The effect of surface treatment of denture acrylic resin on the residual monomer content and its release into water

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The test specimens were processed by autopolymerizing poly(methylmethacrylate) (PMMA), and their surfaces were untreated, polished in a conventional manner with a rag wheel, or coated with a light-curing resin. The residual methylmethacrylate (MMA) content and its release into water from the specimens were measured with high-performance liquid chromatography. The light-curing resin coating reduced most effectively the release of residual MMA into water during a 2-day storage, but conventional polishing of the PMMA surface had a similar effect when the mean values of groups were tested by means of one-way ANOVA ($p < 0.001$). The residual MMA content was lowest in the test specimens coated with a light-curing resin, whereas only a slight difference was seen when the untreated and polished test specimens were compared. This study suggests that not only light-curing resin coating but also the conventional polishing of the denture PMMA reduces residual MMA release into water in vitro. ☐ *Acrylics; dental materials; methylmethacrylate*

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The residual monomer content and its release from denture poly(methylmethacrylate) (PMMA) have been determined in several studies. It is well known that there is less residual monomer in heat-cured PMMA than in autopolymerizing PMMA (1–6). The reason for the higher residual monomer content in the autopolymerizing PMMA is the low degree of polymerization achieved by the use of a chemical activator as opposed to that generated by heat activation. It is also known that a larger amount of residual monomer is released into surrounding water from autopolymerizing PMMA than from heat-cured PMMA (3, 7, 8).

Methylmethacrylate (MMA) released into saliva may cause adverse reactions, such as redness, swelling, and pain of the oral mucosa, even though there is no indication that release of MMA from dentures produces any systemic effect in the patient (9–11). The amount of released MMA can be reduced by coating the denture surface with a light-curing resin (12).

The porosity in the structure of PMMA may affect the release of MMA into water and into saliva when a denture is worn. According to the law of diffusion, the diffusion of MMA into water is dependent on temperature, which has also been shown in a previous study (13). The effect of surface treatment of PMMA by polishing or by coating with another resin on the release of MMA, however, needs further investigation. For instance, it has not been shown experimentally whether surface treatment affects both residual MMA release and the MMA content of denture PMMA.

The aim of this study was to ascertain how surface treatment either by polishing or by light-curing resin coating affects the residual monomer content and the release of the denture PMMA.

Materials and methods

Autopolymerizing PMMA (Pro Base Cold®, Ivoclar, Schaan, Liehtenstein) was used to process the test specimens, which measured 3.0 × 5.0 × 50.0 mm (Fig. 1). The ratio of PMMA powder to MMA liquid was 20.5 g to 10 ml. The PMMA was polymerized in a pneumatic curing unit (Acri-Dense 3, GC-America Inc., Chicago, Ill., USA) with an air pressure of 300 kPa (2 bars) for 15 min. The temperature of the curing water was +40 °C.

After polymerization five of the test specimens were left untreated (group 1), and five were polished in a conventional manner with a 6-mm-thick rag wheel (Polirapid no. 29/100, Riva S. Vitale, Switzerland; polishing apparatus, 300 rpm: Kavo EWL, Leutkirch, Germany), using KMG polishing liquid (Candulor AG, Wangen b. Dubendorf, Germany) (group 2). Five of the test specimens were coated with a light-curing resin (Palaseal, Kulzer GmbH, Wehrheim, Germany), which was cured to the surface of the test specimens in a Dentacolor XS curing unit for 90 sec (group 3) (Fig. 2).

The residual MMA content of the test specimens was determined by high-performance liquid chromatography (HPLC) (LKB 2151, LKB-Produkter AB, Bromma, Sweden) with a reverse-phase column (LiCrosorb RP18, LKB 2134–215, LKB-Produkter AB) (13, 14). After the test specimens had been stored in water at room

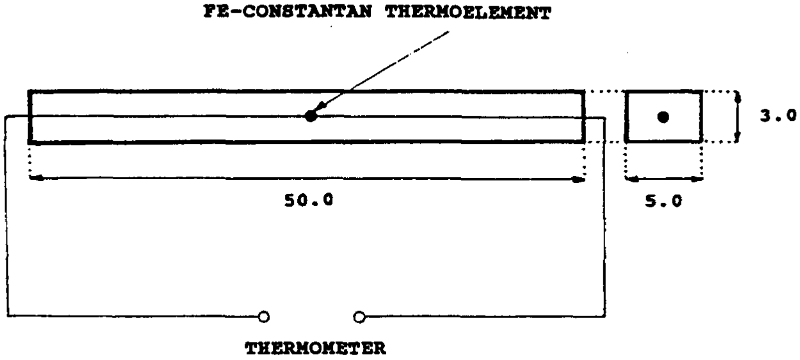

Fig. 1. Shape and dimensions (in mm) of the test specimen and position of a thermal probe.

