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Provisional crown and bridge and its colour unreliability: An investigative approach on the consequences of intraoral thermal changes using reflection spectrophotometry and FTIR

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Abstract

Objectives: Study aims to determine whether the colour stability of different provisional restorative materials are suitable for use in long-term interim prosthesis by cross comparisons and also to assess the changes in material composition due to thermal changes thereby providing a scientific basis for its rapid intraoral colour change.

Methodology: According to ADA specification no 27 thirty samples of three different provisional restorative materials were made for the study; DPI™ self-cure tooth molding powder, Integrity™ & Protemp™. Colour measurements were recorded using spectrophotometer and ΔE values were calculated. To assess the changes in composition the degree of conversion was calculated before and after Thermocycling by assessing the percentage of unreacted C=C double bonds using FTIR analysis.

Results: The ΔE value of the Group C (DPI™) were greater than 3.3 which means the colour change was visually perceptible and clinically unacceptable.

Furthermore the ΔE value of the Group B (Protemp™) represent colour the differences that are just perceptible. The maximum degree of conversion was observed with Integrity™ followed by Protemp™ and the least with DPI™. All the samples irrespective of the material Group showed significant increase in the degree of conversion after thermocycling.

Conclusion: Resin composite-based materials showed superior colour stability than the acrylic resin-based materials. The colour change after thermocycling with an increase in the degree of conversion indicate that the thermocycling induced structural changes (Degree of conversion) could be a causative reason for the colour instability along with other internal and external factors.

Keywords: ADA, FTIR, VITA.

Introduction

The term ‘‘provisional’’ prosthesis is often used as a synonym for ‘‘interim’’ prosthesis. The requirements of an interim restoration are essentially the same as for the definitive restoration, with the exception of longevity and possibly the sophistication of color. [1, 2] When selecting a material for an interim restoration, consideration should be given to the physical properties of the material such as strength, rigidity & reparability, exothermic reaction, polymerization shrinkage, marginal integrity & color stability. [2-5]

As patients become more esthetically aware and demanding, it is paramount that the clinician provides an esthetically acceptable interim restoration. Provisional restorative material and its external colour changes in an external staining environment is a well-studied subject in the literature by using artificial aging & various staining solution methods whereas the effect of various thermal events on the colour stability of the provisional materials have always remained as an inadequately studied aspect. Intra oral thermal changes can cause various changes in the chemical composition of the resin materials as the polymerization process never completes. [6-11]

Methodology

Materials used: Three different provisional restorative materials were selected for the purpose of this study. (Table-1) As described in ADA specification No.27, standard specimens of dimension 25mm diameter and 2mm thickness were used for the study to evaluate colour change more accurately.[12] Standard custom fabricated nickel chromium moulds of same internal dimensions were used to prepare the specimens.

The test materials were dispensed into the nickel chromium mold and polymerized according to the manufacturers' instructions to make the required ten samples of each material. All the obtained sample specimens were finished with lab type micro motor (Marathon, M-3 Champion, Saeyang Microtech, Galsan-Dong, Dalseo-Gu, Korea), Tungsten Carbide burs and using wet or dry sand papers (3M wet or dry paper P400 and 3M wet or dry paper P1000). Until the thermo cycling & FTIR procedure all the specimens were kept in artificial saliva in three different labeled plastic containers as Integrity™-Group-A, Protemp™ Group-B & DPI™ self-cure tooth molding powder-Group-C. Artificial saliva were made up of one liter of double distilled H_2O with 1.6802 gm of $NaHCO_3$, 0.41397 gm of $NaH_2PO_4 \cdot H_2O$ and 0.11099 gm of $CaCl_2$ buffered with lactic acid at pH of 6.72.[13]

Once fabricated the samples are subjected to spectrophotometry (VITA Easy shade®, VITA Zahn Fabrik H. Rauter GmbH & Co, D-79704 Bad Säckingen, Germany) before Thermocycling procedure to provide a baseline data for comparison.

Then the samples were subjected to Thermocycling procedure for varying temperatures for simulating intra oral conditions using a Thermocycling-testing-system

(Wileytec Thermocycler with cooling system HAAKE EK 30, Thermoelectron Coorporation, Germany) which consisted of 1500 cycles from 4 ^{0}C ($\pm$2 ^{0}C) to 55 ^{0}C ($\pm$2 ^{0}C) in water. Immersion times in each bath were 10 seconds and transfer time between baths were 5 seconds. [14]

Once the procedure was completed the samples were subjected to post Thermocycling spectrophotometry for detecting the colour changes after Thermocycling procedure. The post Thermocycling colour values were measured, analyzed and the calculated values were compared with base line data and differences were measured.

