	30 days water	[1]% decrease
G12.5	28.2 (3.9)^{A,a,b}	12 (0.8)^{B,a,b}	56 (7)^{ab}	120 (11)^{A}	103 (21)^{B}	14	4.6 (0.5)^{A,b}	3.9 (0.4)^{A,b,c}	15
G12.10	27.6 (3.5)^{A,a,b}	10 (1.2)^{B,b}	63 (6)^{a}	132 (11)^{A}	97 (15)^{B}	26	4.7 (0.5)^{A,b}	3.5 (0.5)^{B,c}	25
G16.5	27 (2.8)^{A,a,b}	10.8 (0.9)^{B,b}	60 (2)^{a}	142 (24)^{A}	110 (15)^{B}	22	4.8 (0.7)^{A,b}	4.3 (0.4)^{A,b}	8
G16.10	25 (2.5)^{A,b}	10 (0.7)^{B,b}	60 (4)^{a}	139 (9)^{A}	111 (8)^{B}	20	4.7 (0.4)^{A,b}	3.7 (0.4)^{B,c}	21
CG	30.2 (3.2) ^{A,a}	15.2 (2.2)^{B,a}	49 (7)^{b}	138 (22)^{A}	119 (13)^{A}	13	5.9 (1.2)^{A,a}	5.3 (0.5)^{A,a}	10

Different lower case letters indicate statistical differences within a column ($p < 0.05$).
Different upper case letters indicate statistical difference between KHN, FS or EM of the same material between different treatment timing.
For data of each line, standard deviation value is shown in parenthesis.
[1] The percentage of flexural strength and elastic modulus decrease considered a direct and simple comparison between the average results obtained after 24 h and 30 days. Therefore, it is not possible to run statistical analysis test.

3.2. *Sorption and solubility*

Model composites exhibit different behaviors ($p < 0.01$). CG exhibited the lowest water sorption. G12.10 absorbed more water than G12.5 and G16.5 and CG, but it was similar to G16.10. Groups formulated with 5% QAS presented intermediate results. Regarding the solubility test, the CG exhibited the lowest value and G12.10 the highest. G12.5, G16.5 and G16.10 presented intermediate values.

3.3. *Hygroscopic expansion*

CG presented lower hygroscopic expansion than G16.10, while the other tested groups presented intermediate behavior.

3.4. *Polymerization shrinkage*

Model composites varying concentrations and types of QAS had no statistical difference in the polymerization shrinkage and did not differ from CG.

3.5. *Thermal properties*

The thermal analizes (DSC and TGA) have shown that G12.10 and CG tended to be more stable in the degradation process than the other tested composites. Figs. 2 and 3 presented the TGA and DSC curves.

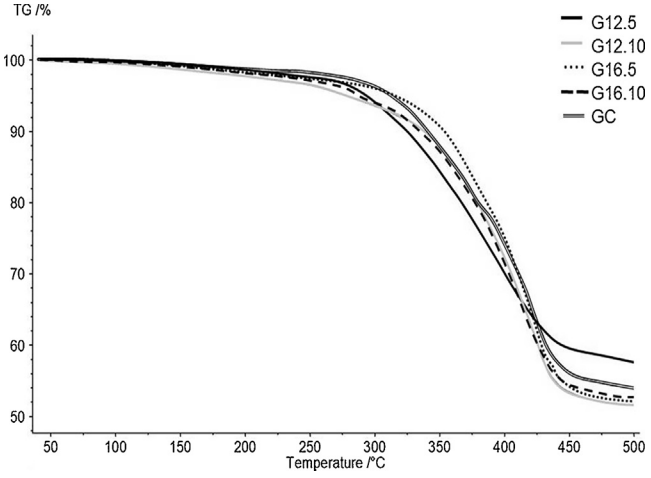

Fig. 2 – TGA curves of model composites.

3.6. *Knoop hardness*

The results obtained after 24 h in dry storage reveal that the CG presented higher KHN than G16.10, while the other materials presented intermediate values. After 14 days ethanol storage, groups formulated with QAS exhibited lower hardness values than the CG, except for G12.5. Similar behavior was observed when considering the percentage of hardness decrease.

