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A Long Term Study on Residual Monomer Release from Denture Materials

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Abstract - *The aim of this long term study was to investigate the release of residual monomer from different denture materials, throughout a 38 months time period after curing and storage in water. Specimens made of four denture base resins (three heat polymerizing, one auto polymerizing) and one hard liner were subjected to residual monomer determination using gas liquid chromatography. The residual monomer estimation carried out on three occasions: one week, 12 months and 38 months after curing. The data obtained were analyzed using two-way Anova followed by Scheffe's test for post hoc multiple comparisons at* $\alpha = 0.05$. *Heat polymerized denture base acrylic resins showed less residual monomer than auto polymerized ones* ($p<0.001$) *and released no statistically significant amounts of monomer* ($p>0.05$)*, during the 38 months storage time period. Auto polymerized denture materials, which had higher residual monomer content, released statistically significant amounts of monomer* ($p<0.001$) *during the first twelve months storage, but not during the last twenty six months period* ($p>0.05$)*. Heat polymerized denture base acrylic resins released insignificant amounts of residual monomer during the storage period; whereas both the auto polymerized denture base resin and the hard liner released significant amounts of residual monomer during the initial storage time period but insignificant ones during the remainder of the storage period.*

KEY WORDS: Complete dentures, denture resins, residual monomer, biocombatibility

INTRODUCTION

Heat and auto polymerized acrylic resins are routinely used in every day prosthodontic practice, despite their shortcomings in ideally meeting the physicomechanical and biological requirements needed (i.e. thermal conductivity, inability to be heat sterilized, shrinkage due to polymerization, possible chemical irritation). It has been widely reported that residual monomer levels produce not only a negative effect on the mechanical properties of denture bases but also are associated with mucosal reactions [1-13].

A number of studies have proved that residual monomer levels are dependent on many variables, such as the type of denture base acrylic resin, its thickness, the curing cycle (polymerization temperature and time) and the processing conditions employed for the polymerization[1,3,5,6,14-20]. So, auto polymerizing resins contain higher levels of residual monomer than the heat cured ones[20]. Acrylic resin specimens produced by a short curing cycle may contain up to 7 times the residual monomer content of specimens cured by a long cycle[11]. The lowest residual monomer content (0.07%) was obtained by polymerizing heat cured denture base resin at 100°C for 12h[18]. It has also been shown that the lowest values of residual monomer (a minimal residual monomer amount of 0.2%-0.3%) can be obtained when a long or overnight curing cycle (i.e. polymerization at 70°C for 7h and 1h at 100°C) is applied [1,15-17].

A number of studies have been devoted to find out if residual monomer leaches out or is bound in the mass of the acrylic resin. In 1956, Smith and Bains[21] reported that part of the residual monomer is leached with time, leaving a residual amount that remains tightly bound to the acrylic resin. The same conclusion was reported by Huggett *et al*[16], who clearly showed that leaching out of monomer is possible if the limiting value of residual monomer is not obtained by the curing cycle employed. Also, the residual monomer content in heat-cured acrylics appears to be very resistant to removal by immersion in water[14]. Most studies have estimated the in vitro release of residual monomer at different time periods (e.g. immediately after the acrylic resin polymerization, one day, 3, 7 days or a month) [18, 22-24].

A release of residual monomer from an acrylic resin appliance into the oral cavity may take place, too. Residual monomer released in saliva was detected for up to one week after wearing either an auto polymerized acrylic appliance or an undercured heat polymerized appliance[25]. Sadamori *et al*[26] reported that the residual monomer contents tended to be decreased to dentures used for long periods than to those for shorter ones. The most of this loss occurred in the first 4-5 years. A very slow additional decrease of residual monomer takes place for many years, since residual monomer was detected in dentures used up to 17 years. In the available literature most studies estimated the in vitro possible leaching of residual monomer for short time periods (from one day up to 3 months) [18, 22-24].

The aim of this long term study was to investigate the release of residual monomer from different denture acrylic resins, one week, 12 months and 38 months after curing and storage in water.

