

Effect of Surface Treatment Methods on Shear Bond Strength between Polyamide and PMMA Denture Base Resins

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Abstract

This study aimed to evaluate the effect of surface treatment on shear bond strength (SBS) between polyamide and denture base resin.

Polyamide surfaces were treated with 6 methods including (1) no treatment (control), (2) air abrasion with aluminum oxide 110 microns, (3) application of 5% acetic acid in ethanol, (4) application of 4-META resin, (5) air abrasion followed by acetic acid and (6) air abrasion followed by 4-META resin prior to bonding with autopolymerizing polymethylmethacrylate (PMMA) resin. All specimens were immersed in 37 °C for one week before being divided into 2 groups: non-thermocycling and thermocycling at 10,000 cycles. Both groups were tested SBS and specified failure mode. Furthermore, the polyamide surfaces after each treatment method were evaluated for surface roughness, surface morphology, and functional groups.

The SBS data were statistically analyzed using two-way ANOVA and Tukey HSD ($P < 0.05$) while surface roughness data were statistically analyzed using one-way ANOVA and Dunnett T3 ($P < 0.05$). Air abrasion followed by 4-META resin yielded the highest SBS in both thermocycling and non-thermocycling groups and had the highest surface roughness. The SBS from applying acetic acid or 4-META resin was not significantly different from the control. Within the limitation of the study, polyamide surface treated with air abrasion followed by 4-META resin is the most effective method to improve SBS to denture base resins.

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Introduction

Polyamide is a thermoplastic resin that has been introduced in dentistry since 1956 as a material for removable partial dentures.¹ Compare with conventional PMMA resin, polyamide has lower modulus of elasticity and surface hardness which may compromise wear resistance of the polyamide denture.^{2,3} However, the high flexibility of the polyamide makes the polyamide denture easy to place and able to use with deep undercuts.⁴

Metal clasps of removable partial dentures are often replaced with polyamide clasps which provide better esthetics and eliminate metal or monomer allergy problems.⁵ However, the high crystallization property of

polyamide makes it unable to bond with acrylic resin, resulting in the difficulty to relines and repair with acrylic resin at the chair side.⁶

Recent research has used several methods to improve the bond strength between polyamide and acrylic resin by treating material surfaces. The methods can be categorized into 3 groups: mechanical, chemical, and mechanochemical approaches.

Mechanical treatments include making holes⁷ and air abrasion with aluminum oxide particles varying in sizes, pressure, and time to increase the surface bonding area.^{5,8,9,10,11} Chemical treatments involve employing chemical solvents such as methyl methacrylate monomer, ethyl acetate, dichloromethane^{5,8,9} and 5% Acetic acid in ethanol¹², as well as using functional monomer 4-methacryloyloxyethyl trimellitate anhydride (4-META) which is the component of the 4-methacryloyloxyethyl trimellitate anhydride/methyl methacrylate-tri-n-butylborane (4-META/MMA-TBB) adhesive resin^{5,8,9}, ultraviolet light¹⁰, and non-thermal plasma¹³. The last method, concerning mechanochemical

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treatment, is the tribochemical-silica coating system which involve changing the surface property by using silica-modified aluminum oxide particles to create a rough surface and silicon oxide layer before applying silane to form chemical bonding between silica and resin.^{5,8,11,12}

Tribochemical-silica coating system was proved to effectively increase the bond strength between polyamide and autopolymerizing resin.^{5,8,12} Furthermore, this coating followed by the application of 4-META resin created even higher bond strength.^{5,8} However, the simple method without special equipment is more suitable for chair-side repair.

To date, there is still no conclusion on which the most effective method to improve bond strength is. This study aimed to examine the effect of different polyamide surface treatment methods on shear bond strength to autopolymerizing resin. The null hypothesis was that various surface treatment methods had no effect on SBS between polyamide and autopolymerizing resins.

Materials and methods

Specimen preparation

A total of 162 polyamide (Valplast®, Valplast International Corp., New York, NY, USA) block specimens (10x10x3mm) were prepared by an injection-molding technique according to the manufacturer's instruction and embedded in an autopolymerizing resin with metal ring. After being grounded with 100-,400-, and 600-grit silicon carbide paper under running water (Grinding Machine, MoPao 160E, MEGA Advance Co., Ltd, China) and ultrasonically cleaned for 15 minutes (Ultrasonic cleaning unit, Easyclean, Rernfert, Hilzingen, Germany), the specimens were stored in distilled water at 37°C for 1 week.

Table 1 shows the materials, manufacturer details, lot numbers, and chemical composition of the materials used in this study.