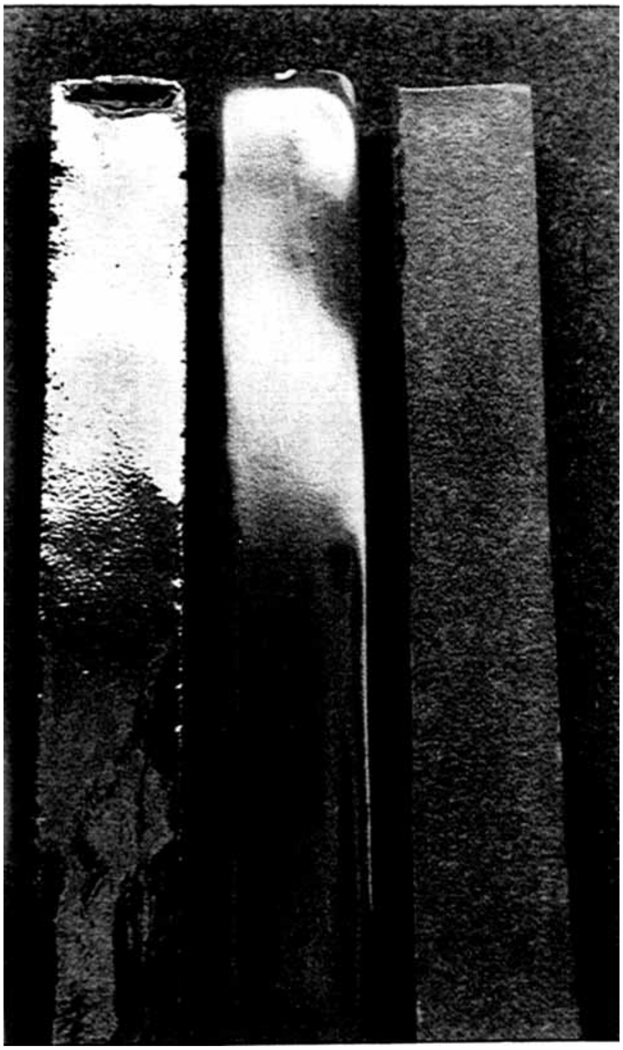

Fig. 2. Photograph of test specimens. From the left: light-curing resin-coated (group 3), rag-wheel-polished (group 2), and untreated (group 1) specimens.

temperature for 6 h, 100 mg of the sample was ground (Fritsch Pulverisette, Fritsch, Idar, Germany). The powder was dissolved in 10 ml of tetrahydrofuran (THF) (Rathburn Chemicals, Walkerburn, Scotland, UK) containing 0.1 wt% hydroquinone. The solution was stirred for 48 h at room temperature; 5 ml methanol (HPLC grade, Rathburn Chemicals) was then added to a 1-ml aliquot of the solution to precipitate the dissolved polymer. After centrifugation the concentration of MMA was determined by HPLC analysis. Concentrations of MMA were calculated from the areas below the curve at the peak produced by the MMA, as previously (14) (Fig. 3). Three measurements were made for each sample. The rate of flow was adjusted to 1 ml/min, and the mobile phase was acetonitrile/water (60:40) (Acetonitrile HPLC Grade, Rathburn Chemicals).

To measure the release of MMA from the test specimens' surface treated in various ways, the specimens were immersed in distilled water (10 ml) for 48 h, and the amount of MMA was determined after three extractions with 0.6 ml of *n*-hexane (Merck 4368, Merck, Darmstadt, Germany). The final volume of the extract was adjusted to 2.0 ml with *n*-hexane. The concentration of MMA was determined with the HPLC method. The amount of released MMA was calculated in ppm (μg/g). The mean content and release of MMA in the different groups were compared by means of one-way ANOVA. *P* values of less than 0.05 were interpreted as statistically significant.

The temperature inside the test specimens during the polymerization of the light-curing resin coating or during the stay of the uncoated specimen in a Dentacolor XS curing unit was measured with the ferro-constantan thermocouple (J-type) of a digital thermometer (Fluke 51K/J, John Fluke Mfg. Co., Inc., Everett, Wash., USA). The temperature of the test specimen during polishing with a rag wheel was measured with the same method. Temperatures were

