Exothermic Behavior, Degree of Conversion, and Viscoelastic Properties of Experimental and Commercially Available Hard Chairside Reline Resins

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ABSTRACT: This study evaluated the exothermic behavior, degree of conversion (DC), and the viscoelastic properties of five reline resins, two experimental (E1 and E2), and three commercially available (Kooliner, K; New Truliner, NT; and Tokuyama Rebase II, TR II), and one denture base resin (Lucitone 550, L). The exothermic behavior was assessed ($n = 4$) using a type-K thermocouple. The DC (%) was measured ($n = 5$) by Fourier transformed infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectroscopy. The viscoelastic properties were evaluated ($n = 2$) by dynamic mechanical thermal analysis (DMTA) under different runs. Storage modulus (E') and loss tangent (tan δ) at 37°C were obtained from the first and last runs. The glass transition (Tg) was measured from the last run. Data were analyzed by analyses of variance (ANOVA) and Tukey tests (α = 0.05). K and NT produced similar peak temperature to TR II and higher than E1 and E2. E1, E2, and TR II showed the lowest time to peak temperature. NT produced the highest DC, followed by TR II and L. E2 produced similar DC to K and higher than E1. No significant differences were found on the E' and tan δ of E1, E2, and TR II. From the last run, L showed similar E' to E1, E2, and K and higher than NT and TR II. The highest Tg was produced by L. K produced lower Tg than TR II and higher than E1, E2, and NT. All reline materials presented suitable exothermic behavior to clinical use. Overall, the materials formulated with difunctional monomers (E1, E2, and TR II) presented similar properties to the denture resin. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1669–1676, 2011

Key words: degree of polymerization; viscoelastic properties; glass transition; crosslinking; thermal properties

INTRODUCTION

Gradual changes in the denture-bearing area occur after tooth extraction. In these situations, the removable prostheses must be relined to re-establish their proper fit and support. A denture may be relined using laboratory procedures or at the chairside in the dental clinic. The laboratory reline materials involve an extra patient visit as well as a laboratory fee. Further, the patient needs to be without wearing the denture during the laboratory procedures. The use of autopolymerizing reline resins allows the dentist to reline removable prostheses directly, intraorally. Thus, this method is not only faster than the laboratory-processed reline systems but can also reproduce the morphologic features of oral soft tissue directly on the denture base.[1] The first relining materials available on the market were all based on

the monomer methyl methacrylate. When compared to the heat-polymerized denture base acrylic resins, these materials had higher porosity,[2] cytotoxicity,[3,4] and heat emission during polymerization[2,5] and also lower mechanical strength[5,6] and color stability.[5] To overcome these limitations, new materials were formulated using polymers and monomers other than polymethyl methacrylate (PMMA) and methyl methacrylate, respectively. Overall, the powder of these polymers was based on polyethyl methacrylate (PEMA), whereas the liquid contained monofunctional monomers such as butyl methacrylate, isobutyl methacrylate (IBMA), and 2-hydroxyethyl methacrylate.[4,7] Although these hard chairside relining materials have produced improvements in controlling setting time and temperature and biocompatibility, studies[7–14] have shown that they still possessed lower physicochemical and mechanical properties in comparison to the heat-polymerized denture base resins. As a result, it has been found that these chairside relining resins affected the mechanical strength of relined denture bases[12,15] and relined specimens.[8,14,16,17] Considering that the mechanical

strength of a relined denture is dependent on the bulk strength of both the denture base and reline polymers,[14] reline materials should have similar properties to denture base resins.

