Addition of Non-Toxic Organic Pigments As Inorganic Cadmium Pigments Replacement In The Denture Base Production from an Aesthetic Perspective

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**Abstract.** The denture base is defined as the base tissue to which the teeth are attached. Materials for denture base must fulfill certain properties such as: good mechanical and aesthetic qualities. For aesthetic quality, the denture base must be able to match the natural color of the gingiva and mucosa. This color adjustment can be done by adding pigment to the denture base resin composition, usually the inorganic pigment cadmium sulfoselenide is used. However, the use of cadmium-based pigments is currently highly restricted due to their potential toxicity. To avoid this effect, most manufacturers are starting to switch to an organic pigment system Cromophtal Red BRN. One of the most influential factors is the pigment concentration, which if too high can reduce the degree of polymerization of the composite and result in poor mechanical properties. However, when the concentration is too low, satisfactory aesthetic results are difficult to achieve. Therefore, the aim of this research is to apply non-toxic organic pigment, Cromophtal Red BRN, in the denture base composition and determine the effect of its concentration on the aesthetic quality of the denture base product through optical analysis. The stages carried out are (1) Making Polymethyl Methacrylate polymer (2) Making denture base specimens (3) Optical Analysis. The result of this research shows that using the organic pigment Cromophtal Red BRN with a minimum concentration of 0.01% in denture base composition can imitate the color of natural aveolar mucosa, so that it can fulfill aesthetic qualities without jeopardize its mechanical properties.

# iNTRODUCTION

Edentulous is a condition where the patient has no teeth, lacks teeth, or experiences tooth loss. Removable dentures have been used for decades to replace function and aesthetics in edentulous patients[1]. Based on data from Badan Pengkajian dan Penerapan Teknologi (BPPT), in Indonesia the need for removable dentures reaches 2,500 pieces per month and fulfillment of this need is still carried out by import activities[2].

Denture base is part of a removable denture which is defined as the base tissue to which the teeth are attached[3]. The material for commercial denture bases is based on acrylic resin with a polymer base of Polymethyl Methacrylate (PMMA) which is available in the form of a powder liquid system which is heat cured[4]. One of the most important factors in materials for denture bases to support the success of restorative treatment in edentulous patients is the aesthetic factor. The base gingival color and pigmentation color must be adjusted to the denture base to make it look more natural[5]. Adjusting the color of the denture base can be done by adding pigment to the resin composition of the denture base to help match the color of the patient's denture base[6].

Inorganic pigments such as cadmium sulfide and sulfoselenide have been used for many years to color denture base resins due to their technical advantages[7]. However, the use of cadmium-based pigments is strictly limited due to their potential toxicity[8]. Therefore, today many prosthodontists are looking for new and better colors to color denture base resin. There are a number of factors that must be considered in choosing pigments such as being easy to mix with acrylic resin, non-toxic, non-irritating, and non-carcinogenic. Because of the considerations above, most manufacturers are starting to switch to organic pigment systems which are considered to have high color strength compared to inorganic pigments, namely, Cromophtal Red BRN (Pigment Red 144)6.

In denture base composites, this pigment is locked in the denture base polymer network and is used in very small concentrations. It is necessary to pay attention to the concentration of pigment in the denture base resin because in some cases when the proportion of color powder is too large, the acrylic resin will not absorb all the color material and this excess powder will interfere with resin polymerization[9]. In Saikaew's[9]. research, increasing the dye concentration significantly reduces the degree of conversion of the composite which causes high residual monomer and produces poor mechanical properties. This means that the pigmentation color of the denture base is limited to a certain range of shades and the best aesthetic restoration results are difficult to achieve. However, if pigments with high color strength are used, such as organic pigments, then just a small amount of pigment added can provide a bright color so that it can better satisfy the aesthetic aspect of the denture base, especially Indonesian denture bases which tend to be darker.

From previous studies, pigment concentration is an important factor that greatly influences the optical, mechanical and resin polymerization properties of denture base specimens. Apart from that, the type of pigment used also produces different optical properties due to differences in color strength. Where in the studies above only used inorganic pigments. So research on adding the organic pigment BRN Red Cromophtal needs to be carried out because of the lack of studies and literature regarding the effect of adding organic pigments.

# MATERIALS AND METHOD

## Materials

Methyl Methacrylate (MMA) (sigma-Aldrich p.a), Hidroksiapatit (HAp) (sigma-Aldrich), 3-(methacryloxy) propyl trimethoxysilane (𝛾−MPS) (sigma-Aldrich p.a), and Ethylene glycol dimethacrylate (EGDMA) (sigma-Aldrich p.a) was purchased from PT. Indofa Utama Multicore. Organic pigment BRN Red Cromophtal and Anorganic pigment Cadmium Sulfoselenida was purchased from Hubei Clf Sci&Tec Co., Ltd.

