

RESEARCH ARTICLE

The effect of TiO₂ coating and coffee immersion on discoloration of thermoplastic nylon denture base

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ABSTRACT

The thermoplastic nylon denture base material is prone to discoloration because its amide bonds absorb water easily. Titanium dioxide (TiO₂) nanoparticle have long been used as a denture base coating. Meanwhile, coffee contains chlorogenic and tannic acid, which can change the color of denture bases. The purpose of this study was to examine the effect of TiO₂ coating and duration of coffee immersion on discoloration of thermoplastic nylon denture base. Samples consisted of 24 thermoplastic nylon in square-shaped (30 x 30 x 2 mm), divided into 4 groups (n = 6). They were control (without TiO₂ coating) and treatment (with TiO₂ coating) groups, which then were immersed in coffee solution for 15 and 30 days. Discoloration test was conducted using spectrophotometer by measuring the delta absorbance of light before and after coffee immersion. The result showed that the lowest delta absorbance was in the 15-day treatment group (0.011 ± 0.005) and the highest was in the 30-day control group (0.077 ± 0.027). Two-way ANOVA test showed that TiO₂ coating and coffee immersion had an effect on discoloration of thermoplastic nylon (p < 0.05). Post hoc LSD test showed that there were significant differences between the control and treatment group at 15 and 30 days of coffee immersion (p < 0.05). In conclusion, TiO₂ as a thermoplastic nylon denture base coating can reduce discoloration by coffee immersion for 15 and 30 days. There were no differences between 15 and 30 days of coffee immersion on thermoplastic nylon's discoloration in the control and treatment groups.

Keywords: coffee immersion; discoloration; spectrophotometer; thermoplastic nylon; titanium dioxide (TiO₂) coating

INTRODUCTION

The denture base is a part of a denture that has a contact with oral mucosa, supports the artificial teeth, distributes occlusal pressure to the supporting tissue, and gives retention and stability to the denture.¹ An ideal denture base is determined based on several criteria, such as biocompatibility in the oral cavity, aesthetics, bonding with artificial teeth, radiopaque, ease of repair, and good physical and mechanical properties.² Thermoplastic nylon material had been introduced as a denture base material since the 1950s for hard or soft tissue undercut cases, repeated fracture of acrylic denture, patient aesthetic issue, and acrylic allergies.³

Thermoplastic nylon is produced by condensation polymerization reaction between hexamethyl diamine NH₂-(CH₂)₆-NH₂ and dibasic

acid COOH-(CH₂)₄-COOH, which produces linear polymer chain NH₂-(CH₂)₆-NH-CO-(CH₂)₄-COOH and residual products in the form of water condensation.⁴ The weakness of thermoplastic nylon is amide (-NH₂) and chromophores (C = O) groups, which easily absorb water and stain, thus susceptible to discoloration and the surface becomes rough.^{5,6} The higher the concentration of amide groups, the greater the absorption of water and discoloration.⁷

Discoloration of denture base material occurs due to intrinsic and extrinsic factors.⁸ Intrinsic factors are caused by changes in physics and chemical conditions of aging polymer matrix. Extrinsic factors occur due to absorption and adsorption of water around the material through water diffusion mechanism. Other factors influencing discoloration

are staining, dehydration, surface roughness, oxidation, and water absorption.⁸

Several drinks such as coffee, tea, soft drinks, yoghurt, and red wine change the color of denture base.^{9,10} Coffee changes the color of denture base due to its chlorogenic acid, which releases H⁺ ions that disrupt the bonding chain of thermoplastic nylon.¹¹ Coffee also contains tannic acid, which gives yellowish brown stain.¹² The duration of coffee immersion also affects the amount of water diffusion so that the longer the thermoplastic nylon is immersed, the more water will be absorbed. Moreover, the more water that is absorbed, the greater the discoloration that occurs.¹³

Several methods have been applied to prevent discoloration and water absorption such as denture base coatings with titanium dioxide nanoparticles.¹⁴ Titanium dioxide (TiO₂) nanoparticles are chemically and physically stable, safe as additives in food and cosmetics,¹⁵ nontoxic, inert, antibacterial,¹⁶ antifungal,¹⁷ and able to inhibit plaque formation.¹⁸ The TiO₂ nanoparticles coating with 5% concentration do not change the brightness of the denture base color¹⁴ and can increase flexural strength.¹⁹

To evaluate the discoloration of thermoplastic nylon after coffee immersion, a spectrophotometer is used to measure the light absorbed by thermoplastic nylon before and after the immersion, which is based on the light and dark measurement. This study aims to investigate the effect of titanium dioxide (TiO₂) nanoparticles coating and the duration of coffee immersion on the color changes of thermoplastic nylon denture base.