To further improve the hard chairside reline materials, dimethacrylate crosslinking agents such as 1,6-hexanediol dimethacrylate and 1,9-nonanediol dimethacrylate have been added to the monofunctional monomer phase to generate a crosslinked matrix.[7,9,10,12] This resulted in copolymers with lower residual monomer content,[4] water sorption, solubility,[7,12] linear dimensional change,[13] and higher mechanical strength.[8–11,14–16] Although difunctional monomers have been used for improving the strength of the reline materials, the type of monomer and concentrations used, and, consequently, the mechanical properties vary widely among materials.[7–15] It is known that highly crosslinked reline materials have significantly high modulus of elasticity, which can result in a low-viscoelastic recovery of the polymer, thus reducing its resistance to fatigue crack propagation.[7] In a previous study,[15] denture bases relined with one highly crosslinked autopolymerizing reline resin had lower resistance to failure than original intact denture bases. Therefore, the development of reline materials with lower brittleness and higher viscoelastic recovery would be recommended. This could be achieved by characterizing and selecting an appropriate combination of crosslinking agents. With that in mind, in the present investigation, two experimental reline resins were formulated using high concentrations of the dimethacrylates ethylene glycol dimethacrylate and 1,4-butanediol dimethacrylate, commonly used in the medical field.[7,18–20]

Among the physicochemical and mechanical properties used for evaluating polymers, the exothermic behavior during polymerization and the degree of conversion (DC) are outstanding.[2,4,5,21] In addition, the dynamic mechanical thermal analysis (DMTA) is one of the most sensitive and specific method used for evaluating the viscoelastic properties of polymeric materials.[22–24] The DMTA analyses are of great importance in evaluating the E', which determines rigidity and depends on the materials' ability to store mechanical energy; E'' that is associated with the energy absorbed during dynamic deformation, and tan δ that is the ratio between E'' and E' and is a measure of the fraction of energy lost.[24] From these properties, the degree of polymerization, presence of plasticizers, effect of postcure treatments, and rigidity can be evaluated.

The aim of this study was to evaluate the exothermic behavior, the DC, and the viscoelastic properties of two highly crosslinked experimental hard chairside reline resins, three commercially available hard chairside reline resins, and one heat-polymerized denture base resin.

MATERIALS AND METHODS

Three commercially available hard chairside reline resins, two experimental highly crosslinked hard chairside reline resins, and one conventional heat-polymerized denture base resin were select for this study. The product names, codes, manufacturers, powder/liquid ratios, compositions, and polymerization conditions are listed in Table I. The experimental materials were formulated using PEMA powder (VIPI Ind. Com. Exp. e Imp. de Prod. Odontol. Ltda; Pirassununga, SP, Brazil) and different ratios (Table I) of the difunctional monomers 1,4-butanediol dimethacrylate (Evonik Degussa; Hanau, Germany; Fig. 1) and ethylene glycol dimethacrylate (Evonik Degussa; Hanau, Germany; Fig. 2). In addition, 1.0 wt % of benzoyl peroxide and 2.0 wt % of N,Ndimethyl p-toluidine (DMT) were added to the powder and liquid, respectively.

Exotherm during polymerization

To evaluate the exothermic behavior of the materials during polymerization, a circular stainless steel split mold (60 mm diameter × 2.0 mm high)[25] with a breakaway compartment was used. This mold was placed inside a stove on the center of a glass plate covered with a nylon sheet. The reline resins were proportioned (Table I), manipulated, and poured to excess within the mold. Subsequently, a type K (chromel-alumel) thermocouple (Instrutherm; São Paulo, SP, Brazil) was carefully positioned in the homogenous dough through the breakaway compartment, so that the sensitive area of the sensor was placed at the center of each specimen ($n = 4$). A second nylon sheet and a glass plate were placed over the material (Fig. 3), and pressure was applied to extrude excess material. The thermocouple was adapted in a portable datalogging thermometer (Instrutherm; São Paulo, SP, Brazil) so that the temperature changes were recorded as a function of time, soon after the mixed materials were placed into the mold. The temperature (°C) was recorded every three seconds from the beginning of polymerization, until the temperature of each specimen returned to 37 ± 1.0°C. From the temperature–time curves (Fig. 4), the mean values of peak temperature (°C), time (s) to peak temperature, and total time (s) of polymerization were recorded (Table II). The total time of polymerization was measured from the beginning of the mix, until the temperature equilibrium was reached (at 37°C).