Measurement of shear bond strength

The bonding area of 120 specimens was defined by an adhesive tape with a 6-mm diameter hole. Surface treatments were performed in which the treatments were categorized into 6 groups (n=10);

Group C: No treatment (control)

Group S: Air abrasion with 110 Aluminum oxide (0.28 MPa 15s distance 10 mm)

Group A: Application of 5% acetic acid in ethanol (30/70, v/v)

Group M: Application of 4-META resin (Super-Bond C&B, Sun Medical, Moriyama, Japan)

Group SA: Air abrasion with 110 Aluminum oxide followed by application of 5% acetic acid in ethanol (30/70, v/v)

Group SM: Air abrasion with 110 Aluminum oxide followed by application of 4-META resin

In groups S, SA and SM, the specimens were ultrasonically cleaned after air abrasion and then blow-dried for 1 minute. Subsequently, acetic acid and 4-META resin were applied in groups SA and SM respectively. The layers of 4-META resin in groups M and SM were created by using the sprinkle-on technique.

Materials, Manufacturer and Lot no.	Composition
Polyamide (Valplast®, Valplast International Corp., New York, NY, USA) Lot No. 16957171230	Poly(lauro lactam), Colorant
Clear autopolymerizing resin (Ortho-jet™ Acrylic resin, Lang, Wheeling, Illinois, USA) Lot No. 1380-18AP	Powder: Methyl Methacrylate (MMA) polymer, Benzoyl Peroxide Liquid: MMA, N, N-Dimethyl-p-Toluidine
Autopolymerizing resin (Unifast™ Trad No.3 Pink, GC, Tokyo, Japan) Lot no. 1701172 (powder) and 1802011 (liquid)	Powder: Dibenzoyl peroxide, Iron(III) oxide Liquid : MMA, Accelerant, UV-light absorber, Dimethacrylate
Resin cement (Super-Bond C&B, Sun Medical, Moriyama, Japan) Lot No. SG15 (powder), SV2 (monomer) and SV11 (catalyst)	Powder: L-Type Clear MMA polymer Monomer: MMA, 4-methacryloyloxyethyl trimellitate anhydride (4-META) Catalyst V: Tri-n-butylborane (TBB) Hydrocarbon
Aluminum oxide 110 micron (Korox®110 Corundum Blasting Material, BEGO, Bremen, Germany)	Aluminum oxide

Table 1. Materials used in the study.

The polymethylmethacrylate (PMMA) autopolymerizing resin (Unifast III live pink, GC, Tokyo, Japan) was filled in a plastic tube mold before being left at room temperature for 24 hours and stored in distilled water at 37°C for 1 week. Thereafter, the shear bond test was performed using Universal testing machine (Instron® 5566; Instron Limited, Massachusetts, U.S.A) at a crosshead speed of 0.5 mm/minute. The exact process was carried out with the thermocycling group which was subjected to 10,000 thermal cycles (Thermocycling HWB332R CWB332R TC301, King Mongkut's Institute of Technology Ladkrabang, Thailand) at 5 °C and 55 °C with a 1-minute dwell time before SBS test. The debonded surfaces were then inspected under a stereomicroscope (SZX7 & SZ2-ILST led illuminator stand & E-330, Olympus, Tokyo, Japan) at 20x magnification. Failure modes were classified as adhesive, cohesive, and mixed failure.

Effect of surface treatment methods

To evaluate the effect of each treatment method on polyamide surface before bonding to PMMA resin, specimens were investigated as follows.

1) Surface roughness (n=4)

Profilometer (Profilometer, Mitutoyo-SurfTest SJ-410, Nfg Co, Ltd., Ninato-Ku. Tokyo, Japan) with a stylus diameter of 5 microns at a speed of 0.5 mm/s travelling 8 mm in 3 directions -- vertical, horizontal and transverse -- was used to measure surface roughness after the process of surface treatments. The data on mean surface roughness in each group were collected and statistically analyzed.

2) Surface morphology (n=2)

After being spattered with gold (Gold coater, SPI-MODULE Sputter Coater, SPI, Wester Chester, PA, US), specimens were evaluated the surface morphology by using Scanning electron microscopy (SEM, JSM-5910LV, JEOL, Tokyo, Japan) at a magnification of 200x at 15kV.

3) Functional groups (n=1)

Fourier transforms infrared spectrometer (FTIR spectrometer, Bruker Tensor 27, Massachusetts, U.S.A.) was used to detect the functional groups formed on polyamide surfaces within electromagnetic wavelength at 400-4,000 cm^{-1} . The graph shows a relation between the intensity of transmitted infrared and wave number.

