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Elution characteristics of residual monomers in different light- and auto-curing resins

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ABSTRACT

The aim of this *in vitro* study was to assess different auto-curing resins based on methylmethacrylate (MMA) and new light-curing resins based on urethane dimethacrylate (UDMA) regarding the residual monomers remaining in the resin and their elution over time. Specimens from three auto-curing and three light-curing resins were produced following the manufacturer's instructions. The concentration of residual MMA and UDMA monomers present in the resins as well as the quantity of the residual monomers released into artificial saliva solution after immersion times of 1, 3, and 7 days were analyzed by high-performance liquid chromatography (HPLC). Data were statistically analyzed using ANOVA and the post hoc Student-Newman–Keuls test. The highest and lowest amounts of residual monomers were found in the group of light-curing resins ($p < 0.05$). The light-curing resins Triad Trans Sheet (0.06 wt%) and Primosplint (0.06 wt%) released over the entire immersion time of 7 days the smallest ($p < 0.05$) quantity of UDMA. These two light-curing resins based on UDMA exhibited lower elution of residual monomers than auto-curing resins (MMA). The elution characteristics of the residual monomers do not seem to correlate with the residual monomer concentration in resins. These observations demonstrate that the quantitative determination of residual monomers alone - as required by the ISO specification 20795-1 – does not seem to be sufficient for an assessment of the biological properties of different resins. Instead, the evaluation of elution characteristics appears to be of higher clinical relevance.

1. Introduction

The resins used in dentistry are predominantly modifications of methylmethacrylates (MMA) while light-curing materials, which are often based on urethane dimethylacrylate (UDMA), represent one of the newer developments within this field of dentistry. Both types of resins are used in restorative dentistry and, e.g., for manufacturing occlusal splints, removable orthodontic appliances and denture bases. During the polymerization process of acrylic resins, the conversion of monomer into polymer is not complete, and varying amounts of free and unreacted monomers remain in the polymerized resin (Zissis et al., 2008), thereby affecting the physical and mechanical properties of these resins (Urban et al., 2007).

Even more, cytotoxic responses seem to be well correlated with substances eluted from the resins (Michelsen et al., 2007). Many investigations reported unfavorable reactions of residual monomers released from methacrylate (MMA)-based restorative materials (Yoshii, 1997; Jorge et al., 2003). The toxic potential of resins is mainly caused by the quantity and the composition of the eluted substances (Hensten-Pettersen, 1998). The potential of cytotoxicity is influenced by residual monomers as well as other additives such as initiators and stabilizers (Michelsen et al., 2003).

Although UDMA shows a lower rate of elution than MMA (Ferracane, 1994), its cytotoxicity is more pronounced compared with the latter (Yoshii, 1997). Maximum acceptable amounts of residual monomers remaining in resins are given by the DIN ISO 20795-1 specification Dentistry – Denture base polymers (International Organization for Standardization, 2008) and are set at 4.5 wt% for auto-curing and 2.2 wt% for light-curing resins. These values consider, however only the residual monomers in the resin and not their elution characteristics. However, this elution behavior has a possible effect on the sensitization risk and the increase of fre-

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Table 1
Characteristics of the investigated resin materials.

Code		Batch No.	Composition[a]	Spectral range (nm)	Manufacturer
AC	Acrylight®	2002003436	Tetrahydrofurfuryl-2-methacrylate, aliphatic urethane-acrylate in TPGDA, aromatic urethane-acrylates, 2-hydroxy-2-methylpropiophenon	320–400 nm (UVA)	Schütz Dental, Rosbach, Germany
PS	Primosplint®	042349	Acrylate-based oligomers, organic and anorganic filler load	320–400 nm (UVA)	Primotec, Bad Homburg, Germany
TS	Triad® TranSheet® Colorless	020205A	Urethane dimethacrylate, copolymer from methylmethacrylate, ethylene glycol dimethacrylate, ethylmethacrylates and styrol	400–500 nm (halogen)	DeTrey Dentsply, Konstanz, Germany
PP	Palapress®		Polymethylmethacrylates/butylacrylate		Heraeus Kulzer,
	Powder	022214	methylmethacrylate, dimethacrylate		Hanau, Germany
	Liquid	031001			
OC	Orthocryl®		Polymethylmethacrylates/methylmethacrylates		Dentaurum,
	Powder	0305776			Ispringen,
	Liquid	120495			Germany
SR	Steady-Resin®		Polymethylmethacrylates,		Scheu Dental,
	Powder (M)	1303 A	dibenzoylperoxyd/methylmethacrylates		Iserlohn, Germany
	Liquid (S+M)	3503 A			

[a] Components as declared in the manufacturer's specification.

quency of hypersensitivity reactions caused by acrylic appliances (Leggat and Kedjarune, 2003).