Method of colour measurement;

Before and after Thermocycling procedures, specimens were measured using VITA Easyshade® spectrophotometer. Each and every specimen was exposed at the center against a white background by the spectrophotometer tip & colour values were recorded. Colour values were recorded using CIE L*a*b colour system (Commission Internationale de l' Eclairage L*a*b colour system). [15]

"L" which represents the lightness or brightness of the object,

"a" which represents the red-green chromaticity of the object,

"b" which represents the yellow-blue chromaticity of the object.

The total colour difference ΔE* for each disk sample was calculated using the following equation and a mean ΔE* value was calculated for each sample Group.[15]

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Fourier Transformation Infrared spectroscopy (FTIR)

Fourier Transformation Infrared spectroscopy (FTIR) assessment was employed to find the absorption of energy in a wavelength or wave number to investigate the chemical structure of the material being tested. Atoms or atomic Groups in molecules are in continuous motion with respect to one another. They vibrate about some mean position. IR spectrum of a compound is the superimposition of absorption bands of specific functional Groups. The subtle interactions with the surrounding atoms or molecules impose the stamp of individuality of the spectrum of each compound and hence can be used for identification of unknown compounds with the help of a database.[16,17]

The specimens were analyzed by FTIR spectroscopy before and after curing and after thermocycling and spectra were acquired on an FTIR spectrometer. The aromatic C…C (peak at 1609.4 cm^{-1}) and N…H (peak at 1537 cm^{-1}) absorbance were used as internal standards for Bis-GMA- and UDMA (Urethane dimethacrylate) - based composites, respectively.[17-19] A baseline was determined for each material (range: 1670 and 1580cm^{-1}) in the uncured (uncured paste of each composite based resin material and liquid component of methacrylate resin-based material) state. The baseline determined the relative peak height (rPH) of absorbance intensity of the aliphatic C =C peak (1638cm^{-1}) as well as aromatic C. C peak (1609cm^{-1}) as an internal reference.[20,21] (graph-1)

As the baseline FTIR measurements were completed three new samples of each material Group were made and after polymerization they were pulverized into fine powder with a lab type micromotor and a tungsten carbide bur. Fifty micrograms of the ground powder was mixed with 5 mg of potassium bromide powder (KBr

PELLET method), and the absorbance peaks were recorded using the diffuse-reflection mode of FTIR. The relative peak height (rPH) of absorbance intensity of the aliphatic C =C peak (1638cm^{-1}) as well as aromatic C .C peak (1609cm^{-1}) were there measured again.

Now in order to find out changes after Thermocycling the three thermocycled samples of each material were pulverized and the absorbance peaks measured as mentioned above. The percentage of the degree of conversions (DC) were calculated after polymerizing (curing) and after Thermocycling as the quotient of the rPH determined for the cured versus uncured and thermocycled versus uncured materials according the following equations:

$$\text{DC (\%)} = \left(1 - \frac{\text{cured (rPH C = C/ rPH aromatic C ... C}}{\text{uncured (rPH C = C/rPH aromatic C ... C}}\right)$$

$$\text{DC (\%)} = \left(1 - \frac{\text{cured \& } thermocycled\ (\ rPH\ C = C/\ rPH\ aromatic\ C \ldots C}{\text{uncured (rPH C = C/rPH aromatic C ... C}}\right)$$

Results

Spectrophotometry: The one-way ANOVA revealed significant differences post Thermocycling with p value 0.0005. The ΔE* value (3.74699) of the Group C (DPI™) were greater than 3.3 which means the colour change was visually perceptible and clinically unacceptable. Furthermore the ΔE* value (2.60252) of the Group B was between 2 and 3 which represent colour the differences that are just perceptible. Whereas the colour difference value (ΔE* value-1.32707) of the Group A was between 0 and 2 which represents imperceptible colour differences. (Table-2 & Graph-2)

Inter Group comparison showed statistically significant difference between Group A (Integrity™) and Group C (DPI™) with p value 0.0001 and 95% confidence interval (upper bound -1.4487 & lower bound-5.6915). Differences between Group A and Group B (Protemp™) were also statistically significant (p value-0.0257). Whereas Group B (Protemp™) and Group C (DPI™) comparison again showed significant differences with p value 0.0435 and 95% confidence interval (upper bound 4.6513 & lower bound 0.4085).