## Procedure

First, PMMA polymer was produced using a suspension polymerization process. Then the hydroxyapatite was silanized with gamma MPS of 8%wt γ-MPS against hydroxyapatite in methanol-aquadest solvent with a ratio of 90:10. Ddenture base specimens were made by mix the powder ingredients (PMMA powder, BPO, pigment, and treated HAp) with a V-Blender at 60 rpm for 30 minutes. There are 2 different types of pigment used in each denture base specimen, namely the organic pigment BRN Red Cromophtal and the inorganic pigment Cadmium Suslfoselenide with a concentration of 0%; 0.01%; 0.02%; 0.04%; 0.06%; 0.08%; 0.1%; and 0.12%wt. Then the powder and liquid (MMA and EGDMA) were mixed in a mixing bowl using the handmixed method until it reaches the dough stage. The dough is molded using standard molds, then the heat cured polymerization process is carried out in a water bath temperature of 78oC for 90 minutes, then the temperature is increased to 100oC for 30 minutes.

## Characterization

Silanized hydroxyapatite was characterized using Fourier Transform Infrared (FTIR) analysis to detect silanol (Si) groups that appeared after the silanization process. Then to get aesthetic perspective from each denture base specimens, optical analysis using digital photography was carried out by measuring the color of each specimen as in the Vafaee10 journal with a digital camera instrument in a series of tools as in **Figure 1** and then measuring it quantitatively using the CIE L\*a\*b\* system with the Photoshop application.

A black and white image of a rectangular object with a number

Description automatically generated

**Figure 1**. Optical Analysis Equipment

Information :

1. Dark box

2. 60 watt halogen flashlight

3. Digital cameras

# RESULT AND DISCUSSION

## Silanized Hydroxyapatite Characterization

The silanization process using 3-methacryloyloxy propyl trimethoxysilane (γ-MPS) aims to increase the compatibility between PMMA and HAp. When silane is activated in an alcohol-water medium, hydrolysis and condensation reactions occur. Activated silane turns into silanol (Si-OH). Later, the bond on the filler surface will occur through a reaction between the silanol groups on the filler surface and the hydrolyzed silane molecules. During the silanization process, several layers of silane molecules form a thin layer around the filler particles, which are chemically or physically attached to the filler particles[11].

A graph of a graph

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**Figure 2. FT-IR** spectrum of Commercial HAp and Silanized HAp

**Figure 2** above shows a comparison of the FTIR graph of commercial HAp with HAp after silanization. Where in commercial HAp, the peak of the phosphate group in hydroxyapatite is seen at a wave number of 1028 cm-1 and the peak of the hydroxyl group is at a wave number of 3570 cm-1. This phosphate group bond (PO43-) appears at the wave interval number 1000–1150 cm-1. Meanwhile, the OH- group waves will appear at 3200-3600 cm-1 waves[12]. Meanwhile, in silanized hydroxyapatite, a peak forms at a wave magnification of 1310-1710 cm-1. In the spectrum of silanized hydroxyapatite, a peak appears at wave number 1310 cm-1 which indicates SiO groups and previously did not appear in commercial hydroxyapatite before silanization which indicates the presence of a silane coupling agent. The peak at 1710 cm-1 shows a carbonyl group (C=O), and at the peak at 2996 cm-1 shows a C-C bond. This proves that the silanization process on hydroxyapatite was successful.

## Aesthetic Perspective of Denture Base Specimens

The photo was taken using a Canon 5D Mark III digital camera with a 24-70 mm macro lens with a speed setting of 60, f = 2.8, ISO = 1000 in a dark box with dimensions (80 x 40 x 40 cm). Lighting is obtained by using two 60 watt halogen lamps on the right and left sides of the box which are angled at 45o with the camera to avoid light reflection. The top box is closed and has holes only for lights and cameras to avoid the influence of light from outside.

Then the color of each specimen was measured using the CIE L\*a\*b\* system which is a 3D color space with 3 axes: L, a, and b with the Photoshop application. The advantage of the CIE L\*a\* b\* system is that color differences can be expressed in units that can be related to visual perception and clinical significance[10]. Where L\* represents (light-dark), a\* represents (red-green), and b\* represents (yellow-blue)[13].

|  |  |
| --- | --- |
| A close up of a red object  Description automatically generated |  |
| (a) | (b) |

**Figure 3.** Optical Analysis Using Photoshop Software (a) Denture Base Specimen with BRN Red Cromophtal 0.02% Organic Dye (b) Denture Base Specimen with 0.02% Cadmium Sulfoselenide Inorganic Dye

From photoshop software we get the average value of L\*a\*b\* for each variable in the denture base specimen as in Table 1 below.

