

An In Vitro Investigation of Water Sorption and Solubility of Two Acetal Denture Base Materials

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Abstract - Acetal resins have been used as an alternative denture base and clasp material recently. The aim of this study was to compare water sorption and water solubility of pink and white acetal resins as compared to a heat-polymerized polymethyl methacrylate resin (PMMA). The tests were performed in accordance with International Standards Organization specification No: 1567. Pink acetal resin showed significantly lower water sorption than heat-polymerized acrylic resin and white acetal resin. PMMA showed significantly higher solubility than pink and white acetal resin. Water sorption and solubility of PMMA, pink and white acetal resins were within the ISO specification limit.

KEY WORDS: Acetal resin; Water sorption; Water solubility

INTRODUCTION

Acrylic resins, introduced in 1937, provide an excellent match to the appearance of oral soft tissues¹. Although acrylic resin is adequate in satisfying esthetic demands, is far from ideal in fulfilling the mechanical requirements of prostheses². Various attempts have been made to improve its mechanical properties.³ However the shortcomings of acrylic resins include mechanical failure, dimensional changes and allergic reactions^{4,5}.

Various polymers have been developed to overcome the strength deficiencies of polymethyl methacrylate (PMMA). Polymers such as polyamides, epoxy resins, polystyrene, vinyl-acrylic, rubber graft polymers and polycarbonate have been introduced. Modification of PMMA and addition of fillers has also been attempted⁶.

Acetal resins are formed by the polymerization of formaldehyde⁷. The homopolymer, polyoxymethylene (POM) is a chain of alternating methyl groups linked by an oxygen molecule⁷. The material has been shown to have good biocompatibility and this has fostered its use in total hip replacements⁸, and as an artificial heart valve occluder⁹. It has been used to form a stress-absorbing component in a dental implant system (IMZ)¹⁰. Smith¹¹ mentioned the possible use of polyacetal resins as denture base materials. These injection-molded resins have been used as an alternative denture base and direct retainer material since 1986 and were promoted primarily on the basis of superior esthetics, which allowed the clasp to better match the color of the abutment tooth¹². Because of its biocompatibility it has been used as a framework material for removable partial denture for patients who have allergic reactions to Co-Cr framework⁷. The manufacturers purport that it has superior physical properties when compared to conventional denture base acrylic resins [PMMA]. It is reported to have a sufficiently high resilience and modulus of elasticity to allow it to be used in

the manufacture of retentive clasps, connectors and support elements for removable partial dentures (RPD)^{7,12}.

The absorption of water by acrylic resin is a phenomenon of considerable importance since it is accompanied by dimensional changes¹³ and results in weight and volume increase^{14,15}. The greater the water sorption, the greater will be the associated dimensional change¹⁶. A further undesirable effect of absorbed water in a denture base resin is the reduction of the tensile strength of the material¹⁷. Water absorbed into the material acts as a plasticizer and decreases the mechanical properties such as hardness, transverse strength and fatigue limit^{15,18}. An ideal material should have a low level of absorption¹⁶. According to International Standards Organization (ISO) specification No 1567 water sorption should not exceed 32µg/mm³ for heat-polymerized or autopolymerized materials^{19,20}.

Solubility represents the mass of the soluble materials from polymers. Denture base resins are insoluble in water and most intraoral fluid¹⁶. The only soluble materials present in denture base resins are unreacted monomers, plasticizers, and initiators^{15,20}. However, these monomers occasionally produce a soft tissue reaction¹⁵. Therefore low solubility of the denture base materials is desired^{15,16,20,21}. According to ISO specification No 1567 the loss in mass per unit volume (soluble matter) should not exceed 1.6 µg/mm³ for heat-polymerized and 8.0 µg/mm³ for chemical polymerized materials²⁰.

The water sorption and solubility of denture PMMA is well documented^{17,21–25}, but have not been studied for acetal resin. The purpose of the present investigation was to compare water sorption and solubility of pink and white acetal resin with one conventional heat-polymerized polymethyl methacrylate denture base resin.

