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A Study to Assess the Colour Stability of Acetal Resins Subjected to Thermocycling

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Abstract - *The purpose of this study was to compare colour stability of pink and white acetal resin with one conventional poly (methylmethacrylate) resin. Five specimen disks 50 ± 0.1 mm in diameter and approximately 1.0 mm thick were prepared from each material. The discs were hydrated for a period of 30 days in distilled water and were then desiccated to a constant weight. Total of fifteen specimens were thermocycled for 100 and 300 hours (4000-12000 cycle) between water baths of 5–55ºC. Changes from baseline colour readings were recorded at each interval. Data were analysed with descriptive statistic, repeated measured analysis of variance and single factor analysis of variance. The colour changes for all materials at 100 hours were in the categories of slight, based upon the National Bureau of Standard System (NBS) for expressing colour difference. At 300 hours, the colour changes of materials were significantly different* (p=0.0001)*. All the materials tested showed clinically acceptable discolouration values.*

KEY WORDS: Colour stability, Denture base materials, Acetal resin

INTRODUCTION

Colour stability is an important clinical character for dental restorative materials and is one factor that provides information on the serviceability of these materials[1,2]. Discolouration of denture base polymers may be caused by either intrinsic or extrinsic factors. Intrinsic factors involve chemical change of the material. Extrinsic factors which contribute to discolouration include staining by adhesion or penetration of colourants as a result of contamination from exogenic sources, coloured solutions such as coffee, tea, other beverages and nicotine[3]. A whitening effect has been observed in several types of denture base materials due to faulty handling or attack by external agents such as denture cleansers[4]. The cause of chemical discolouration has been attributed to the oxidation of amine accelerator after exposure to various energy sources and immersion in water for a long time. Heat polymerised denture base materials have exhibited satisfactory colour stability[5]. Autopolymerised denture base materials have shown relatively poor colour stability[6]. The residual monomer content has been one possible explanation for the colour changes observed[7]. The colouring resistance of polymers depends on both the mode of polymerisation and their chemistry[8]. Denture base materials processed with a rapid-polymerise method have demonstrated up to seven times the level of residual monomer found in conventional heat-polymerise materials[9]. It has been shown that microwave processing resins contain minute level of residual monomer[10]. They are now gaining popularity because of their ease of handling and their physical and mechanical properties[11]. Acetal resin denture base resins have also recently been marketed to compete with conventional acrylic resins.

Acetal resins are formed by the polymerisation of formaldehyde. The homopolymer, polyoxymethylene (POM) is a chain of alternating methyl groups linked by an oxygen molecule[12]. The material has been shown to have good biocompatibility and this has fostered its use in total hip replacement and as an artificial heart valve occluders[13,14]. The possible use of polyacetal resins as denture base materials was considered by Smith over 40 years ago[15,16]. A material 'Dental D' is the first dental product involving these resins to come on to the market. Because of its biocompatibility it was considered to be used as a framework material for removable partial denture for patients with allergic reactions to Co-Cr framework[17]. The colour stability criteria may provide important information on the serviceability of the denture base materials. Several problems arise in colour description of restorative materials, whether this description is by human observation or by colourimetry[18]. Colour measurement by a colorymetry, gives a consistent colour evaluation by other studies[19]. Determination of the acceptability of resins with varying magnitudes of colour differences have found the colour changes less than 3.3 to 3.7 ΔE units have been considered to be acceptable[20–22]

Although there are numerous studies regarding colour stability of denture base materials, there is a paucity of evidence on the colour stability of acetal resin materials. Therefore, the purpose of this study was to determine the colour stability of acetal resins as compared to a conventional acrylic resin.

MATERIAL AND METHODS

White acetal resin, pink acetal resin (Pressing Dental,) and one conventional heat-polymerised acrylic resin (Meliodent) were evaluated in this investigation. The

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Table 1. *Resins, manufacturers and polymerisation conditions used in study*

Resins	*Polymerisation conditions*	*Manufacturers*
Poly(methylmethacrylate) (PMMA)	Heat-cured technique, water, 100°C mixing ratio 23.4 g:10 ml	Meliodent, Dental Bayer Limited, Pharmaceuticals, Berkshire, U.K.
White acetal resin (WA)	Injection technique, 220 Cº, 4 bar, J100 injection machine	Pressing Dental, San Marino, Italy
Pink acetal resin (PA)	Injection technique, 220 Cº, 4 bar, J100 injection machine	Pressing Dental, San Marino, Italy

