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Chemical Characterization and Flexural Strength of a Denture Base Acrylic Resin with Monomer 2-Tert-Butylaminoethyl Methacrylate

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Abstract

Purpose: The objectives of this study were to investigate the flexural strength (FS) and chemical interaction between 2-tert-butylaminoethyl methacrylate (TBAEMA) and a denture base acrylic resin.
Materials and Methods: Specimens were divided into five groups according to the concentration of TBAEMA incorporated in acrylic resin Onda-Cryl (0%, 1%, 2%, 3%, 4%) and were submitted to Fourier transform infrared spectroscopy (FTIR), electron spectroscopy for chemical analysis (XPS-ESCA), and differential scanning calorimetry (DSC) analyses. FS of the specimens was tested, and results were analyzed by ANOVA/Tukey's test ($\alpha < 0.05$).
Results: Different nitrogen ratios were observed on specimens' surfaces: 0.36%, 0.54%, 0.35%, and 0.20% for groups 1%, 2%, 3%, and 4%, respectively. FTIR indicated copolymerization of acrylic resin and TBAEMA, and DSC results demonstrated a decrease in glass transition temperature (T_g). Significant differences were found for FS ($p < 0.05$). The mean values were 91.1 ± 5.5,^{A} 77.0 ± 13.1,^{B} 67.2 ± 12.5,^{B} 64.4 ± 13.0,^{B} and 67.2 ± 5.9^{B} MPa for groups 0%, 1%, 2%, 3% and 4%, respectively (same superscript letters indicate no significant difference).
Conclusions: The incorporation of TBAEMA in acrylic resin resulted in copolymerization and the presence of amine groups on specimens' surfaces, and in decreases of T_g and FS.

Poly(methyl methacrylate) (PMMA) resins have been successfully used in the manufacture of partial and complete dentures since the late 1930s because they are easy to handle and process, do not need special equipment, have a lower density, and provide the possibility of mixing colors.[1,2] However, PMMA resins have certain disadvantages, such as low resistance and thermal conductivity, porosity, water sorption and solubility, in relation to their physical and mechanical properties.[2,3] Another important limitation is the deposition and formation of biofilm on the surface of PMMA resins. Their rough surfaces and/or irregularities facilitate microbial adhesion, thereby enabling the colonization of microorganisms[1,4] that can induce an inflammatory response in the oral mucosa of denture wearers. This condition is known as denture stomatitis.[5]

Some researchers have incorporated antifungals or antiseptics into PMMA resins[4,6,7] to avoid microorganism proliferation; however, these substances may be released from PMMA resins and lose antimicrobial long-term effectiveness.[8,9] This might also cause damage to their mechanical properties. Nowadays, antimicrobial polymers[2,10,11] or monomers[1,5,12,13] represent a plausible alternative to solve such problems, since they are potentially resistant to microbial adhesion, they provide adequate mechanical properties,[1,2] and they may remain attached to the acrylic resin polymer chains by means of copolymerization with the methacrylate monomers.[5]

TBAEMA (2-tert-Butylaminoethyl methacrylate) contains amino groups in its composition and could be incorporated into PMMA resins to inhibit microorganisms from growing on

the denture surface. PMMA resin could possibly display antimicrobial activity if amino groups were found on its surface after TBAEMA incorporation, considering there is an association between amino groups on surfaces and antimicrobial activity.[12-14]

On the other hand, there is a need to investigate the effects of TBAEMA incorporation on the properties of the PMMA resin. The glass transition temperature (T_g) is also an inherent property of polymeric materials, whether semicrystalline or amorphous. T_g is commonly defined as the temperature at which a polymer undergoes a transition from glassy state to a state similar to that of a solid rubber without simultaneous changes in their structure.[15] Therefore, T_g significantly influences the physical and mechanical properties of PMMA resin and denotes consequences for PMMA's potential applications.[15,16] Among the mechanical properties, flexural strength (FS) is a measure of tension and fracture strength that allows us to evaluate the clinical performance of partial and complete dentures,[4,5,13] as they are repeatedly flexed during the chewing cycle and may be deformed.[4]

Therefore, the objectives of this research were to characterize a PMMA resin containing an antimicrobial monomer (TBAEMA) by means of Fourier transform infrared spectroscopy (FTIR), electron spectroscopy for chemical analysis (XPS-ESCA), and differential scanning calorimetry (DSC) and to evaluate the FS of this PMMA resin. The hypothesis tested in this study was that the incorporation of TBAEMA into acrylic resin affects surface properties and FS.