The ΔE* values for three materials; ie Group A, Group B and Group C were illustrated in the overlay graph (Graph 2) and the (Table- 2) shows the mean values of ΔE* for each material Group was analysed.

One way ANOVA for intra Group comparisons to assess the changes in each colour component (ΔL- lightness or brightness, Δa- red-green chromaticity, Δb- yellow-blue chromaticity) revealed that irrespective of the material all the colour components showed significant changes post Thermocycling. Multiple comparisons using Post Hoc Tukey analysis showed statistically significant differences in ΔL values between Group A and Group C with p value 0.0001 and between Group B and Group C with p value 0.003. However the differences between Group A and Group B were statistically not significant (p value- 0.085).

The Δa value comparisons also showed significant differences between Group A & B with p value 0.0001. The differences between Group A & C (0.0261) as well as between Group B & C (0.008) were also significant. Similarly multiple comparisons for the Δb values showed significant difference only between Group B & C with p value- 0.045 and between group A & C with p value 0.032.

FTIR (Fourier transformation infrared spectroscopy)

The measured degree of conversion of each samples were analyzed and listed in the table-3. The maximum degree of conversion was observed with the sample Group A followed by Group B and the least with Group C (Table-3). All the samples irrespective of the material Group showed significant increase in the degree of conversion after thermo cycling.

One way ANOVA for intra Group comparisons to assess the changes in the degree of conversion revealed that there were significant differences in the degree of conversion of Group-A (p value-0.012) Group-B (p value-0.005) and Group-C (p value-0.023) samples before and after the Thermocycling. The sample Group B showed maximum increase in the degree of conversion followed by Group C and Group A.

Discussion

In the literature, the PMMA provisional materials were found to be more colour stable than PEMA and PVEMA provisional materials. Catelan et al's (2011) study on composite resin materials concluded that the aging procedures cause significant color difference in the composite materials.[22] As with other physical properties, colour stability cannot be predicted solely on the chemical classification of the material.[2] Resins change color when they are subjected to various conditions of the oral environment[23,24] as a result of the complex interaction of multiple factors including, but not limited to, incomplete polymerization,[25,26] water sorption,[27,28] chemical reactivity, and the patient's diet and oral hygiene.[29,30]

Whereas very few studies are available showing or questioning the better colour stability of resin composite materials like, the recent study by Dory et al (1997),[31] who concluded that the some resin composites were not as color stable as some acrylic resins under accelerated aging conditions, earlier studies of provisional restorative materials like Crispin et al (1979) and Wang et al (1989) generally concluded that resin composites tended to be more color stable than acrylic resins.[23,24]

The values of measured color difference in the present study (value of ΔE*) were related to a range of values of ΔE* which represent the perceptible color differences as follows:[15]

1. A value of ΔE* of 1 unit is approximately equivalent to a colour difference that is just visually perceptible.
2. Values of ΔE* between 0 and 2 represent imperceptible colour differences, whereas values in the range of 2 to 3 represent colour differences that are just perceptible.
3. Values of ΔE* greater than or equal to 3.3 are visually perceptible and clinically unacceptable.

Colour changes calculated by the materials as extrapolated in the results is significant and visually perceptible. As compared to the acrylic resin-based material Group C (DPI™ self-cure tooth molding powder), wherein the colour change was clinically unacceptable, the Group A (Integrity™) and Group B (Protemp™) Bis acryl-based resins though did demonstrate some colour differences, however these were only imperceptible changes. These results lend credence to the selection of Bis- acryl based provisional restorations in those clinical situations of high esthetic value (such as anterior restorations) and where long-term use of an interim prosthesis is mandated.

The FTIR assessment of all the three material sample groups revealed a constant increase in the percentage of the degree of conversion (DC) after thermocycling. Highest degree of conversion was observed with Group B (Protemp™) followed by Group C (DPI) and the least with Group A (Integrity). FTIR provides an individual, inherent, chemical and molecular composition of materials even to the minutest of details of or as depicted by the relative peak height (rPH) of spectroscopic graphs.

A significant and hallmark feature of this study is that it exclusively concentrates on the effect of thermocycling procedure, which simulate the intra-oral thermal events and its effect on not only the colour, but also reveals the compositional changes of the material. Furthermore, the

change in colour was consistently related to the increases in the degree of conversion of all materials tested by the scientific method of the FTIR. The study has its own few limitations in that only three materials were studied and all were self-cure materials of a single shade and only two groups of materials studied. Nevertheless within such limits, this study brought us to a path breaking & landmark set of scientific findings that provide the basis for both visually perceptible colour changes and as furthermore correlated with compositional & molecular changes as affirmed by FTIR.