Degree of conversion

The DC of the materials was determined by Fourier transformed infrared-attenuated total reflectance

TABLE I
Materials Tested

Product	Code	Manufacturer	Batch number	Powder/liquid ratio	Composition		Polymerization condition
					Polymer	Monomer	
Experimental 1	E1	Not applicable	Not applicable	2.10 g/1.6 mL	PEMA	1,4-BDMA EGDMA (1 : 1)	6 min at room temperature
Experimental 2	E2	Not applicable	Not applicable	2.10 g/1.6 mL	PEMA	1,4-BDMA EGDMA (4 : 1).	6 min at room temperature
Kooliner	K	GC America, Alsip, IL, EUA	0805058	2.10 g/1.5 mL	PEMA	IBMA	10 min at room temperature
New Truliner	NT	Bosworth Co., Skokie, Illinois, USA	0707/409	1.34 g/1.0 mL	PEMA	IBMA di-n-butyl phthalate	20 min at room temperature
Tokuyama Rebase Fast II	TR II	Tokuyama Co., Tokyo, Japan	UF68118	2.40 g/1.0 mL	PEMA	1,9-NDMA AAEM	5.5 min at room temperature
Lucitone 550	L	Dentsply Ind. Com. Ltda, Rio de Janeiro, RJ, Brazil	379209 (powder) 369776 (liquid)	2.10 g/1.0 mL	PMMA	MMA EGDMA	90 min at 73°C + 30 min at 100°C

PEMA, poly(ethyl methacrylate); 1,4-BDMA, 1,4-butanediol dimethacrylate; EGDMA, ethylene glycol dimethacrylate; IBMA, isobutyl methacrylate; 1,9-NDMA, 1,9-nonanediol dimethacrylate; AAEM, 2-(acetoacetoxy) ethyl methacrylate; PMMA, poly(methyl methacrylate); MMA, methyl methacrylate.
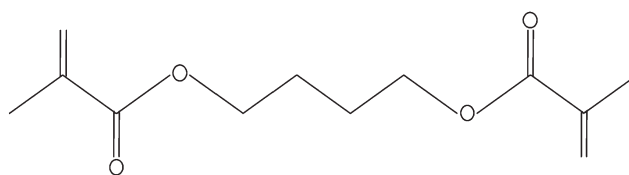

Figure 1 Structural formula of the 1,4-butanediol dimethacrylate (1,4-BDMA).

(FTIR-ATR) spectroscopy.[26,27] Five circular specimens (10 mm diameter $\times$ 4.0 mm high) were fabricated for each material using a stainless steel mold. This mold was placed on the center of a glass plate covered with a nylon sheet. The denture base acrylic resin Lucitone 550 (L) was mixed and packed in the stainless steel mold. Thereafter, a second nylon sheet was placed over the acrylic resin, the steel mold was closed and pressure (1250 kg) was applied for 30 min. The denture base acrylic resin specimens were then polymerized according to the manufacturer's recommendations (Table I). After polymerization, the specimens were bench cooled at room temperature for 30 min and 15 min under running water before being removed from the molds. The specimens were then stored in distilled water at 37 $\pm$ 1.0°C for 50 $\pm$ 2.0 h before testing, following the ISO 1567 recommendations for the physical–mechanical tests.[28] For the fabrication of the reline resins specimens, the materials were proportioned (Table I), mixed, inserted into the metal mold, and pressure (500 kg) was applied until polymerization was complete. The reline resins specimens were subjected to FTIR-ATR spectroscopy, 30 min after processing.

FTIR-ATR spectroscopy

FTIR-ATR spectra of all specimens were recorded at ambient pressure and temperature using a FTIR spectrometer with diamond ATR accessory (Pelkin-Elmer Spectrum BXII; Norwalk, CT). Spectra were obtained with 32 scans at a resolution of 4.0 cm^{-1} within a wavelength from 600 to 4000 cm^{-1}. The DC (%) of monomer-to-polymer was calculated by comparison of the absorbance ratio using a standard baseline technique[29] of the C=C peak from the methacrylate group at 1640 cm^{-1} to that of the unchanging C=O peak from the ester group at 1720 cm^{-1}. The
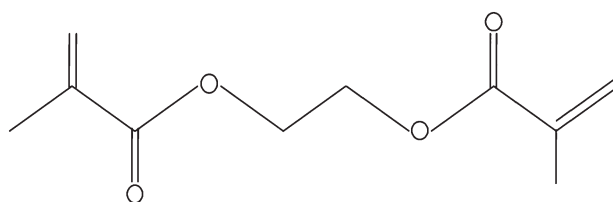