Materials and methods

In this research, five groups of PMMA resin were evaluated, consisting of a control group and four experimental groups. The control group (0%) was composed of a PMMA resin cured by microwave energy (Onda-Cryl, Artigos Odontológicos Clássico Ltda., São Paulo, Brazil), and the experimental groups were composed of PMMA resin + TBAEMA (batch number 126031013, Degussa Creavis, Hanau, Germany), according to the TBAEMA concentration (1%, 2%, 3%, 4%).

Chemical characterization

Each specimen was prepared for chemical characterization by investing glass slides measuring 25 × 75 mm^2 in a plastic flask supported by dental stone (α-hemihydrate of calcium sulfate; Herodent, Vigodent S.A. Ind. Com., Rio de Janeiro, Brazil).[13] Flasks are containers specially designed for denture base resin packing and processing. After the invested material had set, the flask was opened, and the mixtures (Table 1) were placed between glass slides to provide thin specimens of uniform size. Mixtures were then packed and polymerized in a microwave oven (Continental, model AW-30, Continental Eletrodomésticos, Hortolândia, Brazil) according to the cycle recommended by the Onda-Cryl manufacturer (3 minutes at 320 W + 4 minutes at 0 W + 3 minutes at 720 W). One specimen from each group (n = 1) was obtained.[13,17] Excess acrylic resin was trimmed from all specimens with a bur after processing (Maxi-Cut, Lesfils de August Malleifer SA, Ballaigues, Switzerland).

Table 1 Description of TBAEMA incorporation into acrylic resin Onda-Cryl

Group	Powder (g)	Liquid or monomer (ml)	TBAEMA (ml)	Total liquid + TBAEMA (ml)
Control	14	7	0	7
1%	14	6.93	0.07	7
2%	14	6.86	0.14	7
3%	14	6.79	0.21	7
4%	14	6.72	0.28	7

XPS-ESCA analysis

XPS-ESCA was used to analyze the presence of nitrogen ratios on the specimens' surfaces, with a Kratos XSAM HS spectrometer (Kratos, Manchester, UK). The nitrogen ratios detected on the specimens' surfaces represented the percentage of amine groups on the specimens' surfaces.[13] Photoelectrons were excited by MgKα radiation (1253.6 eV, 52 W), and the binding energies of the measured photoelectron peaks were calibrated by the C 1s peak of hydrocarbon contamination at a binding energy of 285.0 eV.

FTIR analysis

FTIR analysis was used to evaluate the polymerization process of acrylic resin specifically in the presence of TBAEMA. For this, 2 mg of each specimen was powdered and mixed with 100 mg of dry alkali halide (KBr)[18,19] powder.

After soaking, we proceeded to press the mixed KBr + specimen to produce small disks of 0.5 mm. The absorption spectra were obtained in a Nexus 670 FTIR spectrometer (Nicolet, ThermoScientific, Waltham, MA) in wavenumbers 3500 to 4000 cm^{-1} using a resolution of 4 cm^{-1} and 64 scans.[20]

DSC analysis

Specimens were subjected to DSC analysis. The objective of this was to evaluate the influence of the TBAEMA incorporation on the glass transition temperature (T_g) of acrylic resin. These tests were performed using a DuPont DSC 20120 TA (TA Instruments, New Castle, DE) instrument and consisted of a scan speed of thermal heating controlled at 10°C/min in a nitrogen atmosphere[18] with the heating programmed for a range of 25°C to 140°C. For T_g measurements, 10 mg of each specimen was contained in an aluminum pan with dry nitrogen streaming through the heating chamber.

Flexural strength

Specimens were prepared for FS analysis by investing metal patterns, measuring 67 × 12 × 5.3 mm^3 into plastic flasks. To facilitate removal from the flask, the master patterns were individually invested in high-viscosity silicone (Zetalabor, Zhermach S.p.A., Badia Polesine, Rovigo, Italy) and were then further supported by dental stone within the flasks. After the invested material had set, the flasks were separated, and the master pattern was removed from the silicone mold.[13,21] Mixtures of acrylic resin (Table 1) were then packed and polymerized

Table 2 Atomic percentage of nitrogen on the specimens' surface

Group	% of nitrogen on surface
0% (control)	–
1%	0.36
2%	0.54
3%	0.35
4%	0.20

in a microwave according to the cycle recommended by the Onda-Cryl manufacturer (3 minutes at 320 W + 4 minutes at 0 W + 3 minutes at 720 W).