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MATERIALS AND METHODS

Four denture base resins (one conventional heat polymerizing, one high impact heat polymerizing, one specially designed for microwaving, one auto polymerizing) and one auto polymerizing hard liner were evaluated for residual monomer. The choice of these 5 types of denture materials addresses the criterion that each one is representative of the most common ones used in every day practice. The materials (trade name, type of material, polymerization mode, curing cycle, manufacturers) are shown in Table 1.

Specimen preparation

I) Moulding method

Wax patterns (John Quayle Dental, Sussex, UK) 90x10x1.5mm in dimension (length x width x thickness), were invested in dental stone (Titanit , Renfert, Singen, Germany) as follows :

a) Twelve (groups A,B,D,E) in conventional denture flasks.

b) Three (group C) in special plastic flasks (FRP Flasks, GC Corp., Tokyo, Japan) in a microwave oven (Siemens Electrogerate GmbH, model HF1210, Germany).

II) Curing method

Specimens were polymerized using the curing cycles presented in Table 1.

III) Storage

After deflasking the specimens were cut into three equal pieces (30x10x1.5 mm) and conditioned as follows: each group of specimens was placed in polyethylene bottles, containing distilled water, and held in controlled temperature at 37 ±1° C.

Residual monomer estimation

The residual monomer estimation carried out on three occasions: one week, 12 months and 38 months after curing. Each time period, three samples of each material were tested for determination of residual monomer by gas liquid chromatography (GLC). The apparatus used for the analysis was a Philips PU4500 gas chromatograph (Pye Unicam Ltd, Cambridge, UK) fitted with a Poropak Q column (80-100 mesh, 1.5m long) and operated at an oven temperature of 230°C with nitrogen as the carrier gas at 60ml min^{-1} flow rate. Samples from the cured specimen were taken in the form of drill cuttings which were reflexed with 10ml of methanol. In the GLC analysis a standard 0.5ml of 2% ethylacetate in methanol was added to the solution to provide a reference by which the quantity of methyl methacrylate monomer in the solution could be measured. Residual monomer content was performed in percentage. The procedure used has been extensively described by Huggett *et al* [16].

STATISTICAL ANALYSIS

Data obtained were analyzed using two-way Anova followed by Scheffe's test for post hoc multiple comparisons at $\alpha = 0.05$. Levene's test for homogeneity of variance was applied, too.

RESULTS

One week after curing and storage in water, residual monomer values ranged from 0.18% (denture base resin SR 3/60 Plus) up to 2.63% (hard liner Rebaron). Twelve months after curing, due to a gradual release, residual monomer values were lowered and ranged from 0.16% (SR 3/60 Plus) up to 0.82% (Probase Cold). Thirty eight months after curing and during storage, residual monomer values ranged from 0.15% (SR 3/60 Plus) up to 0.8% (Probase Cold). Both variables, material and time, presented a significant interaction ($p<0.001$).

Heat polymerized denture base acrylic resins showed less residual monomer than the auto polymerized ones ($p<0.001$) and released no statistically significant amounts of monomer ($p>0.05$), during the 38 months storage time period. Auto polymerized denture materials, holding more residual monomer content, released statistically significant amounts of monomer ($p<0.001$) during the first twelve months storage, but not during the rest twenty six months period ($p>0.05$).

The results of our study, in bar graphs, are shown in Fig.1.

DISCUSSION

All heat polymerized denture materials exhibited lower residual monomer values than the auto polymerized one and the hard liner tested. This finding is in agreement with all previous reports[1,3,11,14,18].

