

Ethanol and Ultrasonic Wave Postpolymerization Treatment Reduced Residual Monomers of Autopolymerizing Acrylic Resins and Maintained their Flexural Properties

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Abstract

Background: Although autopolymerizing resins have advantages in the clinic, they also have disadvantages to patients. The potential for irritation of oral soft tissue by monomers and heat generation during polymerization are areas of clinical concern.

Objective: To evaluate the effect of ethanol and ultrasonic waves on the reduction of residual monomers (RM) and the flexural properties of autopolymerizing acrylic resins.

Methods: After polymerization, the specimens were immersed in water at 50°C for 60 min, 55°C for 10 min, or ethanol/water solutions of 10%, 20%, or 30% in an ultrasonic bath at 55°C for 5 min. Control samples were left untreated. Residual monomers were analyzed by high performance liquid chromatography (HPLC). After treatment, other specimens underwent a 3-point loading flexural properties test. Statistical analysis was performed using one way ANOVA at a significance level of $\alpha = 0.05$.

Result : comparing control specimens, statistic differences in the content of RM were found in other groups that having postpolymerization treatment. Ethanol concentration of 30% and ultrasonic waves promoted a significant reduction in the residual monomers. ($p < 0.05$) and no significant difference from control group in flexural properties. ($p > 0.05$)

Significance: Treatment with ethanol/water solution in an ultrasonic bath was an effective postpolymerization treatment for reducing RM that maintains the flexural properties of autopolymerizing acrylic resins, and also requires only a short time to perform.

Keywords: Autopolymerizing acrylic resins, Residual monomers, Ultrasonic waves, Ethanol, HPLC

Introduction

Autopolymerizing acrylic resins have become available in recent years. They are more convenient to patients than heat-cured acrylic resins because they do not require processing in a lab, resulting in reduced waiting time. However, the autopolymerizing system also has disadvantages. Their unpleasant odor, potential for irritation of oral soft tissue by the monomers and heat generation during polymerization are areas of clinical concern. Some monomers that do not react gradually leach out of the hardened acrylic resin and sometimes may cause a soft tissue reaction.¹⁻³ Their leached concentrations are potentially high enough

to result in irritation, inflammation, and allergic responses of the mucosal tissues.¹ Acrylic resins were first developed in the 1930s and were first used in dentistry in the 1940s.⁴ The physical properties of acrylic resins are that they are hard, brittle and glassy polymers composed of long chains of repeating units, which are called monomers.⁵ Autopolymerizing acrylic resins are composed of pre-polymerized polymethyl methacrylate (PMMA) powder particles that are mixed with methyl methacrylate monomers.⁶⁻⁷ Owing to their advantages in the clinic, they are used for numerous applications including temporary crowns, custom trays, and baseplates for denture fabrication.⁴

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Although autopolymerizing acrylic resins have many advantages, they also have disadvantages. As noted by Hickey and Zarb⁸, these materials can cause lesions in the mouth (i.e. clinical burns on the mucosa), show color instability, are often porous, and develop a bad odor. During the polymerization of acrylic resins, the conversion of monomer to polymer is not complete and some unreacted monomers, called residual monomers, remains in the denture base.⁹⁻¹⁰

MMA monomers causes an allergic reaction on contact with skin or oral mucosa. After the polymerization reaction, various amounts of the MMA monomer remain in the acrylic resin. Allergic reaction can occur, especially contact dermatitis.¹¹⁻¹²

Because of the toxicity of residual monomers, several methods have been proposed to reduce the residual monomers in acrylic resins, including: immersion in hot water¹³⁻¹⁷, microwave irradiation¹³⁻¹⁷ and ultrasonic cleaner.¹⁸

The aim of this study was to find the proper concentration of ethanol/water in an ultrasonic bath that could effectively reduce the concentration of RM without affecting the mechanical properties of auto-polymerizing acrylic resins.

Methodology/Experimental design

Unifast, a well-known autopolymerizing acrylic resins was evaluated in this study. Unifast is composed of polymethyl methacrylate and liquid MMA monomers.

