



## Effect of Diazonium Salt and Aluminum Oxide on Microleakage of PMMA at Co/Cr and Titanium Alloys Interface

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### Abstract

**Aim of the study:** The junction between metal alloy and acrylic resin is an area of clinical concern, failure of removable partial denture may relate to this interface. The purpose of this study was to evaluate the effect of different surface treatments (diazonium salt and aluminum oxide) on microleakage of heat cure acrylic resin at the Co/Cr and titanium alloys interface.

**Materials and method:** Sixty rectangular-shaped specimens divided into 2 main groups, 30 specimens for Co/Cr alloy and 30 specimens for titanium alloy, then subdivided into 3 groups each one consist of 10 specimens, according to the type of surface treatments. Aluminum oxide group abraded with (Al<sub>2</sub>O<sub>3</sub>) 110 μm and diazonium salt group treated based on two steps, first step (primer) and second step (adhesive). Chemical composition of diazonium salt surface treatment was analyze with (FTIR). All specimens thermocycled in artificial saliva (3000 cycles) after clear heat cured acrylic resin application, then immersed in sodium fluorescein dye solution (0.1 g/1000mL) for 24 hours at room temperature. Microleakage was assessed by counting the grids that exhibited dye penetration under ultraviolet light. Data analyzed via One-way ANOVA and LSD test.

**Results:** Microleakage test showed a significant decrease in mean value between PMMA and treated Co/Cr or titanium with diazonium salt by 1.90 and 2.00 respectively (p<0.01). Aluminum oxide surface treatment revealed decrease in the microleakage test mean value between PMMA and treated Co/Cr or titanium by 3.55 and 3.70 respectively (p<0.01). The FTIR analyze showed functional groups of diazonium salt on surfaces for both Co/Cr and titanium.

**Conclusion:** Diazonium salt surface treatments for Co/Cr and titanium alloy showed a significant improvement in bonding strength in comparison to aluminum oxide surface treatment.

**Keywords:** Co/Cr alloy, Titanium alloy, Diazonium salt, Microleakage.

## Introduction

A stable bonding between two surfaces in fabrication of dental prosthesis should exist because it is considered as a primary factor in the prevention of microleakage (1).

Partial dentures are commonly fabricated with acrylic resin and metal framework. Cobalt chromium alloy (Co/Cr) and titanium alloy are commonly used to fabricate the metal framework prosthesis because of their biocompatibility and corrosion resistance as well as desirable mechanical properties. Polymethyl methacrylate (PMMA) is an extensively used denture material for removable partial dentures because of its biocompatibility, excellent esthetic and mechanical properties (2, 3).

Removable partial denture subjected to variations in temperature during oral function; this factor may lead to microleakage (4). Microleakage is defined as the seepage of oral fluids containing bacteria and debris between a tooth and its restoration or between the materials interfaces of the prosthesis; microleakage is a key factor in determining the serviceability of prosthesis and the prevention of microleakage relied primarily on bonding efficiency between materials (1).

The bonding between the metal framework and the acrylic denture base resin plays an important role in the success of the removable partial denture prosthesis (4,5). Several methods have been tested to increase the bond strength between acrylic resin

and alloys in dental prostheses such as electrolytic etching, sand blasting, chemical bonding, silica coating, and metal primer (6).

Mechanical bonding has several types like lattice, mesh, beads, nail heads, pins, and loops that retain acrylic resin to the frame. Lattice design is particularly susceptible to permanent deformation, and the open lattice design provides optimum retention for acrylic resin. Mesh can be used in every particular clinical situation, beads or nail heads are the weakest types among acrylic retentive designs (7).

Chemical bonding is a surface chemistry modification, which is normally liquid and has bonding rapprochement to both surfaces, binds two dissimilar surfaces (8).

Aryldiazonium salts are organic compounds that have been used as a chemical bond to modify material surfaces for many applications (3). The aryl diazonium salts can be induced to provide aryl layers that can "graft onto" many different interesting surfaces with ultrasonic, chemical, or photochemical techniques, and electrochemical that can be covalently bond to a wide range of metallic surfaces. The electrochemistry of diazonium salts in an aprotic solvent medium there are no intermediates between the diazonium cation and the free radical; the free radical is formed directly on the surface, which is a very favorable situation for the grafting reaction (9). The aim of this study was

to develop a method of strong chemical bond between dental alloys and PMMA based on diazonium salt chemistry.