Figure 2 Structural formula of the ethylene glycol dimethacrylate (EGDMA).
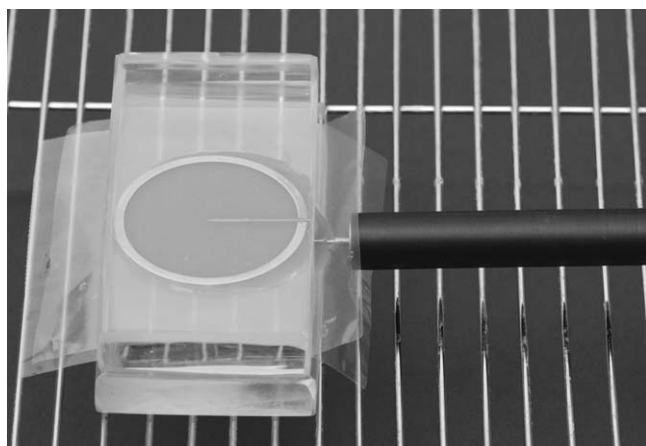
Figure 3 Thermocouple positioned into the reline material, sandwiched between two glass slabs.

C=O peak from the ester group was used as a reference peak, before and after polymerization. By taking the ratio between the two absorbances, the fraction of unreacted double bonds could be calculated using the following formula:

$$\text{Degree of conversion } (\%) = [1 - (P/U)] \times 100,$$

where P is the relationship between the absorbance of C=C and C=O of the polymerized material, and U is the relationship between the absorbance of C=C and C=O of the unpolymerized material.

Dynamic mechanical thermal analysis

For each material, two specimens were fabricated as previously described. After polymerization, the specimens were removed from the molds, and the edges finished with 400-grit silicon carbide paper (3M ESPE, St. Paul, MN) in an automatic grinding and polishing unit (Metaserv 2000, Buehler; Lake Bluff, IL, EUA) to remove irregularities. The accuracy of the dimensions (width and thickness) was verified with a caliper (Mitutoyo Sul Americana; Suzano, São Paulo, Brazil) at three locations of each dimension to within 0.2 mm tolerance. The final
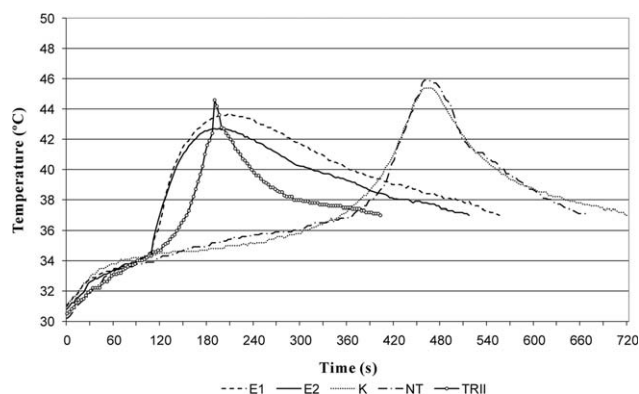

Figure 4 Temperature–time curves obtained during the polymerization of the reline materials.

dimension of each specimen was 40 mm length, 10 ± 0.2 mm width, and 3.3 ± 0.2 mm thickness. To fabricate the denture base resin specimens, acrylic master patterns ($40 \times 10 \times 3.3$ mm) were obtained as described for the reline resin specimens. The acrylic patterns were individually invested in high-viscosity silicone (Zetalabor, Zhermack S.p.A.; Badia Polesine, Rovigo, Italy) to obtain molds, which were further invested in Type IV stone (Vel-Mix; Kerr, Romulus, MI) using conventional flasks. After the stone had set, the flasks were separated, and the denture base acrylic resin L was mixed, packed under pressure, and polymerized according to the manufacturer's instructions (Table I). After polymerization, each processed flask was left to bench cooling at room temperature for 30 min and then placed under running water for 15 min. The specimens were then removed from the molds and finished as described for the reline resin specimens.