Ten specimens from each group (n = 10) were obtained. After processing, the specimens were polished in a polishing machine (Arotec Ind. e Com. Ltda, Cotia, Brazil) to a final dimension of

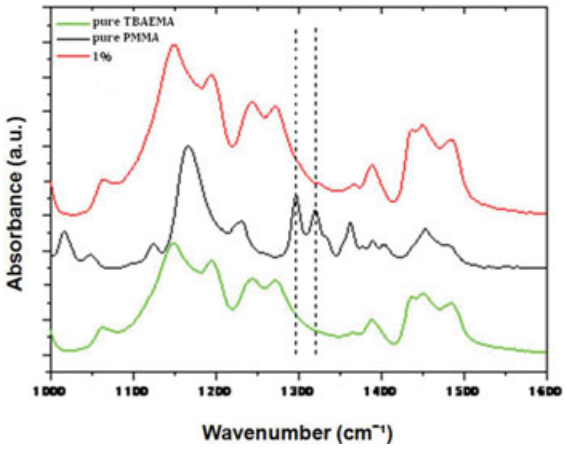

Figure 1 Comparative spectroscopic image of the control specimen, pure TBAEMA, and 1%. Absorption bands (dotted region) are observed in the spectrum of the specimen containing 1% of TBAEMA in the region between 1300 cm^{-1} and 1325 cm^{-1}, which is absent in specimens of pure acrylic resin (control).

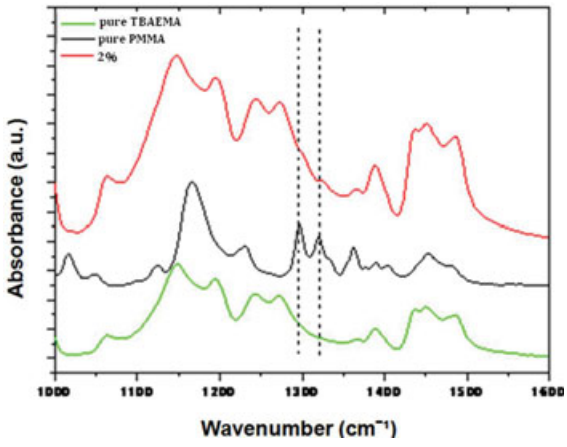

Figure 2 Comparative spectroscopic image of the control specimen, pure TBAEMA, and 2%. Absorption bands (dotted region) are observed in the spectrum of the specimen containing 2% of TBAEMA in the region between 1300 cm^{-1} and 1325 cm^{-1}, which is absent in specimens of pure acrylic resin (control).

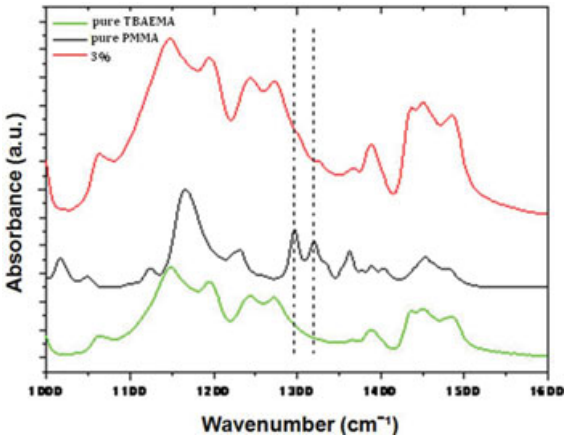

Figure 3 Comparative spectroscopic image of the control specimen, pure TBAEMA, and 3%. Absorption bands (dotted region) are observed in the spectrum of the specimen containing 3% of TBAEMA in the region between 1300 cm^{-1} and 1325 cm^{-1}, which is absent in specimens of pure acrylic resin (control).

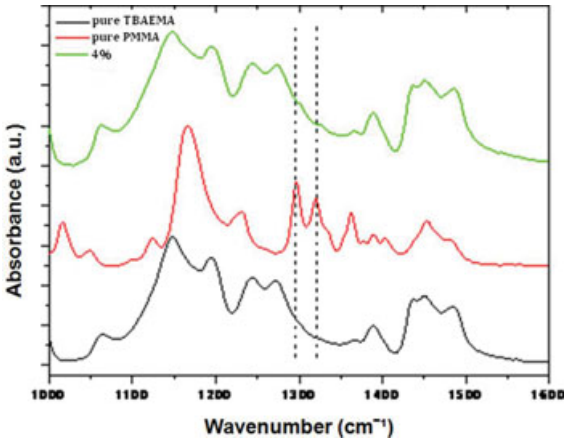

Figure 4 Comparative spectroscopic image of the control specimen, pure TBAEMA, and 4%. Absorption bands (dotted region) are observed in the spectrum of the specimen containing 4% of TBAEMA in the region between 1300 cm^{-1} and 1325 cm^{-1}, which is absent in specimens of pure acrylic resin (control).