Thirty-six specimens were prepared using stainless steel molds as recommended by ISO 20795-1. The resin was prepared following the directions of the manufacturer, and the mixture was placed into a metal mold (disk-shaped, with a diameter of 50 mm and a depth of 3.0 ± 0.1 mm). The specimens were kept in the dark for 24 ± 5 h. The samples were wet-ground until a thickness of 2.0 ± 0.1 mm was obtained.



Figure 1. Metal mold recommended by ISO 20795-1

Determination of residual monomer content

Specimens were randomly divided into six groups (n=6). The first group was the control group, which received no treatment. Groups two and three were immersed in water at 50°C for 1 h, and at $55 \pm 2^{\circ}\text{C}$ for 10 min, respectively. Groups four, five, and six were immersed in ethanol/water solutions of 10, 20, or 30% in an ultrasonic bath at $55 \pm 2^{\circ}\text{C}$ for 5 min, respectively. After the post-polymerization treatment, each specimen was milled into small pieces to prepare three samples weighing 650 mg each. The samples were each placed into 10 ml volumetric flasks. For each sample, 10 ml of acetone was added as an extraction solvent.¹⁹ The sample solutions were magnetically stirred for 72 ± 2 h. To precipitate the dissolved polymer, 8 ml of methanol was added to 2 ml of each of the samples. The monomers were quantified by high performance liquid chromatography (HPLC) (Shimadzu, Kyoto, Japan. Prominence system) using an RP-18-Lichrosphere-Merck column, a mobile phase of water/methanol (34:66), a flow rate of 0.8 ml/min, and a UV light wave length 205 nm detector. The content of RM was determined from standard deviation curve. By Preparing solution of MMA approximately 6mg, 60 mg, 150mg, 300mg, and 400mg. The standard curve was used to determine the concentration in microgram of MMA, C_{MMA} per milliliter of analyzed sample solution.

$$f(x) = (2.21898 \times 10^7)x + 305459 \quad (1)$$

This was standard curve. Where $f(x)$ was absorbance area of MMA by UV detector and x = MMA concentration.

The quantity of residual monomers (μg) in 1 g of each sample was calculated according to the following equation:

$$m_{\text{MMA}} = [C_{\text{MMA}} \times (10/2)^a \times 10^b] \quad (2)$$

Where **a** was the tetrahydrofuran amount and **b** was the methanol amount used for extraction.¹⁴

$$\text{Residual monomer (\% mass fraction)} = (m_{\text{MMA}} / m_{\text{sample}}) \times 100 \quad (3)$$

Where m_{sample} is the mass of sample, in micrograms.¹⁴

Flexural strength and Flexural modulus test

The specimens in the 6 groups ($n=10$) were prepared according to the manufacturer's directions and packed into a mold (64 mm long, 10.0 ± 0.2 mm wide, and 3.3 ± 0.2 mm high). Before testing, the specimens were stored in water at $37 \pm 2^\circ\text{C}$ for 50 ± 2 h, as recommended by ISO 20795-1.¹⁴ Using a Shimadzu universal testing machine, a 3-point bending test was performed at a crosshead speed of 5 mm/min with a 50mm distance between the supports. Each sample was measured three times and the average width and thickness of each specimen was entered into the software before testing. The load was applied while the specimen was in water at $37 \pm 2^\circ\text{C}$ until failure. The fracture load was recorded in N. The flexural strength was expressed in MPa and



Figure 2. Metal mold recommended by ISO 20795-1

calculated using the following formula:

$$FS = \frac{3 * W * L}{2 * b * d^2} \quad (4)$$

Where FS was the flexural strength, W was the maximum load before fracture (N), L was the distance between the supports (50 mm), b was the width of the specimen (mm), and d was the thickness of the specimen (mm).

The flexural modulus was calculated using the following formula:

$$E = \frac{F_1 * L^3}{4 * b * d^3 * h} \quad (5)$$

Where F_1 was the load, in N, at a point in the straight line portion (with the maximum slope) of the load/deflection curve, h was the deflection, in mm, at load F_1 (L, b, d are as previously defined).