Dynamic mechanical thermal analysis tests

The viscoelastic properties were evaluated by DMTA, using a dynamic mechanical thermal analyzer apparatus (PL Thermal Sciences MK II, Polymer Laboratories Ltd.; Loughborough, UK) linked to an IBM compatible computer. The instrumentation was previously calibrated, and the specimens clamped in a

TABLE II
Mean Values and Standard Deviation of Peak Temperature (°C), Time (s) to Peak Temperature, Total Time (s) of Polymerization and Degree of Conversion (%)

Material	Peak temperature	Time to peak	Total time	Degree of conversion
E1	43.7 (0.40) [BC]	209 (1.73) [B]	553 (2.87) [C]	83.58 (1.86) [D]
E2	42.7 (0.59) [C]	187 (7.50) [B]	511 (7.89) [D]	88.14 (1.64) [C]
K	45.7 (0.73) [A]	456 (5.74) [A]	717 (2.45) [A]	85.18 (1.00) [CD]
NT	45.6 (0.22) [A]	439 (27.65) [A]	685 (13.72) [B]	97.37 (0.35) [A]
TR II	44.9 (1.38) [AB]	189 (7.35) [B]	411 (10.68) [E]	91.62 (0.98) [B]
L	NA	NA	NA	92.90 (2.87) [B]

Standard deviation in parenthesis. Vertically, entries with the same superscript letter were not significantly different ($P > 0.05$). NA, not applicable.

Mean Values and Standard Deviation of log E' (Storage Modulus) at 37°C, tan δ (Loss Tangent) at 37°C and Tg (Glass Transition Temperature)

Material	First DMTA run		Last DMTA run		
	log E'	tan δ	Log E'	tan δ	Tg (°C)
E1	8.994 (0.062) [A]	0.127 (0.022) [B]	9.204 (0.006) [AB]	0.067 (0.002) [C]	77.0 (0.2) [D]
E2	8.950 (0.071) [A]	0.126 (0.021) [B]	9.173 (0.021) [AB]	0.067 (0.002) [C]	76.5 (0.3) [D]
K	8.850 (0.073) [A]	0.225 (0.024) [A]	9.089 (0.137) [ABC]	0.124 (0.0003) [B]	90.7 (0.1) [C]
NT	8.837 (0.039) [A]	0.230 (0.003) [A]	8.876 (0.005) [C]	0.184 (0.014) [A]	72.7 (0.7) [E]
TR II	8.995 (0.005) [A]	0.127 (0.062) [B]	9.049 (0.006) [BC]	0.107 (0.0004) [B]	97.5 (0.3) [B]
L	9.253 (0.011) [B]	0.067 (0.001) [B]	9.286 (0.013) [A]	0.065 (0.001) [C]	127.5 (0.2) [A]

Standard deviation in parenthesis. Vertically, entries with the same superscript letter were not significantly different ($P > 0.05$).

dual cantilever configuration at a constant torque of 30 cNm. The removable furnace head was bolted into place, and the transducer was adjusted to ensure that there was no strain on the specimen. The specimens were subjected to a sinusoidal deformation at a fixed frequency of 1.0 Hz (approximately average chewing rate[30]) at heating rate of 3.0°C/min. A strain of 64 μm peak to peak was used, ensuring that each material was tested fully within its elastic limit.

To evaluate any possible postpolymerization effects induced during DMTA, specimens were submitted to consecutive temperature cycling with different temperature ranges. For the reline resins, the first DMTA run was conducted with temperature ranging from 20 to 40°C, and the following "re-runs" were conducted with the maximum temperature being increased by an increment of 20°C. For the denture base resins, the first DMTA run was conducted with temperature ranging from 20 to 100°C. The temperature ranges were from 20 to 120°C and from 20 to 160°C for the last DMTA run of the reline and denture base resins, respectively. Therefore, 5 runs were carried out for each reline resin specimen, whereas 4 were conducted for the denture base resin specimens. After each run, the removable furnace was opened, and the specimens were allowed to cool naturally at room temperature (23°C). Thereafter, the removable furnace was bolted into place, and the sample was cooled to below 20°C by passing liquid nitrogen between the inner and outer casing of the furnace. Values of storage modulus (E') and loss tangent (tan δ) at 37°C were obtained from the first and last DMTA runs. The results of glass transition temperature (Tg) were taken to be the maximum of the tan δ, recorded from the last DMTA run, versus temperature curves.[31] As for the DC, the reline resins specimens were subjected to DMTA runs 30 min after processing, and the denture base resin L specimens were analyzed after storage in water at 37 ± 1.0°C for 50 ± 2.0 h.[28] Therefore, the DMTAs were performed after the same period of storage used to evaluate the DC of the materials.