## Materials and method

### Co/Cr alloy and titanium alloy specimen's preparation

A metal mold designed to reproduce wax pattern in rectangular-shaped with dimension of 15 mm in length, 6 mm in width, and 1 mm thickness with a grid pattern, each grid has 3 mm in length and width for the 30 Co/Cr specimens and 30 titanium specimens. Co/Cr alloy (Adentatec, Germany) casted by using centrifugal casting technique, following the manufacturer's instructions, titanium alloy (Baoji Jinsheng, China) casted by using vacuum-pressure machine, following the manufacturer's instructions. All the surfaces of specimens ground finished using silicon carbide paper (number p60) (Trojan, China) in the grinding machine (160E, Mapao, China) under running water on 300 rpm for 10 seconds to provide uniform and flat surface (10,11) then cleaned ultrasonically for 3 minutes with deionized water and dried with air (12).

After obtaining 30 rectangular shape specimens for each Co/Cr alloy and titanium alloy, a layer of modeling wax (Shanghai, China) adapted all around the Co/Cr alloy and titanium alloy specimens except one end for dye penetration assessment (13). Both specimens Co/Cr alloy and titanium alloy flaked in standard technique for acrylic dentures with dental stone (Easy Dental, Bulgaria) (14,15), then specimens dewaxed and cleaned using boiled water (12). Before packing, the specimens of each Co/Cr and titanium

divided into 3 groups according to the surface treatment that they received (n=10 for each group).

### Surface treatment of the specimens

- Control groups: Without any surface treatment.
- Aluminum oxide groups: Abraded with alumina oxide ( $\text{Al}_2\text{O}_3$ ) 110  $\mu\text{m}$  particle size (Renfert, Germany) with an airborne particle sandblasting machine (Rotex, Turkey) at 2 bar pressure for 15 seconds with 10mm of distance that was standardized by using a specially designed holder (16) then ultrasonically cleaned (Quigg, Turkey) with deionized water for 10 minutes and dried by air (17).
- Diazonium salt group: by using Aryldiazonium salts which is done in two-stages protocol (priming and adhesive) <sup>(3)</sup>. The first stage (priming) conducted as follows: Diaminodiphenyl sulfone (Merck, Germany) (0.248.3 g) and  $\text{NaNO}_2$  (Merck, Germany) (0.07 g) were dissolved in a glass beaker containing 250 ml of 1 Molar HCl temperature of solution should be between (0-5)  $^\circ\text{C}$  <sup>(18)</sup>. The solution mixed with a magnetic stirrer for 5 minutes to produce Aryldiazonium salt, the Co/Cr and titanium specimens (each group separately) were immersed in the previous solution by using (DC) power supply (JYD Inc, China) and two-electrode cell and left to react with a magnetic stirrer for 45 min under  $0.42\pm 0.05$  Volt <sup>(19)</sup>. After that, all specimens were ultrasonication in distilled water and acetone for 5 min to remove any ungrafting matter, this first step leads to spontaneous grafting of polyaminophenylene (PAP) layer on each Co/Cr and titanium specimens. These samples referred to as

(metal-PAP). The second (adhesive) step conducted to optimize the adhesion of monomer (MMA) to (metal-PAP) samples as follows:  $\text{NaNO}_2$  (0.034 g) was dissolved in a glass beaker containing 250 ml of 1 Molar HCl (3), to further emulsify the hydrophobic monomer, sodium dodecyl sulfate (SDS) (0.026 g) and MMA applied, and then Co/Cr and titanium specimens (metal-PAP specimens) immersed in solution by using (DC) power supply and two-electrode cell, and were left to react with a magnetic stirrer for 45 min under  $0.42 \pm 0.05$  Volt <sup>(19)</sup>. All the specimens were ultrasonication in distilled water and acetone for 5 min to remove any ungrafting matter.