MATERIAL AND METHODS

White acetal resin, pink acetal resin and one conventional heat-polymerized PMMA resin were evaluated in this

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Table 1. The names of the resins, manufacturers and polymerization conditions used in the study.

Names of the resins	Polymerization conditions	Manufacturers
Polymethyl methacrylate (PMMA)	Heat-polymerized technique, water, 100 °C, Mixing ratio 23.4 g: 10 ml	Meliodent, Dental Bayer Limited Pharmaceuticals, Berkshire, U.K. Batch no: 106
White acetal resin(WA)	Injection technique, 220 °C, 4 bar, J100 injection machine	Pressing Dental San Marino, Italy
Pink acetal resin(PA)	Injection technique, 220 °C, 4 bar, J100 injection machine	Pressing Dental San Marino, Italy

investigation. The names of the resins, manufacturers and polymerization conditions recommended by the manufacturers are listed in *Table 1*.

Specimen preparation and treatment

Seven discs (50±0.1 mm diameter and approximately 0.5 mm thickness) for each type of resins were prepared by using stainless steel mold which were mounted in a denture flask with Type IV Hard plaster (Cere Rock; GC Germany GmbH, München, Germany). In accordance with the manufacturer's instructions, a 1:3 monomer to polymer ratio, by weight, was used for the heat polymerized PMMA. The polymerization of the resin was performed by immersion in boiling water for 20 min. The specimens were cooled at room temperature for 30 minutes and then, left in tap water for 15 minutes.

Pink and white acetal resin specimens were prepared in accordance with manufacturer's instructions. As the special flask (Muffle-Type 100, Pressing Dental San Marino, Italy) mould with Class IV type plaster (Marble Stone, Pressing Dental San Marino, Italy), the stainless steel mold placed at a distance of about 2.5 cm from the opening of the flask. The flask was closed and hard plaster was poured into the flask through the opening of the special flask cover. The melted wax was removed. One acetal resin cylinder of the selected color was placed into the injection tube and the tube was placed with a special tweezers on the injection machine J-100 (Pressing Dental San Marino, Italy). The flask was then placed into the injection machine that was programmed as follows; melting temperature: 220 °C, pre-injection time with the material kept at the appropriate temperature: 20 minute, post-injection time with the temperature maintained at the desired level: 3 minute, injection pressure: 4 bar.

At the end of the program, the flask was removed from its initial position and the discs were taken out of the plaster. After processing the specimens were smoothed on both sides with 600 grit silicone carbide papers (Struers waterproof silicone carbide, Struers Scientific, Denmark) to a final thickness of 0.5±0.1. The thickness of specimens was determined with a micrometer set at 0 to 25 mm: 0.001 mm (Mitotuyo, Japan)

Test specimens were identified by placing a series of identification notches signifying the type of material and specimen number. Specimens were placed in desiccators (Normax, Fabrica de Vidros Cientificos, Lda, Marinha Grande, Portugal) and stored in the oven at 37 ±1 °C for 23 ± 1h and weighed by electronic balance (HM-200, AND Company Limited, Japan) in accordance with the procedure described in the International Specification for denture base polymers¹⁹. Specimens were reweighed at

regular intervals, until constant mass was reached (until the loss in mass of each specimen was not more 0.2 mg). This was considered to be the initial mass of the specimen (m_1).

Before they were immersed in water, test specimens were measured with the micrometer set at 0 to 25 mm: 0.001 mm (Mitotuyo, Japan) in the center and at four equally spaced locations around the circumference. Specimen volume was determined for calculation of water sorption. Specimens were then separately stored and immersed in distilled water, which was thermostatically controlled and maintained at 37°C±2°C for 7 days.