Statistical analyses

Data from exotherm during polymerization, FTIR-ATR spectroscopy, and DMTA tests were evaluated statistically using one-way analyses of variance (ANOVA). Tukey Honestly Significant Difference (HSD) *post hoc* test was used to determine differences between means ($\alpha = 0.05$). SPSS software (Version 16, SPSS Inc.; Chicago, IL) was used for these statistical analyses.

RESULTS

The one-way ANOVAs showed a significant effect for the factor material ($P < 0.005$) for all properties evaluated. The mean values for the peak temperature, time to peak temperature, total time of polymerization, DC, and the results of Tukey HSD *post hoc* test ($\alpha = 0.05$) are presented in Table II. Table III presents the mean values and the results of Tukey HSD *post hoc* test ($\alpha = 0.05$) for log E', tan, δ and Tg.

DISCUSSION

The effect of the exothermic release of the hard chairside relining materials should always be a consideration, as the heat released might harm the oral mucosa.[2,21,32] According to Kim and Watts,[21] as the polymerization proceeds, carbon–carbon double bonds (C=C) are converted to new carbon–carbon single bonds (C—C), and the difference in energy between the two bonds (80 kJ/mol) emits as heat. In the present study, the exothermic reaction of the acrylic resins was evaluated by the thermocouple method, a reliable and easy approach to measure temperature changes.[21,25,32] The stove temperature (37°C) was constantly maintained because the temperature may affect the resultant net temperature rise for a given amount of energy dissipation.[21] All materials showed exothermic reaction during polymerization. The rise in temperature during polymerization ranged from 12 to 15°C. Although the peak

temperature results differed statistically, the mean values ranged from 42.7 to 45.7°C, which are suitable to use in the oral cavity and well below the maximum recommended by the ADA no. 17.[25] Previous studies[2,5,32] corroborated the peak temperature (45.7°C) of K material. Another fact that must be considered is that the materials formed by monofunctional monomers (K and NT) produced higher time to peak temperature than the materials formulated with difunctional monomers (E1, E2, and TR II). Similar results were found in another study,[21] in which a monofunctional polymer presented higher time to peak temperature (10 min) than two dimethacrylate-based materials (2 min). This may be considered an advantage as it reduces the chair time required to reline the denture base. The faster setting reaction of the dimethacrylate-based polymers may be related to its greater reactivity. According to Ruyter and Svendsen,[19] the increased distance between the methacrylate groups of the crosslinked materials enhanced the reactivity of the second double bond, thus favoring the monomer to polymer conversion. Based on the exothermic behavior of the materials, the use of dimethacrylate-based reline materials should be preferred because the faster setting reaction can reduce the time consumed for the chairside relining procedures. Although the method used for determining the total time of polymerization does not reflects the total time required to a complete monomer-to-polymer conversion, it is reasonable to suppose that after exothermic reaction (equilibrium at 37°C), most of the molecules are converted, allowing comparison between the results of different materials.

The DC of the materials was measured by FTIR-ATR spectroscopy, which is a special infrared spectroscopy method based on the physical phenomena of light reflection at the interface of two media of difference indices of refraction.[26] During reflection, the infrared beam penetrates the surface layers of the specimens, providing a surface spectrum of the material. From the obtained spectra of unpolymerized and polymerized samples, the DC of the materials is calculated using the standard baseline technique.[29] The results from the present investigation are in accordance with the few previous studies on the DC of hard chairside reline materials.[4,10] NT produced the highest DC (97.37%), followed by TR II which showed similar DC to L and higher than E1, E2, and K. Despite the differences, the DC of all evaluated materials was higher than 80%, a percentage that has been demonstrated to be adequate for acquiring optimal mechanical properties.[10,33] Considering that there is an inverse correlation between the DC and the residual monomer content of denture base polymers,[34,35] the elevated DC produced by NT was not expected. In a previous study,[10] NT showed