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

A total of 15 discs (50±0.1 mm diameter and approximately 1.0 mm thickness), 5 for each type of resins were prepared by using stainless steel mold mounted with Type IV Hard plaster stone (Cere Rock) in a denture flask. After being processed the samples were abraded on both sides with 600 grit silicone carbide paper (Struers waterproof silicone carbide) to a final thickness of 1.0±0.1 units of measurements should be mentioned. The thicknesses were determined with a micrometer (0 to 25 mm:0.001 mm). The samples were 0.5 mm thicker than the dimensional requirements for colour stability testing as described in the American Dental Association (ADA) specification No: 12 to more accurately evaluate colour changes as function of accelerated aging[6]. In accordance with the manufacturer's instructions, 1:3 liquid to powder ratio by weight were used for the heat polymerised PMMA. The polymerisation of the resin was performed by immersion in boiling water for 20 min. The specimens were cooled at room temperature for 30 min and then left in tap water for 15 min. Pink and white acetal resin specimens were prepared in accordance with manufacturer's instructions. First the stainless steel mould placed at a distance of about 2.5 cm from the injection hole of the special flask (Muffle-Type 100) mould with hard plaster (Marble Stone). One acetal resin cylinder of the selected colour was placed into the injection tube and the tube placed with a special tool on the injection machine (J-100 Pressing Dental). The injection machine was programmed as follows: melting temperature 220ºC, 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 and 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.

Test samples were identified by placing a series of identification notches signifying the type of material and sample number. The discs were hydrated for a period of 30 days in distilled water and were then desiccated to a constant weight. With this procedure all of the specimens had the same level of saturation when the experimental procedure began. After initial colour measurements, specimens were thermocycled for 100 and 300 hours (4000–12000 cycle) at between baths of 5–55ºC. After 100 and 300 hours of thermocycling, the colour measurements of all samples were repeated. Colour was measured according to CIE L*a*b* colour scale relative to standard source C against a white background on a reflection spectrophotometer (Spectra flash SF 600 CT). According to this system, all colours in nature are obtained through the blending of 3 basic colours, red, blue and green in certain proportions. The CIE Lab system has been developed on the basis of this system. In examining various materials with regard to colour, this technique is also being used quite extensively by researches in dentistry. Colour differences $(\Delta E^*) = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$.

Colour measurements were made in 3 selected areas near the center of each specimen. The colour of each specimen was measured three times. The average of this three reading was recorded and the mean of each sample was calculated.

To determine the average colour change after 100 hours and 300 hours, the mean and standard deviation of each material was calculated. The statistical analysis consists of: (1) descriptive statistic, (2) analysis of variance for the change of colour (ΔE) at each time, and (3) repeated measurement analysis to determine the overall effect of material on the colour change. To determine the average colour changes after 100 hours and 300 hours, the mean and standard deviations of the three materials were calculated .

The three materials were compared with respect to the mean colour change at 100 and 300 hours, using the analysis of variance (ANOVA) method. The colour changes measured after 100 hours and 300 hours, specimens consisted of repeated measurement on the same experimental unit. An overall comparison of the mean colour changes at both times was made[6].

RESULTS

The mean and standard deviations for all materials after 100 and 300 hours of thermocycling are shown in *Table 2*.

The one way ANOVA showed no significant difference ($p = 0.30$) (*Table 3*) between the means of the test samples at 100 hours *(Figure 1)*. The colour changes for all materials at 100 hours were in the categories of slight, based upon the National Bureau of Standard System (NBS) for expressing colour difference (*Table 4*).

At 300 hours of the colour changes of materials were significantly different ($p=0.0001$) (*Table 3* and *Figure 1*). When the ΔE means were subjected to repeated measurements analysis (*Table 5*), there were significant differences between materials ($p=0.0001$), there was a significant colour difference (ΔE) of all materials from 100 hours to 300 hours ($p=0.0001$). The colour changes for PMMA and PA materials at 300 hours were in the category 'slight', for WA materials were noticeable based upon the NBS system for expressing colour difference (*Table 4*).