**Table 1.** Average Value of L\*a\*b\* for All Denture Base Specimen variables

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Pigment** | **C (%)** | **L** | **a\*** | **b\*** |
| Cromophtal Red BRN | 0,01 | 37,67 | 47,00 | 16,00 |
| 0,02 | 36,67 | 46,67 | 16,33 |
| 0,04 | 30,33 | 46,67 | 27,67 |
| 0,06 | 29,67 | 46,00 | 30,00 |
| 0,08 | 26,33 | 44,67 | 30,00 |
| 0,10 | 26,67 | 44,00 | 29,67 |
| 0,12 | 26,33 | 44,00 | 31,00 |
| Cadmium sulfoselenida | 0,01 | 65,00 | 7,67 | -2,67 |
| 0,02 | 50,33 | 25,33 | 4,33 |
| 0,04 | 44,00 | 36,67 | 11,67 |
| 0,06 | 41,67 | 39,33 | 13,33 |
| 0,08 | 39,33 | 43,33 | 17,67 |
| 0,10 | 38,33 | 45,67 | 20,33 |
| 0,12 | 37,00 | 48,67 | 25,00 |

The higher the concentration of BRN Red Cromophtal pigment added, the lower the L\* value, this is because L\* is an indication of lightness. Where the higher the L\* value, the higher the brightness[13]. The a\* value also decreases but is not significant and starts to remain unchanged at a value of 44.00 when pigment is added with a concentration of 0.10%. This a\* value indicates red-green. Where a positive a\* value indicates red and a negative a\* value indicates green. Meanwhile, the b\* value is increasing, where the increase is quite large from 0.02% to 0.04%, after which there is only a slight increase, this is an indication of yellow-blue, where a positive b\* value indicates yellow and a negative b\* value indicates blue[14].

**Figure 4.** Graph of the average L\*a\*b\* value for the addition of BRN Red Cromophtal pigment

For the cadmium sulfoselenide variable pigment, the higher the concentration of cadmium sulfoselenide pigment added, the lower the L\* value, the a\* value increases very significantly, and the b\* value also increases significantly in each variable.

Figure 5. Graph of the average L\*a\*b\* value for the addition of Cadmium Sulfoselenide

From the results of adding pigments, both the organic BRN Red Cromophtal pigment and the inorganic cadmium sulfoselenide pigment, it can be seen that the L\* value decreases as the pigment concentration increases, this is in accordance with research by Azhar15 which states that with the addition of red pigment to dental composite materials, the brightness which is indicated by the L\* value decreasing with increasing pigment concentration while the b\* value as an indication of sample yellowness increases. When red pigment is added a red and yellow shift occurs. This shows that with the addition of red pigment, the yellow color indicated by the b\* value of the sample also increases. Meanwhile, the a\* value increases along with increasing red pigment concentration. However, for the BRN Red Cromophtal pigment type variable, the a\* value actually decreased slightly and then did not change in certain variables. This is because the BRN Red Cromophtal pigment has a strong color strength[16] therefore by increasing the minimum pigment concentration only the a\* value which is an indication of red is already high, and as the concentration increases the change in the a\* value decreases slightly and does not change any more.

The color range of healthy gingiva and alveolar mucosa has a different color range from pale pink, coral pink, red, to deep bluish purple. Where the color of the alveolar mucosa is usually darker and redder than the color of the gingiva[17] In Huang's[18] research, in Taiwan, 101 human subjects had a healthy gingival L\* value range of 30.15 - 62.69. Meanwhile, in Ho's14 research, in Asia, 120 human subjects with healthy gingiva had an a\* value range of 13.14 - 36.7. Meanwhile, the b\* value is 9.2 – 22.2. Meanwhile, for the darker alveolar mucosa, the highest a\* value is up to 47 and the highest b\* value is up to 30.

By adding pigment with the organic pigment BRN Red Cromophtal with a minimum concentration of 0.01%, it can imitate the color of healthy human aveolar mucosa and less than 0.01% to imitate the color of gingiva. Meanwhile, the addition of the inorganic pigment cadmium sulfoselenide requires a minimum pigment concentration of 0.04% to imitate the color of healthy gingiva and a greater concentration to imitate the color of aveolar mucosa.

# CONCLUSION

The results of FTIR analysis of silanized hydroxyapatite show the presence of SiO groups at a wavelength of 1310 cm-1, which indicates that the hydroxyapatite silanization process was successful. The results of optical analysis of denture base specimens show that the addition of the organic pigment BRN Red Cromophtal at a minimum concentration of 0.01% alone can imitate the darker color of aveolar mucosa. so that the use of the organic pigment Cromophtal Red BRN can prevent disturbances in mechanical properties caused by disruption of composite polymerization.

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