Specimens were removed from water with tweezers wiped dry until free from visible moisture, waved in the air for 1 minute and 15 seconds after removal from the water. The mass was recorded as m_2 . This represented the weight of specimen after absorption of distilled water. The water sorption (mg/mm³) calculations were made using the following formula¹⁹:

$$\text{Water sorption} = (\text{mg/mm}^3) \quad \frac{m_2 - m_1}{V}$$

Where m_1 = initial mass (mg)
 m_2 = mass after absorption (mg)
 V = Volume (mm³)

The amount of soluble material lost was measured by drying the specimens to constant weight (m_3) in the desiccators after absorption. The amounts of soluble material lost per unit volume were determined as follows:

$$\text{Water solubility} = (\text{mg/mm}^3) \quad \frac{m_1 - m_3}{V}$$

Where m_1 = initial mass (mg)
 m_3 = final mass after desiccation (mg)
 V = Volume (mm³)

Data were analyzed by using non-parametric Kruskal-Wallis test (significant $p < 0.05$)

RESULTS

Water sorption and solubility amounts of each specimen are shown in *Table 2*, *3* and *4* represent mean values and standard deviations of water sorption and solubility test. The mean increase in weight was 17.19µg/mm³ for PMMA, 12.99µg/mm³ for pink acetal resin and 17.03µg/mm³ for white acetal resin. The non-parametric Kruskal-Wallis test showed significant difference ($p = 0.001$) (*Table 3*) between water sorption values of the test specimens. Pink acetal resin showed significantly lower water sorption than heat-polymerized acrylic resin and white acetal resin.

Table 2. Water sorption and solubility amounts of three materials (polymethyl methacrylate (PMMA), white acetal resin (WA), pink acetal resin (PA)) in ($\mu\text{g}/\text{mm}^3$).

	Sorption ($\mu\text{g}/\text{mm}^3$)	Solubility ($\mu\text{g}/\text{mm}^3$)		Sorption ($\mu\text{g}/\text{mm}^3$)	Solubility ($\mu\text{g}/\text{mm}^3$)		Sorption ($\mu\text{g}/\text{mm}^3$)	Solubility ($\mu\text{g}/\text{mm}^3$)
PMMA 1	17.42	1.85	WA 1	15.27	0.07	PA 1	13.71	0.06
PMMA 2	14.76	1.74	WA 2	15.64	0.10	PA2	11.38	0.10
PMMA 3	16.44	2.65	WA3	15.95	0.03	PA 3	13.75	0.18
PMMA 4	20.54	0.91	WA 4	16.51	0.03	PA 4	13.62	0.07
PMMA 5	15.09	1.38	WA 5	16.15	0.07	PA 5	13.42	0.07
PMMA6	16.98	1.34	WA 6	16.87	0.18	PA 6	13.30	0.10
PMMA 7	19.08	1.32	WA 7	22.81	0.06	PA 7	12.83	0.16

Table 3. Non-parametric Kruskal-Wallis analysis of water sorption test

Material	N	Mean Rank	Chi-Square	df	Asymp. Sig.
PMMA	7	15.00			
PA	7	4.00			
WA	7	14.00			
Total	21		13.455	2	.001

Table 4. Non-parametric Kruskal-Wallis analysis of the water solubility test.

Material	N	Mean Rank	Chi-Square	df	Asymp. Sig.
PMMA	7	18.00			
PA	7	8.86			
WA	7	6.14			
Total	21		14.181	2	.001

Water solubility was $1.60\mu\text{g}/\text{mm}^3$ for PMMA, $0.11\mu\text{g}/\text{mm}^3$ for pink acetal, and $0.13\mu\text{g}/\text{mm}^3$ for white acetal resin. The non-parametric Kruskal-Wallis test showed significant difference ($p=0.001$) (Table 4) between the water solubility values of the test specimens. PMMA showed significantly higher solubility than pink and white acetal resin. Solubility of pink acetal resin was higher than white acetal resin but it was not statistically significant. Overall, both the quantity of water absorbed and solubility of the three materials tested were relatively small and within the ISO specification¹⁹ limit ($32\mu\text{g}/\text{mm}^3$ and $1.6\mu\text{g}/\text{mm}^3$).