Table 2. *Colour change (ΔE) means and standard deviations (Sd) at 100 and 300 hours of accelerated aging.*

Materials	*no*	*100 hours mean (ΔE)(Sd)*	*300 hours mean(ΔE) (Sd)*
PMMA	5	0.69 (0.05)	1.33(0.07)
WA	5	0.74(0.07)	1.67(0.07)
PA	5	0.77(0.05)	1.13(0.01)

Table 3. *ANOVA of ΔE data on materials at 100 and 300 hours.*

Source	*d.f*	*Sum of squares*	*Mean square*	*f.test*
100 hours				
Between groups	2	0.02	0.01	1.31
Within groups	12	0.08	0.01	p=0.308
Total	14	0.09		
300 hours				
Between groups	2	0.73	0.36	91.53
Within groups	12	0.05	3.97E-3	p=0.0001
Total	14	0.77		

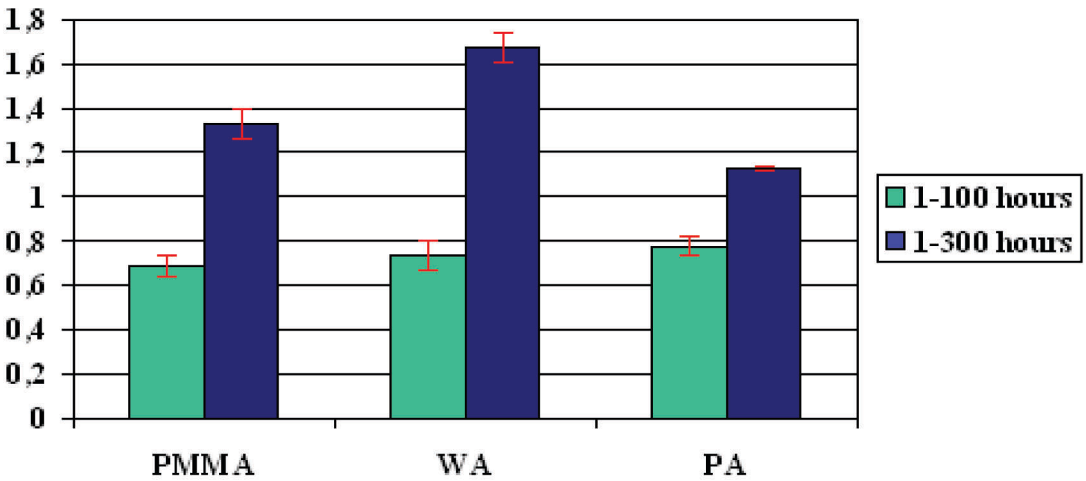

Figure 1. *Materials mean colour change (ΔE) values at 100 and 300 hours of thermocycling*

Table 4. *National Bureau of Standards (NBS) system of expressing colour difference*

Critical remarks of colour difference	*(AE) NBS units*
Trace	0.0–.05
Slight	0.5–1.5
Noticeable	1.5–3.0
Appreciable	3.0–6.0
Much	6.0–12.0
Very much	12.0+

Table 5. *ANOVA table for repeated measurements analysis results of colour change (ΔE) values of denture base resins.*

Source	*Df.*	*Sum of squares*	*Mean square*	*F.test*	*P value*
Materials	2	0.34	0.17	35.95	0.0001
Subjects vs.groups	12	0.06	4.77E-3		
Repeated measure (B)	1	3.09	3.09	542.49	0.0001
AB	2	0.4	0.2	35.12	0.001
Bxsubjects vs.groups	12	0.07	0.01		

DISCUSSON

Colour changes became an aesthetic problem when a long service is required and are effected by many parameters including type of the base resin, polymerisation process, using denture cleansers, diet and oral hygiene of patients. Discolouration of denture base resins can be evaluated visually or by colourimetry. Johnston and Kao evaluating the assessment of appearance match by visual observation and clinically colourimetry, stated that the mean colour difference between compared teeth that were rated as a match in the oral environment was 3.7

(ΔE)[18]. They observed that, if ΔE less than 1, this chromatic value is seemed to be slight and between 1 and 2, and the situation is clinically acceptable. Seghi *et al.* also presumed that an acceptable colour difference can often be 2 or 3 times greater than the detectable limits[19]. The upper limit of acceptability in subjective visual evaluations has been confirmed by Ruyter *et al.* and Um and Ruyter who suggested that a perceptible discolouration must be referred to as acceptable up to value of ΔE = 3.3[21,22]. In the study, discolouration below or above value of ΔE =3.3 was referred to as 'acceptable' or 'unacceptable' respectively. In our study, the colour changes exhibited by all specimens after 100 and 300 hours thermocycling are clinically acceptable levels.