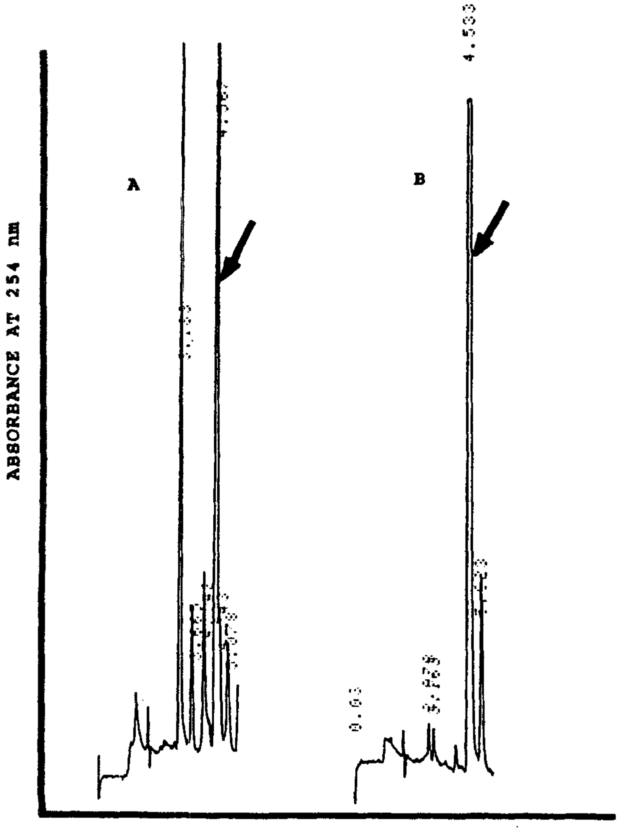

Fig. 3. Chromatograms obtained from the high-performance liquid chromatography determination of residual methylmethacrylate (MMA). A) MMA extracted with tetrahydrofuran from dissolved poly(methylmethacrylate). B) MMA extracted with *n*-hexane from storage water. Arrows indicate the peaks for MMA.

plotted against the treatment time at 10-sec intervals. The distance of the test specimen from the bottom of the curing box in the light-curing unit was 30 mm.

Results

The residual MMA release into water was highest from the untreated test specimens (821 ppm) and lowest from the light-curing resin-coated test specimens (30 ppm) during 2 days of storage (Table 1). The residual MMA content was almost the same in the untreated and polished test specimens (6.9 and 6.7 wt%), but it was lower in the light-curing resin-coated test specimens (4.8 wt%) (Table 2).

The temperature inside the test specimen while treated in a Dentacolor XS curing unit for 90 sec rose to 75 °C. The highest temperature inside the test specimen polished by a rag wheel for 110 sec was 52.6 °C (Fig. 4).

Discussion

In the present study HPLC was used for determination of residual MMA. HPLC chromatography has been used by other researchers for similar purposes (1, 15), but there are also other chromatographic methods available for the determination of residual MMA, such as gas chromatography (2, 3, 7, 16–18). The rather high residual MMA content and MMA release from autopolymerizing PMMA found in this study agree well with previous results obtained using the same MMA extraction and determination technique (13).

Table 1. Mean residual methylmethacrylate release (in ppm ± SD) into water from test specimens surface-treated in various ways. Means are compared by means of ANOVA

Group	M ± SD		*n*	*F*	d/f	*p*
1 Uncoated	821	246	15			
2 Polished	292	36	15			
3 Light-curing resin	30	19	15	117.4	2/42	0.000

Table 2. Mean residual methylmethacrylate content (in wt% ± SD) of the test specimens surface-treated in various ways. Means are compared by means of ANOVA

Group	M ± SD		*n*	*F*	d/f	*p*
1	6.9	0.5	15			
2	6.7	1.3	15			
3	4.8	0.8	15	25.3	2/42	0.000