high-residual monomer content (519 μg mL^{-1}), when compared to other three chairside reline resins including K (207.2 μg mL^{-1}). Similarly, as the short-cured denture base resin L contains just 0.08% of residual monomer content,[4] its higher DC in comparison to NT was also not expected. Probably, the high DC produced by the reline resin NT is related to its low viscosity (tan δ = 0.230) and Tg (72.7°C). According to Pereira et al.,[36] an increased DC may be expected when mobility and flexibility of the starting monomer is high. Therefore, materials with lower viscosity and Tg are likely to exhibit higher DC. Although the reline resin K present similar chemical composition to NT, with the exception of the plasticizer di-n-butyl phthalate,[37] its DC was lower than the former. Similar results were found in a previous study,[10] in which NT produced higher DC (94.1%) than K (81.3%). The high Tg of K (90.7°C) in comparison to NT (72.7°C) may have played a role in the difference in DC between NT and K. Further studies are needed to confirm this hypothesis. TR II showed favorable DC (91.62%), which was close to that of the denture base resin L (92.90%). The DC of the dimethacrylate-based materials has an inclination to be higher due to its increased reactivity of the second double bond.[19] Therefore, the 1,9-nonandioldimethacrylate (NDMA) crosslinking agent present (39%) in the liquid of TR II may have increased its reactivity, thus resulting in elevated DC. The high percentage of acetoacetoxyethyl methacrylate (AAEM; 59%) in the liquid of the reline resin TR II may have also contributed to its high conversion. From another study,[27] there is a direct relationship between the increase in AAEM concentration and DC. According to the authors, this was most probably a result of the resin system being less viscous and the polymer having more flexibility and thus being able to polymerize further before vitrification. Although the experimental resins E1 and E2 contain high percentages of crosslinking agents and low Tg, their DC were lower than most of the materials evaluated. Several authors[19,38,39] have observed that part of the dimethacrylate-based monomers react only to one of the double bond, resulting in pendant molecules which remain bound within the polymer network and are not eluted. Based on these observations, it is possible that these unreacted molecules were detected as double bonds by the infrared analysis.[38] Further studies on the residual monomer content of the experimental materials are necessary to confirm this hypothesis. Despite these results, the DC produced by E1 and E2 (83.58% and 88.14%, respectively) was similar to those of three reline resins evaluated by Urban et al.[10] Considering these results and that the pendant molecules are not elute, a low-residual monomer content may be expected for the experimental reline

resins. Another fact that must be considered is that the DC of the materials was obtained after a short period of time. Therefore, considering that the monomers radicals may be active over a long period of time, the obtained results might not be related to the maximum DC. Additional studies are necessary to evaluate the maximum DC of the experimental and commercially available reline materials.

The DMTA was used in the present investigation, because it has far greater sensitivity to both macroscopic and molecular relaxation process than conventional thermal analysis techniques.[31,40] An "ideal" reline resin would demonstrate a high E' and a low tan δ, as is preferable that the material return to its initial shape shortly after the load is removed.[41] Therefore, E1, E2, and TR II produced the most ideal viscoelastic properties and appeared to perform similar to the denture base resin L. The results from the first DMTA run showed that the denture base resin L produced higher E' than the reline resins. These results are in agreement to those of Murata et al.,[41] in which the E' of two heat-polymerized denture base resins was higher than those of different chairside reline materials. Similarly, several studies[9–11,16,17,42] have demonstrated that chairside reline resins have lower physicomechanical properties than denture base resins. Therefore, the results of this study may be attributed to the differences in the chemical composition and polymer network structure of the materials tested. The crosslinking agents may increase the E' and Tg of a polymer by introducing restrictions on the molecular motions of the polymeric chains,[39] reducing its damping.[43] This may help explain the lower tan δ showed by the reline materials E1, E2, TR II, which present high percentages of crosslinking agents. Based on this observation, the high content of crosslinking agents may produce polymers with high stiffness and brittleness, which is a nondesired property of denture base and reline materials. According to Arima et al.[7] highly crosslinked reline materials demonstrated a significantly high modulus of elasticity, which reflects the rigidity of a material. Therefore, the low plasticity of the high-crosslinked polymers may result in a decreased resistance to fatigue crack propagation. Studies are still needed to evaluate the effect of cyclic loading on the properties of materials formulated with high percentages of crosslinking agents. Despite this information, the experimental materials did not produced lower tan δ results than the largely used denture base resin L, either in the first or last DMTA runs. Contrastingly, the reline materials K and NT, which do not contain crosslinking agents in its composition, showed the highest tan δ mean values. The plasticizer di-n-butyl phthalate contained (8.0%)[18,37] in the liquid of material NT may have also contributed to its greater flexibility. These findings are in agreement with other investigations, where mechanical properties such as flexural modulus[7,11] and Vickers[9] hardness were higher for those acrylic resins having crosslinking monomers.