#### **Application of Heat Cured Acrylic Resin**

The clear heat cured acrylic resin (RODEX, Turkey) was mixed with powder: liquid ratio of 3:1 and packed by placing the flask in a hydraulic press (Rotex, Turkey), with 5 MPa pressure applied slowly (20). All the specimens were cured according to the manufacturer's instructions. The 60 specimens of all groups for each Co/Cr alloy and titanium alloy were subjected to 3,000 thermocycles between 5 °C and 50 °C with a dwell time of 1 minute in artificial saliva (21) using thermocycling system (Cooler: Beko, Turkey; Herter: Windom, China; Custom made holder) (1).

#### **Preparation of specimens for (FTIR) analysis**

Two specimens of (Co/Cr and titanium alloys) that treated with diazonium salt are selected randomly and prepared for FTIR analysis by scrapping a few amount from the surface of the specimen and mix it with potassium bromide (KBr) salt. A mini hand press used to produce disk shape

for the mixture, and then placed inside the FTIR analyzer to be analyzed (1).

#### **Preparation of specimens for microleakage test**

The thermocycled specimens immersed in sodium fluorescein dye solution (0.1 g/1000mL) for 24 hours at room temperature. Then the specimens cleaned with ultrasonic cleaner by distilled water for 20 minutes in order to remove any stain on the surface. The specimens allowed to bench dry for 24 hours to ensure that the fluorescein dye penetration ended (12). The depth of dye penetration between the heat curing acrylic resin and Co/Cr or titanium denture base materials was assessed under ultraviolet light (Escolite, China) with wavelength 395 nm and digital microscope (Dino-Lite, Taiwan) with a magnification of 8x as shown in figure (1) (7). Each square that exhibited any evidence of dye penetration was recorded as positive.

#### **Statistical Methods**

The study data analyzed via One-way ANOVA and least significant difference (LSD) test used to determine the pair differences.

## **Results**

#### **Microleakage test**

The microleakage test for all studied groups showed in figure (2), Co/Cr alloy with diazonium surface treatment group showed the lowest mean value (1.90) when compared with other studied groups. The means and standard deviations with One-way ANOVA difference tests for the microleakage test of PMMA to each Co/Cr alloy and titanium alloy presented in table (1). The lowest mean value for Co/Cr alloy groups showed for Co/Cr diazonium surface treatment (1.90) followed by Co/Cr aluminum oxide (3.55), whereas the highest mean value was related for Co/Cr control

group (4.15). LSD test used for comparisons between all microleakage studied groups, table (2).

### Fourier Transforms Infrared Spectroscopy (FTIR)

All various functional groups present are studied through FTIR analysis, the characteristic bonds of benzene ring for diazonium that bind with Co/Cr alloy are peaks at  $3127.01\text{ cm}^{-1}$ ,  $1597.73\text{ cm}^{-1}$ ,  $3283.21\text{ cm}^{-1}$ ,  $1407.78\text{ cm}^{-1}$ , and  $1254.74\text{ cm}^{-1}$ . The functional groups of monomer that entanglement the diazonium are peaks at  $1646.91\text{ cm}^{-1}$ ,  $1091.51\text{ cm}^{-1}$ , and  $2923.59\text{ cm}^{-1}$ , figure (3). The functional groups of diazonium that characterize the chemical reactions with titanium alloy are peaks at  $3118.33\text{ cm}^{-1}$ ,  $1518.67\text{ cm}^{-1}$ ,  $3238.86\text{ cm}^{-1}$ ,  $1407.78\text{ cm}^{-1}$ , and  $1261.22\text{ cm}^{-1}$ . The functional groups of monomer that entanglement the diazonium are peaks at  $1638.23\text{ cm}^{-1}$ ,  $1107.9\text{ cm}^{-1}$ , and  $2927.41\text{ cm}^{-1}$ , figure (4).

### Discussion

Removable partial dentures subjected to various temperatures during oral functions, which may lead to microleakage and make clinical difficulties. Thermocycling procedure is an important method for evaluating adhesion durability of bonding between metal alloy and acrylic resin. Several factors caused leakage like thermal contraction, materials dimensional changes due to polymerization shrinkage, mechanical stress, and water absorption. Several studies explain microleakage due to the discrepancies in coefficient of thermal expansion between framework material and resin denture base that lead to create a gap at the materials interface thus induce the microleakage extension (1,16). The good bonding is important

to increase bond strength thus lead to control and prevent the microleakage extension (23).