Statistical analysis

If the data were normally distributed, one-way analysis of variance (ANOVA) was used to assess the significance of the differences in treatment on RM and flexural strength tests at a significance level $\alpha = 0.05$. If the data were not normally distributed, the Kruskal–Wallis test (i.e. the non-parametric alternative to ANOVA) was used at the same significance level. Statistical analyses were performed using SPSS software (SPSS ver.17, IBM, New York, NY, USA).

Results and Discussion

RM content

The RM content of the autopolymerizing acrylic resins samples after treatment is shown in Table 1. The one-way ANOVA analysis of the RM data found that time, temperature, ultrasonic waves and the concentration of ethanol significantly decreased RM in the autopolymerizing acrylic resins ($p < 0.05$). All experimental groups presented significantly lower RM than that of the control group ($p < 0.05$). The specimens treated with 30% ethanol in an ultrasonic bath at 55 ± 2 °C for 5min demonstrated the lowest level of RM ($p < 0.05$).

Table 1: Mean (% mass fraction) and SD of RM of the experimental groups.

	control	water 50°C 60min	water 55°C 10min	ultð 10% 5min	ultð 20% 5min	ultð 30% 5min
MN	3.09	2.134 ^a	2.508 ^b	2.204 ^a	2.360 ^{ab}	1.644 ^c
SD	0.132	0.125	0.153	0.098	0.185	0.139

Horizontally, the same letters mean not significantly different. ($p > 0.05$)

Flexural Strength and flexural modulus

Compared with the control group, the experimental groups presented no significant differences in flexural strength or flexural modulus ($p > 0.05$) (Tables 2 & 3)

Table 2: Mean and SD of the flexural strength (MPa) of the experimental groups.

	control	Water 50°C 60min	Water 55°C 10min	ultð 10% 5min	ultð 20% 5min	ultð 30% 5min
MN	49.527	49.976	52.401	47.323	46.798	47.160
SD	2.954	3.443	4.590	3.493	3.675	4.271

Table 3: Mean and SD of the flexural modulus (MPa) of the experimental groups.

	control	Water 50°C 60min	Water 55°C 10min	ultð 10% 5min	ultð 20% 5min	ultð 30% 5min
MN	1445.37	1603.90	1684.13	1526.63	1404.30	1382.09
SD	84.40	121.79	176.13	123.75	107.96	136.64

One factor that may have influenced the amount of RM is the length of time of postpolymerization treatment. Tsuchiya et

al.²¹ reported that immersing acrylic resin dentures in 50°C water for 60 minutes before insertion significantly decreased RM. However, this method is not practical in clinical situations because they waste chair time. Treatment with ultrasonic waves can decrease the amount of RM.¹⁸ Kuijpers et al.¹⁹ also found that ultrasonic treatment promotes chemical reactions through ultrasonic polymerization.

Our results also demonstrated that the RM was decreased by ethanol solutions. It is important to consider the chemistry of different solvents in postpolymerization treatments²², because solvent chemistry influences monomer solubility in the extraction media. Bettencourt et al. found that the amount of RM released from acrylic polymer was linearly related to ethanol concentration.²³ Thus, the results of the present study showed that ultrasonic waves and ethanol concentration strongly decreased the amount of RM.

We also tested flexural properties to confirm that the material can be used in the clinic. Although the flexural properties of the samples receiving ultrasonic wave and ethanol solution treatment were less than that of the control group, the differences were not significant.

Autopolymerizing acrylic resins are commonly used for direct applications including temporary crowns, custom trays and baseplates for denture fabrication in the clinic.⁴ The results of the present study can be applied in the dental office to reduce the amount of residual monomer exposure to patients. Moreover, this treatment is easy to achieve with simple equipment in a dental office, and only requires a short amount of time.

Conclusion

Under our experimental conditions, postpolymerization treatment reduced the residual monomers content while maintaining the flexural properties of autopolymerizing acrylic resins. Immersion in 30% ethanol solution in an

ultrasonic cleaner at 55±2C° for 5 minutes was the most effective treatment.

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