In this context it is discussed controversially at which time the major part of residual monomers is eluted. Some authors propose a continuous process (Mikai et al., 2006) while others assume that the majority is released within the first 24 h (Ferracane and Condon, 1990).

The aim of this *in vitro* study was to assess different auto-curing resins based on MMA and newer light-curing resins based on UDMA regarding the amounts of residual monomers remaining in the resin and their elution behavior over time.

2. Materials und methods

Three auto-curing and three light-curing resins were investigated (Table 1). The light-curing resins were polymerized in the light oven Targis Power (Ivoclar, Schaan, Liechtenstein). The oven emits light at frequencies between 400 nm and 500 nm using eight ralutec long lamps (18 W/2 G11/71, Radium Lampenwerk, Wipperfürth, Germany) and between 320 nm and 400 nm by the use of eight ralutec long lamps (18 W/2 G11/78, Radium Lampenwerk, Wipperfürth, Germany). The auto-curing resins were mixed manually. After mixing in a modeling technique, the polymerization took place in a pressure cooker (Palamat, Heraeus Kulzer, Hanau, Germany). All resins were prepared according to the manufacturer's instructions.

2.1. HPLC analysis

In order to quantify the residual monomers a high-performance liquid chromatography device (HPLC) (Agilent 1100, SP 200 Hewlett Packard, Böblingen, Germany) with an Octadecyle silanised hypersil column (Dr. Maisch, Ammerbuch, Germany) (length 250 mm and bore of 4.6 mm) with a pore size of 5 μm was used. An isocratic eluent of 66% methanol (CH_3OH) and 34% H_2O was used as mobile phase. The flow velocity was 0.8 mL/min, and the monomers were detected by a UV light detector (Hewlett Packard, Böblingen, Germany) with a wavelength of 205 nm. To ascertain that constant volumes of sample and calibration solutions were injected a sample loop with a fixed volume of 20 μL was used. All samples were evaluated regarding the content of MMA and UDMA. To establish the retention times, pure samples of MMA (Primotec, Bad Homburg, Germany) and UDMA (Dentaurum, Ispringen, Germany) (HPLC grade; 500 μg/mL) were injected consecutively. The retention times of MMA and UDMA were 5.982 and 20.371 min, respectively (Fig. 1).

For quantitative evaluation calibration solutions with concentrations of 6, 12, 60, 120, 300, 600 and 800 μg/mL were prepared by mixing pure MMA and UDMA with an acetone/methanol solution (solution C; Table 2). The peak areas of these calibration solutions vs. the respective concentrations (mg/10 mL) were taken to obtain calibration curves. The correlation coefficient was not less than 0.999. The assay limit for MMA and UDMA was 6 μg/mL.

For the quantitative determination of the residual monomers the data of the peak areas measured with the UV detector were integrated and employed in the calibrating curve formula. For the determination of percentage amounts (% mean) of the residual monomers in the samples, formula 1 of the analysis software (Chemstation, Agilent Technologies, Santa Clara, CA, United States) was used.

$$\%Mean = 10^{(a)} \cdot \left[\frac{c(m_{(monomer)}/10\,\mathrm{mL})}{c(m_{(specimen)}/10\,\mathrm{mL})} \cdot 100 \right]$$

Formula 1 Determination of the percentage amount [% mean] of residual monomers.

2.2. Determination of the quantity of residual monomers

For each of the six different resins, six samples were made using metal rings (diameter 50 mm and height 2 mm) and prepared from separate mixtures. Each sample was weighed three times (Sartorius Le 324S-0CE, accuracy 0.1 mg, Göttingen, Germany) and the mean value was recorded. Two polished glass plates served as a counter for the light-curing resins, and for the auto-curing resins two polished metal separating tiles were used.

In order to produce standardized samples, the resins were pressed in a cuvette with a pressure of 40 bars. The produced tiles were visually inspected to be free from bubbles and homogeneous.

Table 2
Solutions used in this study.

Acetone solution (A)	Methanol solution (B)	Methanol/acetone solution (C)
0.02 g hydrochinone filled up with acetone (HPLC grade) to a total volume of 1 L	0.02 g hydrochinone filled up with methanol (HPLC grade) to a total volume of 1 l	Solution A was mixed with solution B in a ratio of 1 to 4