### Aluminum oxide surface treatment

The surface treatment with aluminum oxide particles abrasion has been recommended methods to establish an acceptable surface condition to improve bond strength, eliminate the contaminated layer, debris and/or metal oxides and increase the surface area by creating micromechanical roughness. In addition, this treatment increases the surface wettability of the material (24).

In this study, aluminum oxide group of each Co/Cr alloy and titanium alloy that treated with  $110\text{ }\mu\text{m Al}_2\text{O}_3$  exhibit lower microleakage than the specimens without surface treatment. This is maybe due to the variation of surface morphology that advances a micromechanical interlocking sites as well as greater wettability, which allows the heat cured acrylic resin be mechanically joined and increase the mechanical bonding. The non-significant difference between Co/Cr aluminum oxide surface treatment group and Co/Cr alloy control group may be due to the used of silicon carbide p60 during the grinder polisher procedure that made the surface of Co/Cr alloy control group rough and nearly similar to the Co/Cr aluminum oxide group that treated with  $\text{Al}_2\text{O}_3$  ( $110\mu\text{m}$ ). In comparison to the titanium alloy control group, the aluminum oxide surface treatment group shows a highly significant difference, sandblasting with aluminum oxide particles removed the superficial oxide layer and cleaned the surface of titanium alloy.

### Diazonium salt surface treatment

Diazonium salts can graft easily by covalent bonding on the metal surface (25). The diazonium chemistry used to bind PMMA with (Co/Cr alloy and titanium alloy) strongly. The chemical

mechanism began in the first step when the amino one ends  $\text{NH}_2$  ( $\sim \text{C}_6\text{H}_4\text{-NH}_2$ ) of diaminodiphenyl sulfone transformed into diazonium cation ( $\sim \text{C}_6\text{H}_4\text{-N}_2^+$ ) by adding  $\text{NaNO}_2$ , the electrochemical reduction will reduce the diazonium cation into benzene ring free radical ( $\sim \text{C}_6\text{H}_4 \bullet$ ) and grafted on the surface of each (Co/Cr alloy and titanium alloy) specimen and then forming (PAP) layer. The second step was designed to change the second end of amino  $\text{NH}_2$  of diaminodiphenyl sulfone the same as in the first step into diazonium cation ( $\sim \text{C}_6\text{H}_4\text{-N}_2^+$ ) and then into ( $\sim \text{C}_6\text{H}_4 \bullet$ ). The free radical of carbon benzene ring ( $\sim \text{C}_6\text{H}_4 \bullet$ ) will react with double bond ( $\text{C}=\text{C}$ ) of monomer, (SDS) disperse the monomer in the aqueous reaction solution by forming micelles around the monomer droplets, the polymerization of monomer leads to the formation of an adhesive layer (26,27).

The non-significant difference that is shown between Co/Cr alloy and titanium alloy diazonium salt group could be explained due to diazonium salt grafted in the same manner on the different metal substrates by a covalent bond that formed between diazonium layers Polyaminophenylene (PAP) and metal substrate, also diazonium salt is capable to increase the wettability of metal substrate (3).

## Conclusion

Within the limitations of this study, diazonium salt surface treatments decreased the microleakage level for both Co/Cr and titanium alloys. However, aluminum oxide surface treatment showed lower reduction in the microleakage level when compared with diazonium salt surface treatment for both Co/Cr and titanium alloy.

## Conflicts of Interest

The authors reported that they have no conflicts of interest.