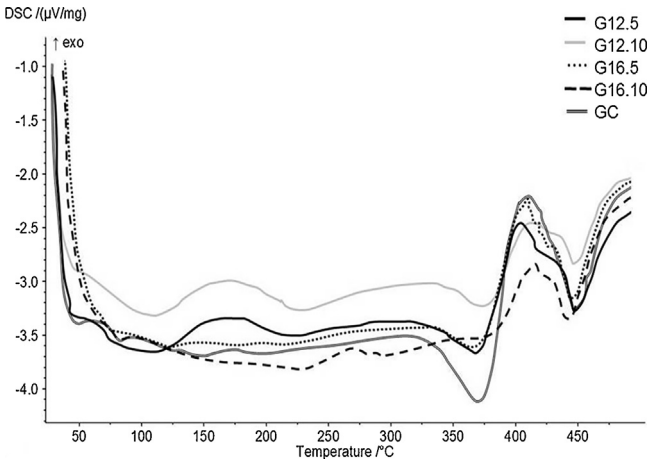

Fig. 3 – DSC curves of model composites.

3.7. *Flexural properties*

3.7.1. *Flexural strength*

Considering those values obtained after 24 h and 30 days in water storage, neither the concentration nor the type of QAS added to the model composites affected the flexural strength results. The CG was the only material not adversely affected by 30 days storage in water.

Considering a direct and simple comparison between the average results obtained after 24 h and 30 days it was possible to observe that the CG and the material formulated with 5% short-chained QAS (G12.5) tend to present lower decrease after the storage period than the other materials.

3.7.2. *Elastic modulus*

The CG showed the highest values for tests performed after 24 h of dry storage and after 30 days water storage. Groups containing 10% QAS (G12.10 and G16.10) showed a reduction in elastic modulus after storage for 30 days in water.

4. Discussion

The present work research hypothesis was that QAS addition would not affect the tested properties. If the variables degree of conversion, polymerization shrinkage and flexural strength were considered, this hypothesis could be confirmed, since there was no statistical difference between the groups evaluated. However, the addition of antibacterial monomers resulted in properties decrease if the following variables were considered: sorption, solubility, hygroscopic expansion, Knoop hardness and elastic modulus before and after water storage. Thus, the research hypothesis was rejected.

Keeping constant the weight of Bis-GMA/TEGDMA and varying just the type and concentration of QAS at the model composites allow to evaluate its influence on the degree of conversion. According to the current outcomes, QAS incorporation had no influence on degree of conversion compared with the CC. Although statistical significant difference was only observed between G12.10 and G16.5, consequently it is important to consider that shorter chained QAS (DMADDM) tended to produce superior conversion than the long chained QAS (DMAHDM). This could be related to the greater mobility of monomers formulated with shorter alkyl chain [27]. As QAS were added by weight percentage of the organic matrix, DMADDM (alkyl chain length 12) was incorporated in larger amounts due to differences in molecular weight of both chains [13]. This could explain the tendency to produce a polymer with higher degree of conversion. In regards to concentration of QAS, some previous studies showed that by increasing the concentration, an increase in degree of conversion were detected [28,29]. Although no statistically significant difference was observed among concentrations in the present study, by analyzing numerical results, it was possible to detect that by adding QAS at 10% either at longer or shorter chains degree of conversion tended to increase.

The CG had the lowest value of water sorption and solubility and statistically differed from other groups. A variety of chemical and physical processes are directly related to sorption and solubility. This process can produce deleterious effects, such as volumetric, physical and chemical changes in the structure and function of polymers [30]. As previously mentioned, G12.10 and G16.10 were the model composites that had the greatest amount of QAS added. Since QAS is a polar and hydrophilic molecule [21] and the polarity of the composite appears to dictate water sorption [31], it could be rationale that, the more molecules of QAS, more hydrophilic the composite is. This hydrophilicity associated with the heterogeneous network due to the presence of QAS can increase water sorption. The high absorption of water swells the polymer network and makes the unreacted monomers leach out the material leading to greater water solubility [32]. This was observed in this study, and findings agreed that the incorporation of QAS has increased the sorption and solubility [21,32].

The hygroscopic expansion coefficient of some restorative materials may exceed the polymerization shrinkage and have catastrophic consequences for the remaining tooth structure [33]. The QAS increasing concentration and chain length were proportional to the hygroscopic expansion increase. As previously discussed, model composites containing QAS had higher water sorption. Studies report that the more hydrophilic restorative materials tend to be, the greater hygroscopic expansion is, when compared to hydrophobic materials [34]. Previous researches show the relation between crosslinking density and hygroscopic expansion [23,35]. G16.10 was statistically different of the GC, which possibly shows a lower crosslink density of this group due to the concentration and QAS chain size used. These results are in agreement with the results obtained in thermal properties, discussed below.