$65 \times 10 \times 3.3\ mm^3$, according to the International Organization for Standardization (ISO/FDIS 1567).[22] Each specimen surface was finished with a 280-, 320-, 400-, and 600-grit wet-dry abrasive paper (Norton, Saint-Gobain Abrasivos Ltda, Vinhedo, Brazil). Specimen measurements were verified using a digital caliper (Mitutoyo, Kawasaki, Japan). All specimens were stored in distilled water at 37°C for 50 ± 2 hours before testing.[13,21-22]

The FS of the groups was measured using a three-point bending test in a material testing system machine (Model 810, MTS System Corp, Eden Praire, MN) at a 5 mm/min crosshead speed. FS was calculated using the formula: $FS = 3WL/2\ bd^2$, where FS is flexural strength, W is the maximum load before fracture, L is the distance between supports (50 mm), b is the specimen width, and d is the specimen thickness. Statistical analysis was performed using one-way ANOVA and Tukey's test for

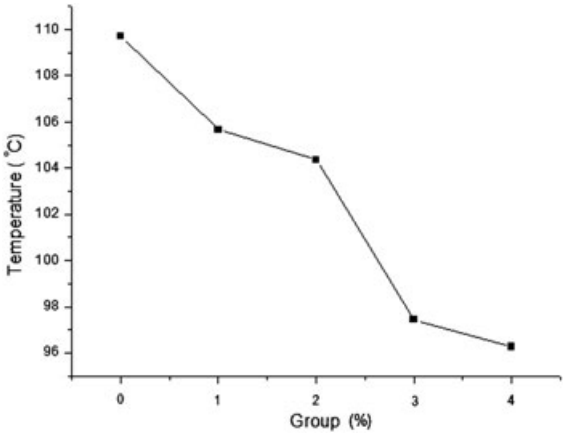

Figure 5 Effect of TBAEMA incorporation on the glass transition temperature (T_g) of the acrylic resin Onda-Cryl.

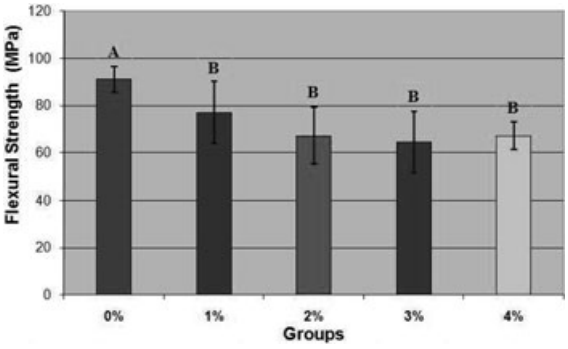

Figure 6 Flexural strength of acrylic resin Onda-Cryl, according to the TBAEMA concentration. Similar capital letters represent statistical similarity (Tukey's test, $p < 0.05$).

post hoc comparisons, performed at a 95% level of confidence. Data were analyzed with SPSS for Windows software (v.12.0.0, Chicago, IL).

Results

The presence of amino groups on the specimens' surface was analyzed by XPS-ESCA, represented by nitrogen ratios. Table 2 shows the nitrogen ratios on specimens' surfaces (%) for all groups. The results showed that TBAEMA incorporation into acrylic resin resulted in different nitrogen ratios on specimen surfaces. The addition of 2% of TBAEMA to acrylic resin showed the highest nitrogen ratio. The lowest nitrogen ratio was observed when 4% of TBAEMA was incorporated into acrylic resin.

The results obtained from FTIR analysis are shown in Figures 1 to 4 and provide evidence supporting copolymerization between PMMA resin and TBAEMA. The evidence of this fact is the presence of absorbance bands in the spectra of specimens containing TBAEMA (1%, 2%, 3%, 4%) observed in the region 1300 to 1325 cm^{-1}, which are absent in specimens of pure PMMA resin.

TBAEMA incorporation decreased the glass transition temperature (T_g) of PMMA resin (Fig 5). The highest values were found for groups 0%, 1%, and 2%, whereas the lowest values were found for the 3% and 4% groups.

Mean values and standard deviations for FS are shown in Figure 6. ANOVA revealed significant differences among the groups ($p < 0.05$). Tukey's test revealed differences among the control group (91.1 ± 5.5 MPa) and 1% (77.0 ± 13.1 MPa), 2% (67.2 ± 12.5 MPa), 3% (64.4 ± 13.0 MPa), and 4% groups (67.2 ± 5.9 MPa); however, there were no differences among the 1% to 4% groups.