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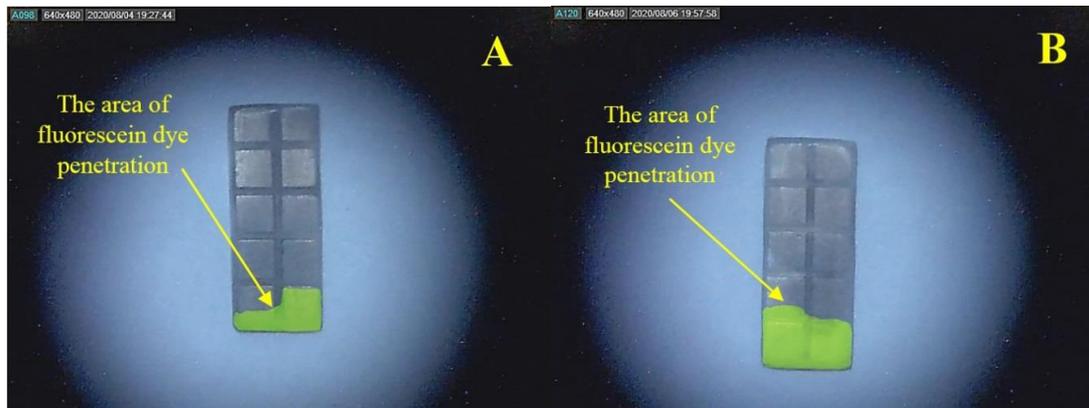


Figure 1. Microleakage specimens under the digital microscope with a magnification of 8x.

(A): Co/Cr specimen. (B): Titanium specimen.

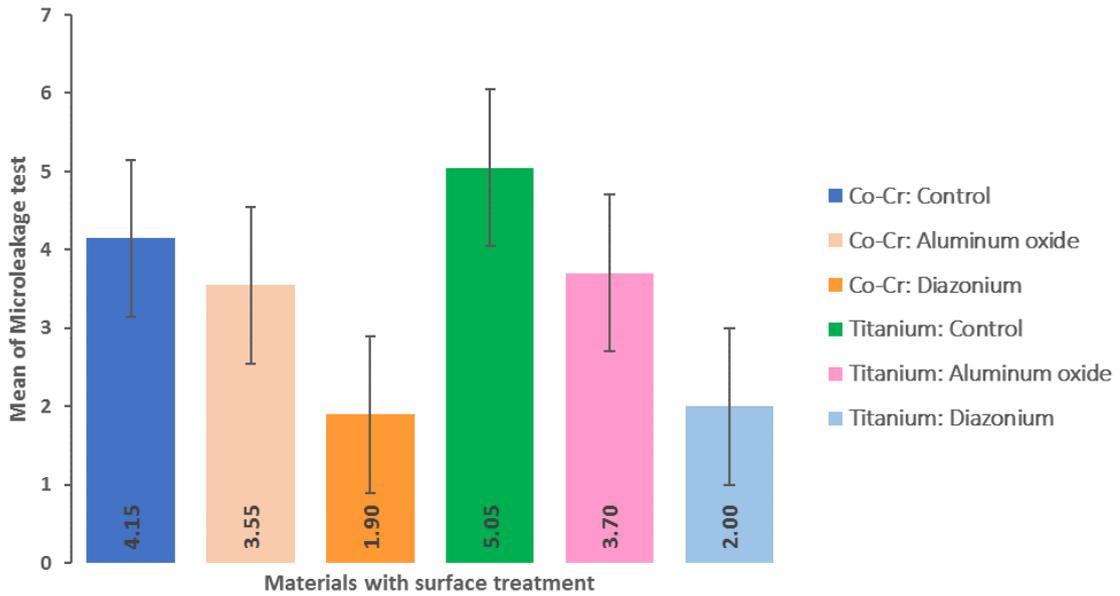


Figure 2. Bar chart for microleakage test.