Shrinkage of commercial available methacrylate-based composite is between 1–5% [36,37] and is similar to the values of all model composites in this study. Polymerization of methacrylate composite is combined with volumetric shrinkage [38], which is caused by the separation of carbon double bonds and formation of single bonds [39]. Even though the problem of secondary caries can be minimised by the addition of QAS to the composites, the polymerization contraction stress could still produce deleterious effects. However, the addition of QAS did not adversely affect the model composites polymerization contraction. These results were different

from those obtained previously [40,41] and are probably due to differences in molecular structure and concentration of QAS used, since until now there is not any study with DMADDM and DMAHDM testing polymerization shrinkage.

Thermal properties were influenced by the addition of QAS at the model composites. In DSC and TGA analysis of onset decomposition temperature and the T_g, model composite containing 5% of DMADDM presented the highest values. These results are an indicative of a higher crosslink density [35,42]. On the other hand, DMAHDM presented lower values, thus, longer chains could have affected the glass transition temperature by changing polymerization and chain formation characteristics [43]. DSC curves figures that CG required more energy for phase transitions. This is probably due to greater interaction between organic and inorganic phases. It must be highlighted that CG presented higher load concentration, as the other groups had 5 or 10% more organic matrix added as QAS.

Chain length and QAS concentration affected Knoop hardness before and after ethanol immersion in the current investigation. Since Knoop hardness indirectly reflects crosslink density, results obtained before storage are correlated to thermal analysis in which shorter chains groups presented the highest values of T_g. [25,26,44]. The higher values of CG before and after storage are probably attributed to larger concentrations of the inorganic portion. After ethanol storage, CG presented lower hardness decrease than those groups containing QAS. This behaviour could be associated with the polymeric network. The CG is formed mainly by dimethacrylates, that are able to form dense, crosslinked, networks [30,35]. In contrast, model composites containing QAS were more susceptible to chemical degradation probably due to more linear networkś, derived from methacrylates, that enables solvent penetration. The attractive forces between the polymer networks are exceeded by the attractive forces between the molecules of the solvent and the chains, thus solvent penetrates into the polymer matrix and breaks the chains [30]. Previous studies with MDPB [45] and DMAE-CB in a pit fissure sealant with fluoride [46] reported no drop in hardness values.

A high flexural strength is necessary to composites resist masticatory forces and to prevent fractures [47]. Commercial composites have flexural strength between 96–180 MPa [48], and the values found in the current investigation ranged from 120 to 142 MPa. The values before and after storage demonstrated that neither QAS concentration nor chain length influenced the flexural strength and similar results were found previously [12,18,32]. These values are related to thermal properties of the model composites. Comparing the flexural strength values before and after storage, a statistical decrease was observed only in materials formulated with QAS. The sorption values could justify the higher drop of the QAS model composites compared to the CG. This decrease can be explained by the plasticization due to hydrophilic characteristics, which can reduce the polymers mechanical strength [30]. A lower concentration of inorganic content compared to the CG was detected in 10% QAS groups. It is known that the module is directly affected by the amount of fillers; as a result groups containing 10% concentration of QAS presented a decrease after water storage. This phenomenon also occurred in a previous study [12].

5. Conclusion

According to the current outcomes it was possible to state that the addition of QASs:

(1) Exhibited a low effect on the degree of conversion.
(2) Reduced the degradation resistance – by increased water sorption and solubility, hygroscopic expansion, and reduced hardness and elastic modulus – when compared with a model composite without QAS.
(3) QAS concentration and chain length had an impact on the tested properties. Within the tested QAS, the addition of DMADDM at 5% concentration resulted in a less degradable material.

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REFERENCES

[1] Ferracane JL. Resin composite—state of the art. Dent Mater 2011;27(1):29–38.
[2] Demarco FF, Corrêa MB, Cenci MS, Moraes RR, Opdam NJ. Longevity of posterior composite restorations: not only a matter of materials. Dent Mater 2012;28(1):87–101.
[3] Padovani G, Fúcio S, Ambrosano G, Sinhoreti M, Puppin-Rontani R. In situ surface biodegradation of restorative materials. Oper Dent 2014;39(4):349–60.
[4] Delaviz Y, Finer Y, Santerre JP. Biodegradation of resin composites and adhesives by oral bacteria and saliva: a rationale for new material designs that consider the clinical environment and treatment challenges. Dent Mater 2014;30(1):16–32.
[5] Aljabo A, Xia W, Liaqat S, Khan MA, Knowles JC, Ashley P, et al. Conversion, shrinkage, water sorption, flexural strength and modulus of re-mineralizing dental composites. Dent Mater 2015;31(11):1279–89.
[6] Tavassoli Hojati S, Alaghemand H, Hamze F, Ahmadian Babaki F, Rajab-Nia R, Rezvani MB, et al. Antibacterial, physical and mechanical properties of flowable resin composites containing zinc oxide nanoparticles. Dent Mater 2013;29(5):495–505.
[7] Xu X, Ling L, Wang R, Burgess JO. Formulation and characterization of a novel fluoride-releasing dental composite. Dent Mater 2006;22(11):1014–23.
[8] Kim JS, Shin DH. Inhibitory effect on *Streptococcus mutans* and mechanical properties of the chitosan containing composite resin. Restor Dent Endod 2013;38(1):36–42.
[9] Beyth N, Farah S, Domb AJ, Weiss I. Antibacterial dental resin composites. React Funct Polym 2014;75:81–8.
[10] Tiller JC, Liao CJ, Lewis K, Klibanov AM. Designing surfaces that kill bacteria on contact. Proc Natl Acad Sci U S A 2001;98(11):5981–5.