Conclusions

Among the materials studied for the colour stability after thermocycling procedure the DPI™ material showed visually perceptible colour change which was clinically unacceptable. Whereas from the resin composite-based materials, the colour differences were just perceptible for Protemp™ and the colour difference of Integrity™ was imperceptible.

Hence while selecting the material for temporization the resin composite-based materials were found to have superior colour stability than the acrylic resin-based materials.

Thermocycling significantly increased the degree of conversion of all the materials thereby thermal changes definitely cause changes in the material's molecular composition or in the chemical structure

The colour change after thermocycling with an increase in the degree of conversion indicate that the thermocycling induced structural changes could be an important causative reason for the colour instability along with other internal and external factors and not just the degree of conversion alone.

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Legend of tables

Table 1: Products, Shades, and Manufacturers of Provisional Restorative Materials Tested

Sn.	Product	Shade	Manufacturer
	Integrity™ (Resin composite material)	A2	Densply/Caulk, Milford, DE
	Protemp™ (Resin composite material)	A2	3M ESPE, Seefeld, Germany
	DPI™ self-cure tooth molding powder (PMMA acrylic resin material)	A	Dental products of India LTD, Wallace Street, Mumbai

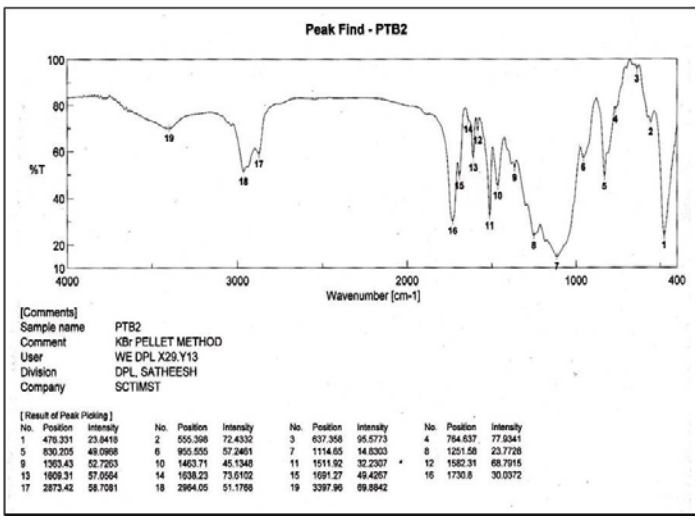
Table 2:The mean ΔE* values for three materials.

Sl No	Material	Grouping	Mean ΔE* value
1.	Integrity™	A	1.32707
2.	Protemp™	B	2.60252
3.	DPI™ self-cure tooth molding powder	C	3.74699

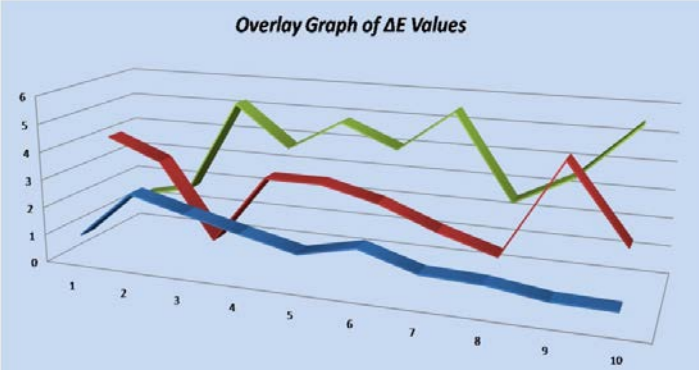
Table 3: Mean degree of conversion of samples before and after Thermocycling.

Sample Group- A		Sample Group- B		Sample Group- C	
Before	After	Before	After	Before	After
65.33	69.13	63.93	68.60	57.07	61.80

Graph 1: FTIR graph showing peaks at 1609cm-1 & 1638cm-1



Graph 2: Overlay graph showing the ΔE* values for Group I(A), II(B) and III(C).



	1	2	3	4	5	6	7	8	9	10
Group I	0.91104335	2.62488095	2.11896201	1.64012194	1.18321595	1.62480768	1	0.92736185	0.64031242	0.6
Group II	4.06571027	3.30302891	0.54772255	3.04302481	3.04138126	2.56124969	1.77482393	1.14455231	4.60977222	1.93390796
Group III	1.28840987	1.73781472	5.18169856	3.67423461	4.78121323	3.96610640	5.46351535	2.42899156	3.5	5.44793538