MATERIALS AND METHODS

This study was an experimental laboratory using 24 subjects in the form of square-shaped thermoplastic nylon samples (30 x 30 x 2 mm). Twenty four samples were divided into 4 groups (n = 6): the control (without TiO₂ coating) and treatment (with TiO₂ coating) group, which were immersed in robusta coffee for 15 and 30 days. Materials that were used in this study were thermoplastic nylon (Valplast, USA), TiO₂ nanoparticles sized 25 nm

(Sigma-Aldrich, Germany), silane (Monobond, Ivoclar, Netherland), robusta coffee (Singa Brand, Indonesia), and ethanol as TiO₂ solvents. The tools used in this study were digital scales and measuring cups, nirbaken, microwave oven, staining jar as coffee immersion containers, and UV Vis spectrophotometer (Pharmaspec 1700, Shimadzu, Japan) to measure the discoloration based on the absorbance of light.

The coating method that was used was dip-coating. The treatment group was given a pre-treatment with silane (Monobond, Ivoclar) using a micro brush on the entire surface, then it was allowed to dry. Subsequently, it was immersed in coating solution that contained 5% of TiO₂ nanoparticles (5 grams TiO₂ in 100 ml ethanol) for 5 seconds and dried in an oven (Panasonic, Japan – 220 V / 50 Hz) at 70 °C for 10 minutes. After control and treatment groups were ready (Figure 1), the initial color measurement was performed using spectrophotometer before coffee immersion.



Figure 1. The color of all thermoplastic nylon sample before coffee immersion



Figure 2. The coffee immersion of control and treatment group in the staining jar for 15 and 30 days

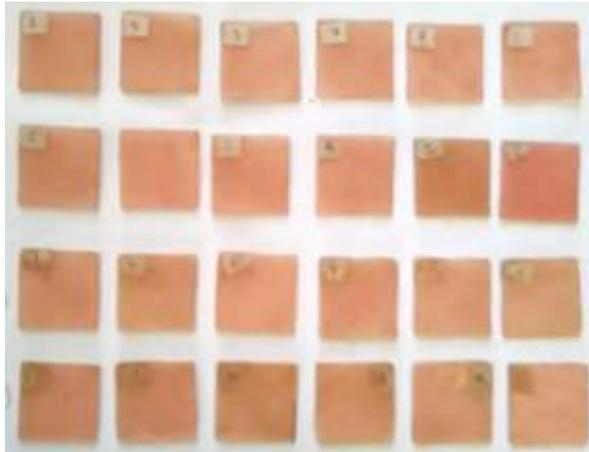


Figure 3. The color of all thermoplastic nylon sample after coffee immersion

All samples were immersed in robusta coffee (6 grams of coffee powder in 180 ml of water) using a staining jar so that the entire surface of the sample was exposed to the coffee. Immersion was carried out for 15 and 30 days. The coffee solution then was changed every day (Figure 2).

After the coffee immersion was complete, (Figure 3) the final color measurement was performed using a spectrophotometer. Statistical analysis was performed using two-way ANOVA test with 95% significance level followed by LSD post hoc test. This research has been reviewed and approved by the Ethical Committee of the Faculty of Dentistry with Ethical Clearance Letter No. 001526/KKEP/FKG-UGM/EC/2018.

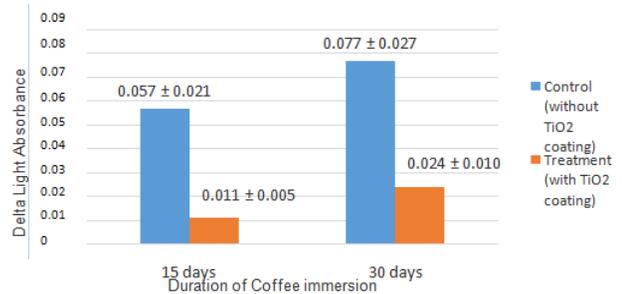


Figure 4. The diagram of means and standard deviation of delta light absorbance of control and treatment groups before and after coffee immersion for 15 and 30 days

RESULTS

The means and standard deviation of delta light absorbance of thermoplastic nylon before and after coffee immersion were shown in Table 1, the data were also presented in the form of bar diagrams in Figure 4. As presented at Table 1 and Figure 4, the treatment group with TiO₂ coating showed a smaller delta light absorbance than the control group. It implies that the treatment group had fewer discoloration than control group.