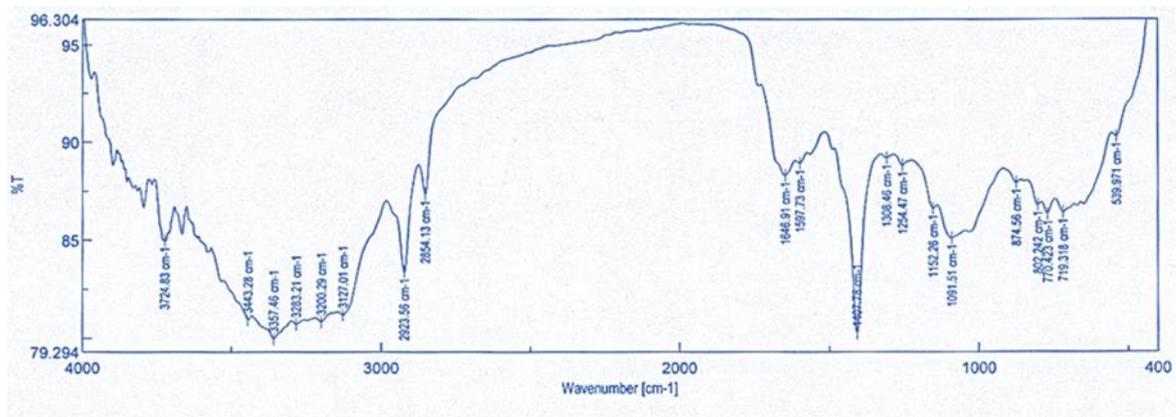


Figure 3. FTIR spectrum of diazonium salt treated Co/Cr alloy.

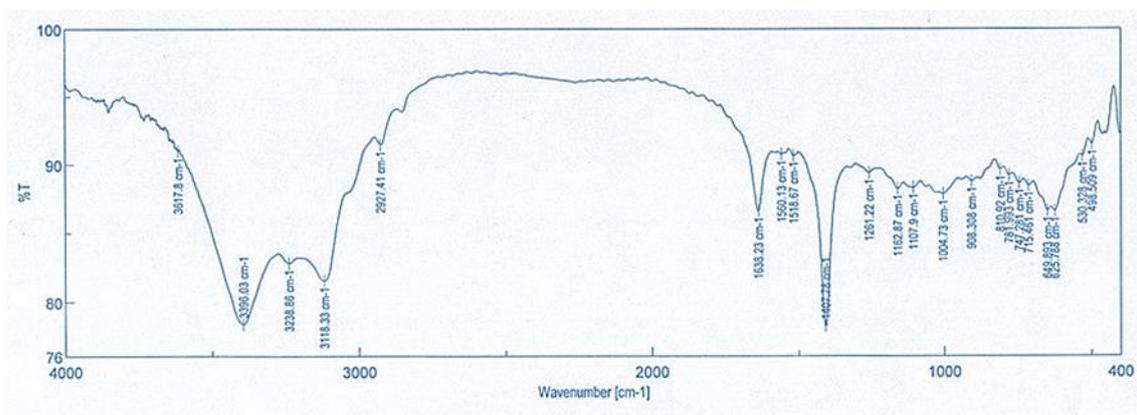


Figure 4. FTIR spectrum of diazonium salt treated titanium alloy.

Table 1. Descriptive analysis statistics with Levene's and one-way ANOVA tests for microleakage

Groups	No.	Materials		ANOVA Difference rest	
		Co/Cr alloy	Titanium alloy	Levene`s Test	F-test
		Mean value $\pm$ SD	Mean value $\pm$ SD		
Control	10	4.15 $\pm$ 1.23	5.05 $\pm$ 1.21	p=0.095 (NS*)	p=0.000 (HS**)
Aluminum oxide	10	3.55 $\pm$ 1.34	3.70 $\pm$ 1.27		
Diazonium salt	10	1.90 $\pm$ 0.78	2.00 $\pm$ 0.75		

\* NS: Non-Sig. at P>0.05  
\*\* HS: Highly Sig. at p<0.01

Table 2. Least Significant Difference (LSD) test of all studied groups for microleakage

Groups	Co/Cr control	Co/Cr aluminum oxide	Co/Cr Diazonium salt	Titanium control	Titanium aluminum oxide	Titanium Diazonium salt
Co/Cr control	-	*NS	**HS	NS	NS	HS
Co/Cr aluminum oxide	-	-	HS	HS	NS	HS
Co/Cr diazonium salt	-	-	-	HS	HS	NS
Titanium control	-	-	-	-	HS	HS
Titanium aluminum oxide	-	-	-	-	-	HS
Titanium diazonium salt	-	-	-	-	-	-

\* NS: Non-Sig. at P>0.05  
\*\* HS: Highly Sig. at p<0.01