[11] Beyth N, Yudovin-Farber I, Bahir R, Domb AJ, Weiss EI. Antibacterial activity of dental composites containing quaternary ammonium polyethylenimine nanoparticles against Streptococcus mutans. Biomaterials 2006;27(21):3995–4002.
[12] Liang X, Söderling E, Liu F, He J, Lassila LV, Vallittu PK. Optimizing the concentration of quaternary ammonium dimethacrylate monomer in bis-GMA/TEGDMA dental resin system for antibacterial activity and mechanical properties. J Mater Sci Mater Med 2014;25(5):1387–93.
[13] Li F, Weir MD, Xu HH. Effects of quaternary ammonium chain length on antibacterial bonding agents. J Dent Res 2013;92(10):932–8.
[14] Zhou H, Li F, Weir MD, Xu HH. Dental plaque microcosm response to bonding agents containing quaternary ammonium methacrylates with different chain lengths and charge densities. J Dent 2013;41(11):1122–31.
[15] Li F, Weir MD, Chen J, Xu HH. Effect of charge density of bonding agent containing a new quaternary ammonium methacrylate on antibacterial and bonding properties. Dent Mater 2014;30(4):433–41.
[16] Li F, Weir MD, Fouad AF, Xu HH. Time-kill behavior against eight bacterial species and cytotoxicity of antibacterial monomers. J Dent 2013;41(10):881–91.
[17] Zhang K, Cheng L, Weir MD, Bai YX, Xu HH. Effects of quaternary ammonium chain length on the antibacterial and remineralizing effects of a calcium phosphate nanocomposite. Int J Oral Sci 2016;30(8):45–53.
[18] Zhou C, Weir MD, Zhang K, Deng D, Cheng L, Xu HH. Synthesis of new antibacterial quaternary ammonium monomer for incorporation into CaP nanocomposite. Dent Mater 2013;29(8):859–70.
[19] Zhang K, Cheng L, Wu EJ, Weir MD, Bai Y, Xu HH. Effect of water-ageing on dentine bond strength and anti-biofilm activity of bonding agent containing new monomer dimethylaminododecyl methacrylate. J Dent 2013;41(6):504–13.
[20] Li F, Weir MD, Chen J, Xu HH. Comparison of quaternary ammonium-containing with nano-silver-containing adhesive in antibacterial properties and cytotoxicity. Dent Mater 2013;29(4):450–61.
[21] Xu X, Wang Y, Liao S, Wen ZT, Fan Y. Synthesis and characterization of antibacterial dental monomers and composites. J Biomed Mater Res B Appl Biomater 2012;100(4):1151–62.
[22] Alrahlah A, Silikas N, Watts DC. Hygroscopic expansion kinetics of dental resin–composites. Dent Mater 2014;30(2):143–8.
[23] Al Sunbul H, Silikas N, Watts DC. Resin-based composites show similar kinetic profiles for dimensional change and recovery with solvent storage. Dent Mater 2015;31(10):201–17.
[24] Watts DC, Marouf AS. Optimal specimen geometry in bonded-disk shrinkage-strain measurements on light-cured biomaterials. Dent Mater 2000;16(6):447–51.
[25] Schneider LF, Moraes RR, Cavalcante LM, Sinhoreti MA, Correr-Sobrinho L, Consani S. Cross-link density evaluation through softening tests: effect of ethanol concentration. Dent Mater 2008;24(2):199–203.
[26] Cavalcante LM, Schneider LF, Silikas N, Watts DC. Surface integrity of solvent-challenged ormocer-matrix composite. Dent Mater 2011;27(2):173–9.
[27] Elliott JE, Lovell LG, Bowman CN. Primary cyclization in the polymerization of bis-GMA and TEGDMA: a modeling approach to understanding the cure of dental resins. Dent Mater 2001;17(3):221–9.
[28] Hoshika T, Nishitani Y, Yoshiyama M, Key 3rd WO, Brantley W, Agee KA, et al. Effects of quaternary ammonium-methacrylates on the mechanical properties of unfilled resins. Dent Mater 2014;30(11):1213–23.