Shapiro-Wilk normality test results showed that the data in each group had a normal distribution ($p > 0.05$). The homogeneity test results using Levene's test also exhibited the value that all population variances were the same ($p > 0.05$). Two-way ANOVA test was performed to compare the mean difference between group of TiO₂ coating

Table 1. The means and standard deviation (sd) of delta light absorbance of control and treatment groups before and after coffee immersion for 15 and 30 days

Groups	Duration of coffee immersion (mean ± sd)	
	15 days	30 days
Control (without TiO ₂ coating)	0.057 ± 0.021	0.077 ± 0.027
Treatment (with TiO ₂ coating)	0.011 ± 0.005	0.024 ± 0.010

Table 2. The two-way ANOVA results of the effect of TiO₂ coating and duration of coffee immersion on the discoloration of thermoplastic nylon

Variabel	F	p value
TiO ₂ coating	45.204	0.000
Duration of coffee immersion	4.854	0.039
TiO ₂ coating * duration of coffee immersion	0.264	0.613

*: significant difference if $p < 0.05$

Table 3. Post hoc LSD test for each group

Groups	Control, 15 days	Control, 30 days	Treatment, 15 days	Treatment, 30 days
Control, 15 days	-	-.0198333	.0453333*	.0330000*
Control, 30 days	.0198333	-	.0651667*	.0528333*
Treatment, 15 days	-.0453333*	-.0651667*	-	-.0123333
Treatment, 30 days	-.0330000*	-.0528333*	.0123333	-

*: The mean difference is significant at the 0.05 level

nanoparticles and the duration of coffee immersion on the color change of thermoplastic nylon denture base (Table 2).

The results of the two-way ANOVA test showed a significant effect of TiO₂ coating on thermoplastic nylon discoloration ($p < 0.05$). Moreover, it exhibited a significant effect of the duration of coffee immersion on thermoplastic nylon discoloration ($p < 0.05$). There was no interaction between TiO₂ coating and duration of coffee immersion to thermoplastic nylon discoloration ($p > 0.05$).

The results of the post hoc LSD test of the treatment group immersed in 15 days of coffee (treatment, 15 days) exhibited a significant difference compared to the whole control group ($p < 0.05$) (Table 3). The control group without TiO₂ coating which was immersed in coffee for 30 days showed the highest delta light absorbance compared to all groups with a value of 0.077 ± 0.027 . Post hoc LSD test in Table 3 also exhibited significant differences compared to all treatment groups ($p < 0.05$). However, there were no significant differences between treatment groups immersed in coffee for 15 and 30 days ($p > 0.05$). There were no significant differences between the

control group immersed in coffee for 15 and 30 days ($p > 0.05$).

Test investigation of thermoplastic nylon surface using a light microscope (Leica, DM 500) with 100 times magnification showed that the TiO₂ coating group had a smoother surface than the control group because of the covering of TiO₂ nanoparticles on the surface of porous microstructure (Figure 5). The color surface examination using a digital microscope (Dino-Lite, 20 times magnification) also showed the effect of coffee immersion in the control group whose surface became darker than that of the treatment group (Figure 6).

DISCUSSION

The result of this study indicated that TiO₂ coating on the thermoplastic nylon is effective to reduce discoloration due to coffee immersion for 15 days. Coffee immersion for 15 days is equivalent to exposure of coffee consumption for 2 years. These results imply that the TiO₂ coating is effective to prevent discoloration for 2 years due to coffee exposure.