DISCUSSION

This study was carried out on a small number of specimens to compare the water sorption and solubility of acetal resins with polymethyl methacrylate. Information on this parameter is important for clinical application of acetal resin as water uptake may affect dimensional stability and other physical properties of denture bases.

According to earlier studies the water sorption of different types of acrylates is 10 to $25\mu\text{g}/\text{mm}^3$. The results of this study revealed that PMMA used in this study was in accordance with the other studies in terms of water sorption and solubility^{14,15,17,21}. Pink acetal resin showed significantly lower water sorption than PMMA and white acetal resin.

The rate at which the materials absorbed water or lost soluble components varies considerably with the type of material, the amount of the plasticizer or filler content, and the solution in which they were immersed³. The chemical nature of the polymer versus that of the water molecule directly affects the water sorption of denture

base resin²¹. Distribution of molecules and their geometric disposition also influence the curing of fluids by solid bodies²¹. The macromolecules of polymethyl methacrylate are large and highly complex molecules with a heterogeneous conformation, having discontinuous empty spaces and unequal interstices, which also vary according to their composition²⁰. One of the primary properties of acrylic resins is related to polar properties of polymers and to the physical presence of these spaces, or their capacity to absorb water when immersed in liquid environments¹⁴. The absorption process of a liquid by a solid is diffusion¹⁴. Clearly, the solid will increase in weight due to the imbibitions of the liquid. The mechanism of liquid absorption originates from the diffusion of water molecules among polymeric macromolecules, as set forth by the laws of diffusion¹⁴.

Chow *et al.*³ found that fiber content of denture base polymers significantly reduces the water sorption of denture base resins. Both acetal resin materials have the same structure, but pink acetal resin has color fibers in structure. Piattelli²⁷ stated that pink acetal resin is more resistant to stress than white variety. This is because, in coloring it, acrylic fibers are added to the rough material and they amalgamate with the matrix and produce 2 fundamental aspects. These are: 1) varying the quantity and shade of the fibers can modulate the final color and 2) modifying the quality of the fiber in the mixture enables one to alter the overall resistance. This might indicate that water is less absorbed into the pink acetal resin. Overall, the quantity of water absorbed by the three materials was relatively small.

Solubility represents the mass of the soluble materials from polymers. The only soluble materials present in

denture base resins are unreacted monomers, plasticizers, and initiators that likely leached out during the 7 days the specimen was immersed in water^{15,20}. Correlation between residual monomer leaching and residual monomer content of the denture base polymers has been established^{21,22}. Takahashi *et al.*²⁵ found that denture base polymers of different monomer compositions and polymerization activator systems have different resistance to the influence of water. Acetal resins are formed by the polymerization of formaldehyde. The homopolymer, polyoxymethylene (POM) is a chain of alternating methyl groups linked by oxygen molecule⁸. Polymer losses and by-product formation can be minimized during stabilization⁷. The amount of residual monomer in heat polymerized PMMA also affects the solubility values more than the acetal resin does, of which does not contain monomer. Acetal resins could be clinically used as a denture base material from the standpoint of water absorption and solubility based on ISO specification. But, this is an *in vitro* study and does not replicate the clinical situation.

On the same level as water sorption and water solubility, color changes became a problem when a long service is required and are effected by many parameters including type of the base resin, polymerization process, using denture cleansers, diet and oral hygiene of patients. Ozkan *et al.*²⁶ indicated that acetal resin perform as favorably as acrylic resin, when the discoloration of the denture is considered. However, further research is needed for the evaluation of clinical application of acetal resins.

CONCLUSIONS

The results of this study indicated that water absorption and solubility of PMMA, pink acetal resin and white acetal resin were relatively small and within the ISO specification limit (32µg/mm³ and 1.6µg/mm³).

MANUFACTURERS' DETAILS

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