[29] Antonucci JM, Zeiger DN, Tang K, Lin-Gibson S, Fowler BO, Lin NJ. Synthesis and characterization of dimethacrylates containing quaternary ammonium functionalities for dental applications. Dent Mater 2012;28(2):219–28.
[30] Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006;22(3):211–22.
[31] Ito S, Hashimoto M, Wadgaonkar B, Svizero N, Carvalho RM, Yiu C, et al. Effects of resin hydrophilicity on water sorption and changes in modulus of elasticity. Biomaterials 2005;26(33):6449–59.
[32] Huang QT, He JW, Lin ZM, Liu F, Lassila LV, Vallittu PK. Physical and chemical properties of an antimicrobial Bis-GMA free dental resin with quaternary ammonium dimethacrylate monomer. J Mech Behav Biomed Mater 2016;56:68–76.
[33] Martin N, Jedynakiewicz NM, Fisher AC. Hygroscopic expansion and solubility of composite restoratives. Dent Mater 2003;19(2):77–86.
[34] Versluis A, Tantbirojn D, Lee MS, Tu LS, DeLong R. Can hygroscopic expansion compensate polymerization shrinkage? Part I. Deformation of restored teeth. Dent Mater 2011;27(2):126–33.
[35] Alshali RZ, Salim NA, Satterthwaite JD, Silikas N. Post-irradiation hardness development, chemical softening, and thermal stability of bulk-fill and conventional resin-composites. J Dent 2015;43(2):209–18.
[36] Kleverlaan CJ, Feilzer AJ. Polymerization shrinkage and contraction stress of dental resin composites. Dent Mater 2005;21(12):1150–7.
[37] Ferracane JL. Developing a more complete understanding of stresses produced in dental composites during polymerization. Dent Mater 2005;21(1):36–42.
[38] Pfeifer CS, Shelton ZR, Braga RR, Windmoller D, Machado JC, Stansbury JW. Characterization of dimethacrylate polymeric networks: a study of the crosslinked structure formed by monomers used in dental composites. Eur Polym J 2011;47(2):162–70.
[39] Dewaele M, Truffier-Boutry D, Devaux J, Leloup G. Volume contraction in photocured dental resins: the shrinkage-conversion relationship revisited. Dent Mater 2006;22(4):359–65.
[40] He J, Söderling E, Lassila LV, Vallittu PK. Preparation of antibacterial and radio-opaque dental resin with new polymerizable quaternary ammonium monomer. Dent Mater 2015;31(5):575–82.
[41] Beigi Burujeny S, Atai M, Yeganeh H. Assessments of antibacterial and physico-mechanical properties for dental materials with chemically anchored quaternary ammonium moieties: thiol-ene-methacrylate vs. conventional methacrylate system. Dent Mater 2015;31(3):244–61.
[42] Miyazaki CL, Medeiros IS, Santana IL, Matos Jdo R, Rodrigues Filho LE. Heat treatment of a direct composite resin: influence on flexural strength. Braz Oral Res 2009;23(3):241–7.
[43] Stansbury JW. Dimethacrylate network formation and polymer property evolution as determined by the selection of monomers and curing conditions. Dent Mater 2012;28(1):13–22.
[44] Ferracane JL. Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. Dent Mater 1985;1(1):11–4.
[45] Imazato S, McCabe JF. Influence of incorporation of antibacterial monomer on curing behavior of a dental composite. J Dent Res 1994;73(10):1641–5.
[46] Li F, Li F, Wu D, Ma S, Gao J, Li Y, et al. The effect of an antibacterial monomer on the antibacterial activity and

mechanical properties of a pit-and-fissure sealant. J Am Dent Assoc 2011;142(2):184–93.
[47] Yap AU, Teoh SH. Comparison of flexural properties of composite restoratives using the ISO and mini-flexural tests. J Oral Rehabil 2003;30(2):171–7.
[48] Boaro LC, Gonçalves F, Guimarães TC, Ferracane JL, Pfeifer CS, Braga RR. Sorption, solubility, shrinkage and mechanical properties of "low-shrinkage" commercial resin composites. Dent Mater 2013;29(4):398–404.