TiO₂ nanoparticles coating will make a thin layer that covers the porous microstructure, which

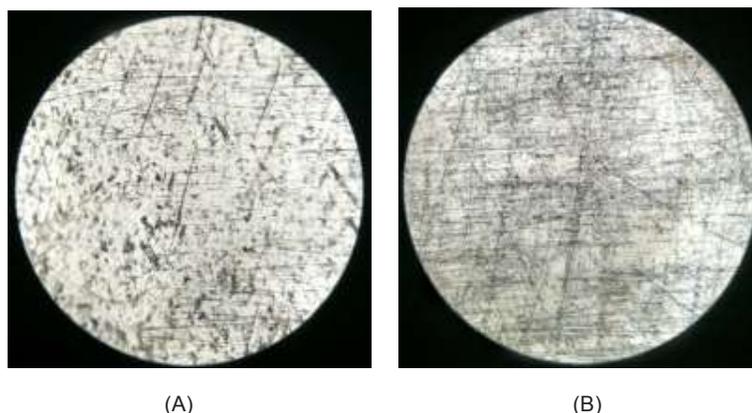


Figure 5. Description of thermoplastic nylon surface using a light microscope (Leica, DM 500) 100 times magnification, (A) Control group without TiO₂ coating, (B) Treatment group with TiO₂ coating

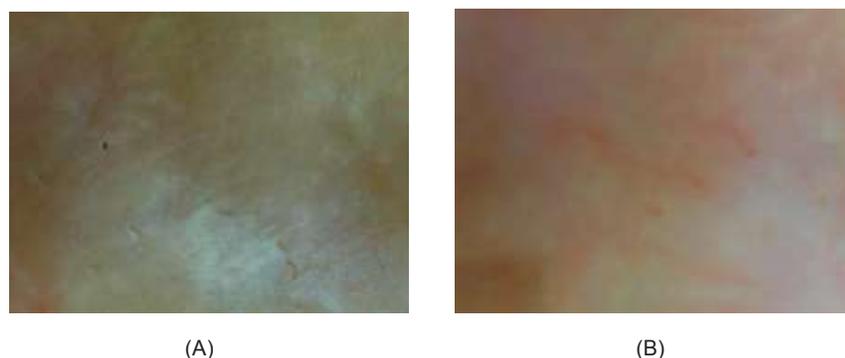


Figure 6. The color of thermoplastic nylon surface after coffee immersion (digital microscope, Dino-Lite, 20 times magnifying) (A) Control group, (B) Treatment group

inhibits water and stain absorption. Zuo et al.²⁰ stated that coatings with organic and inorganic materials reduce absorption and solubility of water. Feng's study showed that the coating process close the porous microstructure formed after polymerization.²¹ Closure of porous microstructure prevents absorption of water into the matrix of thermoplastic nylon to maintain color stability. Grumezescu stated that the layer formed on the thermoplastic nylon surface is due to the very small size of nanoparticles (<100 nm) that could enter through a micro gap.²² The layer formed is very thin with the thickness only about 1 - 1000 nm, which is stable against dimensional change.²³

The high difference in light absorbance showed that the control group became darker, thus it absorbed lighter than the treatment group. It occurred because the amide -NH group absorbed more water and coffee stain without any protection layer. The ability of coffee to change the color of the thermoplastic nylon is due to its chlorogenic acid, which disrupts the thermoplastic nylon bond chain, thus making it easier for the diffusion process of water molecules. Amaliyah et al.¹¹ stated that chlorogenic acid disrupts the thermoplastic nylon bond chain by releasing H⁺ ions that break the linear bond of thermoplastic nylon so that the deformation occurs. Coffee has tannic acid, which gives brownish yellow stain on the material attached. Guler et al.¹² stated that tannic acid in coffee provides yellowish stain on composite resin polymers. The two-active substances in coffee which are chlorogenic acid and tannic acid contribute to alter the color of

thermoplastic nylon by damaging chemical bonds and giving brownish yellow stain.

The results showed no significant difference between the control groups immersed in coffee for 15 and 30 days. It can be explained that the absorption of coffee solution by the thermoplastic nylon reaches its maximum point at 15 days as a result the absorption of coffee solution is no longer significant after 15 days. This result is in accordance with Navarro et al.²⁴ study, which stated that there were no significant differences between acrylic and thermoplastic nylon denture base immersed in coffee for 15 and 30 days.

CONCLUSION

Titanium dioxide (TiO₂) nanoparticles as a coating material on thermoplastic nylon denture base prevent discoloration due to coffee immersion for 15 and 30 days. There were no differences between 15 and 30 days of coffee immersion on thermoplastic nylon discoloration in the control and treatment groups.

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