Heat polymerized denture base materials showed low levels of residual monomer and released insignificant amounts during the whole storage period. The low levels of residual monomer were obtained since an optimum curing cycle was employed. Conventional heat polymerized (Trevalon) and microwave polymerized acrylic resin (MC Acron) exhibited residual monomer levels of ~ 0.5%, whereas high impact acrylic resin (SR 3/60 Plus) presented the lowest residual monomer content ~ 0.2% and the most insignificant release. The residual monomer values esti-

Table 1. *Materials tested*

Code	*Trade name*	*Type*	*Polymerization mode*	*Curing cycle*	*Manufacturer*
A	Trevalon	Denture base	Heat polymerizing	2 h at 70°C +1h at 100°C	Dentsply/DeTrey
B	SR 3/60 Plus	Denture base	Heat polymerizing	2 h at 70°C +1h at 100°C	Ivoclar
C	MC Acron	Denture base	Microwave curing	3 min at 500W	GC
D	Rebaron	Hard liner	Auto polymerizing	10 min at room temperature	GC
E	Probase Cold	Denture base	Auto polymerizing	30 min at room temperature	Ivoclar

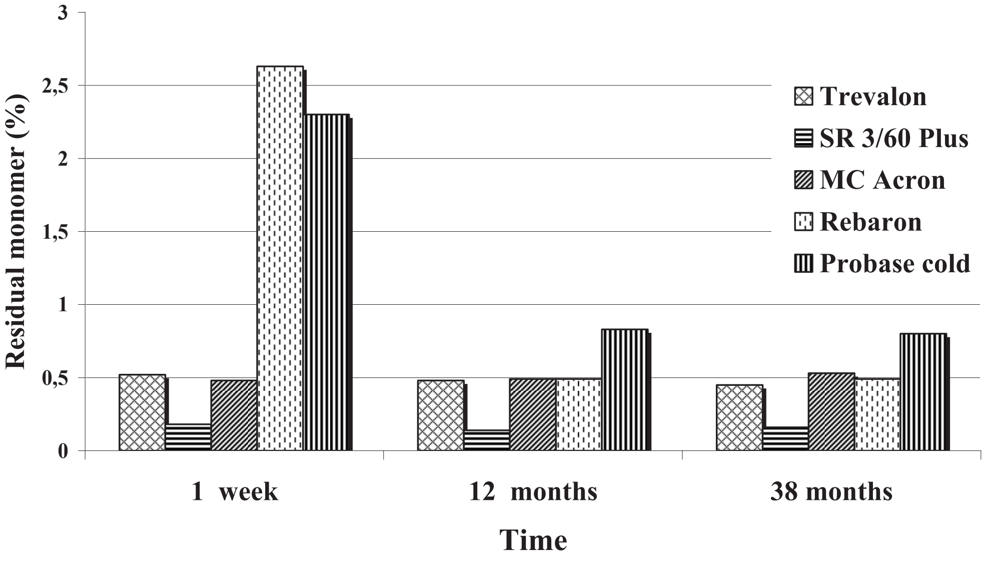

Figure 1. *Residual monomer estimation*

mated in this study confirm previous reports for the same materials[4,24,25]. Especially, the finding for Trevalon confirms previous report [20] that the levels of residual monomer were not to be different after 28 days of saturation.

Auto polymerized denture resin and hard liner released significant amounts of residual monomer during the first 12 months storage period but insignificant ones during the rest 26 months. This is due to the continuing polymerization during saturation and is in agreement with previous studies[20,21,24,25].

At the end, our results fully support the early statement[16] that leaching out of monomer is possible when the limiting residual monomer level is not obtained by the curing cycle employed. As it concerns the time occasions chosen for the estimation of the residual monomer leaching, 38 months is really a long term period since the obtained values arithmetically and statistically gave similar results with the 12 months. Also, the 38 months also represents about the half time period of the clinical life of a complete denture before a replacement is needed.

This long term in vitro study suggests that in clinical practice, heat polymerized denture materials should be cured using an optimal curing cycle in order a minimal residual monomer level could be obtained. Since residual monomer levels continue to be high more than one week after curing, auto polymerized and hard liners should be handled with caution to patients in order mucosal reactions to be avoided.

CONCLUSIONS

Under the limitations of this study the following conclusions can be drawn.

1. All heat polymerized denture materials exhibited lower residual monomer values than the auto polymerized one and the hard liner tested.
2. There was a gradual release of residual monomer during the 38 months storage period.
3. Heat polymerized denture base materials released insignificant amounts of residual monomer during the whole storage period.
4. Auto polymerized denture resin and hard liner released significant amounts of residual monomer during the first storage time period but insignificant ones during the rest period.

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