Discussion

According to Ottersbach and Sosna,[23] when amine groups remain attached to the methacrylate main chain, this can result in antimicrobial activity. Therefore, our results suggest that PMMA resin containing TBAEMA could display antimicrobial activity due to the presence of amine groups on its surface, since previous studies found an association between amine groups on surfaces and antimicrobial activity.[11,12,14,24]

Paleari et al[13] incorporated the antimicrobial agent TBAEMA into a conventional water bath-polymerized PMMA resin and also found different nitrogen ratios on the specimens' surface. Similar to our results, in this previous study,[13] nitrogen atomic percentages decreased in high concentrations of TBAEMA. It could be explained by a possible saturation of the PMMA/TBAEMA system, allowing only incorporation lower than 2% of TBAEMA for acrylic resin Onda-Cryl. Additionally, it could occur due to a possible decrease in the conversion degree of PMMA resin for concentrations greater than 2%, which may result in less nitrogen on the specimens' surface.

Another possible explanation could be that PMMA resin presents a greater amount of unreacted residual monomers that bind to TBAEMA, or the test itself, since XPS-ESCA can detect chemical elements to a depth of 100 Å. In this case, TBAEMA could be heterogeneously dispersed within the matrix PMMA resin, resulting in lower rates of atomic nitrogen in the evaluated PMMA resin surface. Moreover, there is the possibility phase separation occurs during polymerization, explaining the nonlinear presence of the amine at the surface, a presence beyond a certain threshold value of the amine-based monomer (concentrations of TBAEMA greater than 2%).

The results of FTIR corroborate those of Park et al,[5] who incorporated carboxyl groups to an acrylic resin and observed the increase of the absorption bands on the modified resin, indicating incorporation into PMMA. In addition, our findings are consistent with those previously reported by Imazato et al,[7] who attempted to develop a composite resin with antibacterial activity after monomer methacryloyloxydodecylpyridinium bromide (MDPB) incorporation. These authors affirmed that monomer MDPB, a nonreleasing antibacterial agent, was able to copolymerize with composite resin.

The results of the present study support the fact that TBAEMA chemically attaches itself to PMMA resin with pendent amino groups on its surface. These findings allow for the possibility of obtaining a PMMA resin with long-term antimicrobial activity, since the releasing effect of TBAEMA is

no longer expected; however, microbiological evaluations are needed to confirm the preliminary evidence found in this research.

The results obtained in DSC analysis for the control group (109.7°C) are similar to the results obtained by Phoenix et al,[16] who evaluated the mechanical and thermal properties of various brands of acrylic resins and found that the T_g ranged between 102.5°C and 104.7°C for all brands tested. For the other groups, T_g decreased with an increased concentration of TBAEMA. According to Phoenix et al,[16] the incorporation of antimicrobial agents into acrylic resin detrimentally affects the T_g by causing a plasticizing effect.

The extreme peaks of orally achievable temperatures, due to the intake of hot and cold food and drinks, may be situated between 0°C and 67°C.[25] Our results allow us to presume the behavior of a denture base PMMA resin within TBAEMA in a clinical situation, where the temperature of dentures may vary considerably. Upon increasing the temperature, the material will become closer to its T_g temperature, which can result in rapid and irreversible deformation.[15,26] However, our results demonstrated T_g values between 96.3°C and 109.7°C for all groups evaluated, suggesting no clinical implication regarding T_g for PMMA resin incorporated with TBAEMA.

In accordance with previous studies,[1,4,5,13] our results showed that TBAEMA incorporation decreased the flexural strength of acrylic resin. These results could be associated with the presence of residual monomer, which acts as a plasticizer and negatively affects the mechanical properties of acrylic resins.[4,13] It could be hypothesized that TBAEMA incorporation increases the intermolecular distance of monomers, affecting polymer chains and consequently decreasing resistance values.[1,5]

Future studies should be conducted to investigate other mechanical and physical-chemical properties of acrylic resins after incorporating TBAEMA. Cytotoxic and microbiological tests are also necessary to evaluate if TBAEMA incorporation into acrylic resins may offer improvements in the oral health of denture wearers and consequently increase their quality of life.

Conclusion

Within the limitations of this study, the following may be concluded:

(1) The presence of amine groups on the specimen surface indicates possible antimicrobial activity of modified PMMA resin.
(2) There was evidence of copolymerization between TBAEMA and PMMA resin.
(3) Glass transition temperature and flexural strength were affected after TBAEMA incorporation into PMMA resin, depending on the percentage.

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