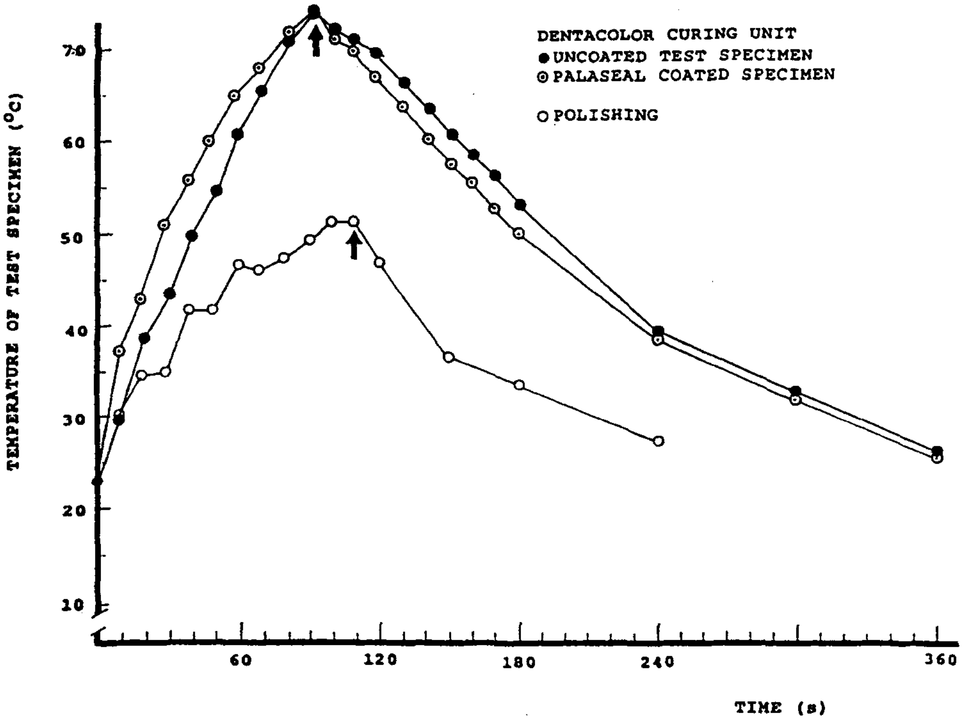

Fig. 4. Thermograms of the poly(methylmethacrylate) test specimens during surface treatment, plotted against treatment time. Polishing refers to rag wheel polishing. Arrows indicate end of the treatment.

The results of this study showed that polishing the surface of the PMMA specimen can reduce the amount of residual MMA released. This study was based on the hypothesis that either the increased temperature inside the test specimen during the polishing of the PMMA or the reduced diffusion surface of the specimen brought about by polishing decreases the MMA release into water. The increased temperature was thought to precede the polymerization of the MMA, which would obviously decrease the MMA content and release from the specimen. To test this hypothesis, the temperature of the PMMA during polishing and the residual MMA content after polishing were measured for the test specimens. The temperature increased during polishing, but no clear indication of a reduced MMA content of the specimen was noted. Consequently, the reduction of residual MMA release from the polished PMMA test specimens seems to be caused by the diminished diffusion surface rather than by the reduced MMA content inside the test specimen.

The light-curing resin coating effectively decreased the release of the residual MMA from the test specimens. This finding supports the results reported by Szabo et al. (12). It is not difficult to understand that the light-curing resin coating applied to the surface of the PMMA specimen will provide an effective barrier against residual MMA release into surrounding water. However, the present study showed that the light-cured resin coating is not the only mechanism at work in reducing the MMA release from denture PMMA. The polymerization of a light-curing resin coating in a curing apparatus increases the temperature of a PMMA specimen up to 75 °C. Benzoyl peroxide as an initiator of the polymerization reaction of PMMA forms oxygen radicals, which initiate the polymerization at temperatures above 70 °C, which is considered a critical temperature (19). After polymerization, some unreacted peroxide that reacts at the critical temperature is still present in PMMA (20). Consequently, the amount of residual MMA should be lower in the PMMA specimens after being treated in a light-curing unit. This theory is supported by the finding in the present study that there is a smaller amount of residual monomer in the test specimen treated in a light-curing unit than in the specimens polished with a rag wheel.

Another interesting observation was that there was no difference between the peak temperatures of the uncoated and light-curing resin-coated test specimens when they were treated in a light-curing unit. The temperature increase was, however, more rapid in the test specimen coated with the resin, possibly because of the type of exothermic polymerization reaction the coating resin underwent. It can be concluded that the reduction of residual MMA release from light-curing resin-coated test specimens seems to be caused by the coating acting as a barrier and by the preceding polymerization of the residual MMA. The use of light-curing resin coating in reduction of the release of residual MMA is not without complications; it has been shown that the use of resin coating on dentures may increase the cytotoxicity of the denture (21).

The release of MMA into saliva may cause redness, swelling, and pain of the oral mucosa. In the oral cavity the residual MMA may be affected by some chemical reactions, such as oxidation and hydrolysis. The oxidation converts MMA into formaldehyde, and hydrolysis converts MMA into methacrylic acid (11, 22). Furthermore, phenyl benzoate and phenyl salicylate have been identified in saliva samples from patients wearing autopolymerizing PMMA appliances (18).

Means of decreasing the amount of released chemicals from PMMA in clinical use should be considered. These means include 1) storing a denture in water before use; 2) polishing denture surfaces adequately, as was done in the present study; or 3) coating the denture surface with a light-curing resin. The polishing of the mucosal surface of a denture involves certain difficulties. The polishing affects the dimensions of a denture, which may reduce the fitting of the denture to the supporting tissues. This question and the effect of polishing on residual MMA release in vivo need further investigation. The effect of polishing on the reduction of released chemicals from dental resins may also have implications for restorative dentistry.

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