The DMTA was performed under different temperature ranges (runs)[31] within the average chewing rate.[30,43] The ability to re-examine the DMTA specimens after heating cycles is an important advantage. According to Jacobsen et al.,[31] the DMTA induces some postpolymerization, and the magnitude of this will depend on the efficiency of the original conversion.[35] Therefore, at the last cycle, all specimens were probably analyzed in a full postcure condition. This may explain why a decrease in tan δ was observed for all reline materials after the last DMTA run as opposed to the heat-polymerized denture base resin L, for which no change was observed. As a result, E1 and E2, which produced lower E' and tan δ than the denture base resin L at the first DMTA run, showed similar results to L after the last run. Similarly, while a significant difference in tan δ was observed between materials K and TR II at the first run, no difference was observed after the last run. These results might be related to the further polymerization of the materials. In a previous study, Urban et al.[4] observed that material K produced higher residual monomer content (1.52%) than four hard chairside reline resins and one denture base resin. However, the residual monomer content and the monomer release of reline materials may be reduced after immersion in hot water or dry microwave heating.[4,10] It is known that high temperatures increased the mobility of the residual monomer, which was stationary in the polymer network, thus resulting in higher DC.[10,42] Other studies have shown that the reduction of residual monomer content may improve the mechanical[10,44] and viscoelastic[45] properties of the acrylic resins. From this previous discussion, it would be advisable that the hard chairside reline materials evaluated in the present study be submitted to a postpolymerization heat treatment before the denture is inserted into place, as suggested by several authors.[3,9–11]

The Tg of the materials can be arranged as L > TR II > K > E1 = E2 > NT. It has been observed that the DC, the residual monomer content and the presence of crosslinking agents are associated to the Tg of polymers.[22,39,42,43,46] The dimethacrylate-based materials generally present low flexibility and higher Tg than the non-crosslinked polymers.[39,46] In this context, the low Tg of the experimental resins were not expected. Probably, these results are associated to the plasticizer effect of the pendant methacrylate groups, commonly observed in highly crosslinked polymers.[22,39] Although TR II contains high percentage of crosslinking agent (39%), this reline material has also high concentration of AAEM (59%) in its

composition. According to Viljanen et al.,[27] the use of this monomer may result in copolymers with high DC and Tg. Thus, the differences among the results of Tg seem to be depending on the composition of the reline materials. Despite the differences observed here, these results corroborate findings in the literature, which show that the Tg of the dental polymers can vary considerably.

Overall, the experimental reline resins E1 and E2 produced similar properties to the denture base acrylic resin L. Despite the enhancements produced by these materials in comparison to some extensively used commercially available reline resins, properties such as flexural strength, water sorption and solubility, polymerization shrinkage, and bond strength to denture base resins must be evaluated prior to clinical use and will be the focus of a detailed investigation in the future.

CONCLUSIONS

From the results of this study it can be concluded that:

(1) All reline materials presented suitable peak temperature for direct use in the oral cavity.
(2) Differences in chemical composition may influence the DC and viscoelastic properties of a hard chairside reline resin.
(3) Overall, the materials formulated with difunctional monomers (E1, E2, and TR II) presented similar properties to the denture base acrylic resin L.

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