This test study was carried out on a small number of specimens to compare the colour stability of acetal resin with poly (methymethacrylate). Information on this parameter is important for clinical application of acetal resin. Dentures placed in water for periods of 12 to 24 hours before insertion leach excess tertiary amines and unreacted monomer[5]. In this test study, specimens were placed in water for 30 days and were desiccated to constant weight before thermocycling. Using this procedure, all specimens had the same level of saturation before study began. The one-way ANOVA at 100 hours showed no statistically significant differences in ΔE of the materials. But there was a statistically significant difference between materials at 300 hours of thermocycling. In accordance with NBS System of expressing colour differences, all the materials could be categorised slight after 100 hours of thermocycling. After 300 hours of thermocycling, the materials were grouped into two NBS categories of colour changes 'slight' and 'noticeable'. The mean colour change ΔE values at 100 hours were 0.69 for PMMA, 0.74 for white acetal resin, 0.77 for pink acetal resin, at 300 hour, 1.33 for PMMA, 1.67 for white acetal resin, 1.13 for pink acetal resin, which represent imperceptible colour differences. The results of this study indicated that acetal resin perform as favorably as acrylic resin, under these experimental conditions. The colouring resistance of polymers depends on both the mode of polymerisation and their chemistry. Other possible reason for the changes observed could be attributed to the colourants added for characterisation[9].

Conventional denture base materials, when processed according to the manufacturer's instruction, have demonstrated adequate colour stability under conditions of accelerated aging[5]. The residual monomer content could be explanation for the colour changes observed[7]. De Clerck concluded that microwave processing provided a more thoroughly processed denture base acrylic resin that contained minute levels of residual monomer while preserving the physical properties of the conventionally cured acrylic resins[10]. Polyoxymethylene (POM), which is formed by polymerizing formaldehyde may be used as an alternative to conventional denture base materials[16]. Acetal resin is a thermoplastic technopolymer with a monomer-free crystalline structure and is a product of formaldehyde polymerisation[17]. Therefore, it is likely that there are other factors involved when colour changes are seen.

Other possible reasons for the changes observed could be attributed to colourants added for characterisation. The colourants may leach out or change in colour on accelerating aging. In our study, white acetal resin showed suprisingly less colour stability than pink acetal resin. Pink acetal resin may be more resistant to stress than white variety because, the addition of acrylic fibers may: 1) vary the quantity and shade of the fibers can modulate the final colour, and 2) modifying the quality of the fiber in the mixture may enable one to alter the overall resistance.

Another possible source of colour change may be associated with porosity caused by overheating or insufficient pressure during polymerisation. It was shown that acetal resins resist temperatures from –40 to +90^{0}C. The colour differences shown are supported by the statistical analysis. The processing method may not be as significant factor in the colour stability of these materials as the effect of thermocycling.

CONCLUSIONS

This study involved subjecting white acetal resin, pink acetal resin and one conventional heat-cured acrylic resin to conditions of thermocycling 100 and 300 hours to test colour stability. Within the limitation of this study, the conclusions are:

1. Use of thermocycling (5–55°C) 100 hours all materials tested showed no significant colour changes from baseline values.
2. After 300 hours thermocycling all materials exhibited significant colour changes from baseline values.
3. All materials tested showed clinically acceptable colour changes after 300 hours thermocycling.
4. ΔE values of acetal resins are similar to PMMA.

MANUFACTURERS' DETAILS

- Pressing Dental, San Marino, Italy
- Meliodent, Dental Bayer Ltd Pharmaceuticals, Berkshire, UK
- Cere Rock, Germany
- Struers waterproof silicone carbide, Struers Scientific, Denmark
- Muffle-Type 100, Pressing Dental, San Marino, Italy
- Marble Stone, Pressing Dental, San Marino, Italy
- J-100 Pressing Dental, San Marino, Italy
- Spectra Flash SF 600 CT, Data Color

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