Statistical Analysis

Statistical analysis was performed using SPSS software (version 23). The SBS data were analyzed using two-way ANOVA and Tukey HSD while the mean surface roughness data were analyzed using one-way ANOVA and Dunnett T3. For all analyses, $P < 0.05$ was considered statistically significant.

Results

In non-thermocycling groups, the shear bond strength of groups C, A, and M was not significantly different from the control. Nevertheless, the shear bond strength of groups S, SA, and SM increased dramatically, with the SM group revealing the highest value at 9.65 MPa. In thermocycling groups, specimens in groups C, A, and M could not complete the 10,000 thermocycling process. According to the two-way ANOVA analysis, bond strength values after the thermocycling decreased considerably

in all groups. Similar to the above result, group SM yielded the highest bond strength at 7.99 MPa. However, groups S and SA were not statistically different. All specimens in both thermocycling and non-thermocycling groups were classified as an adhesive failure mode. Figure 1 shows the mean SBS of all groups.

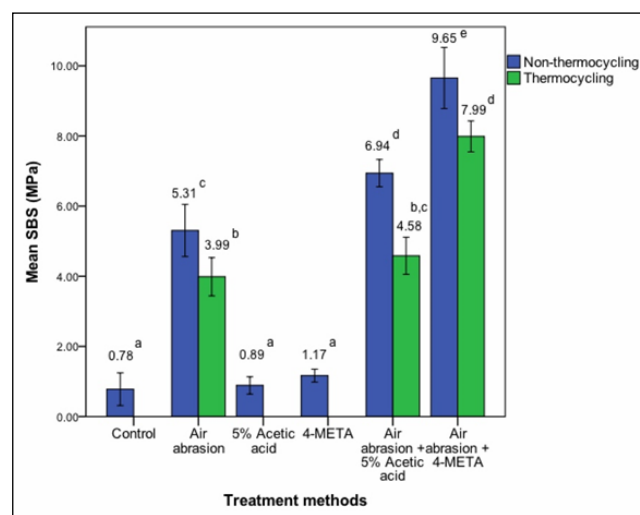


Figure 1. Graph showed mean SBS in each treatment groups. The value with identical alphabet indicated no statistically significant differences at $p=0.05$.

According to one-way ANOVA analysis and Dunnett T3 post hoc, group SM demonstrated the highest surface roughness at 4.44 microns. No statistical differences were found among groups SM, M, S, and SA while group A was not statistically different from the control. Figure 2 presents the mean surface roughness of all groups.

FTIR graphs, as shown in Figure 3, illustrate similar patterns of groups C and A, S and SA, and M and SM. Groups C and A had a strong broad peak at 3,000 – 3,500 cm^{-1} indicating O-H stretching. A strong peak at 1,650 cm^{-1} referred to C=O stretching band and N-H bending at 1,540 cm^{-1} . On the contrary, groups S and SA found a weak broad peak of O-H stretching at 3,200 cm^{-1} and C-H bending at 2,840 and 2,916 cm^{-1} . Groups M and SM had nearly identical graphs which showed a strong peak at 1,730-1,715 cm^{-1} introducing C=O stretching vibration of the carboxylic group. Furthermore, a broad peak at 2,840-3,000 cm^{-1} and a strong peak at 1,144 cm^{-1} indicated C-H and C-O stretching respectively.

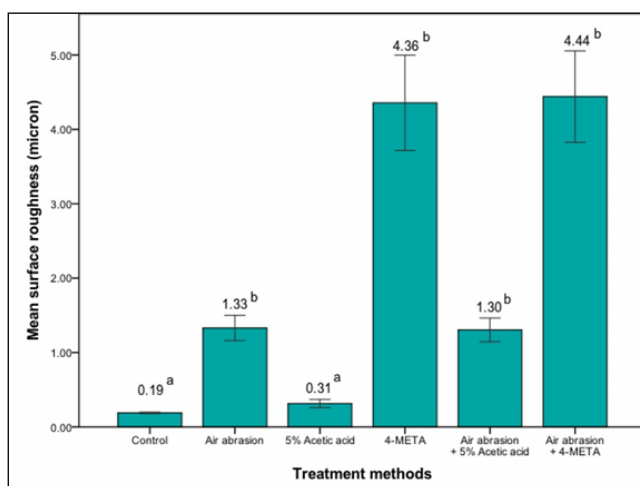


Figure 2. Graph showed mean surface roughness in each treatment groups. The value with identical alphabet indicated no statistically significant differences at $p=0.05$.

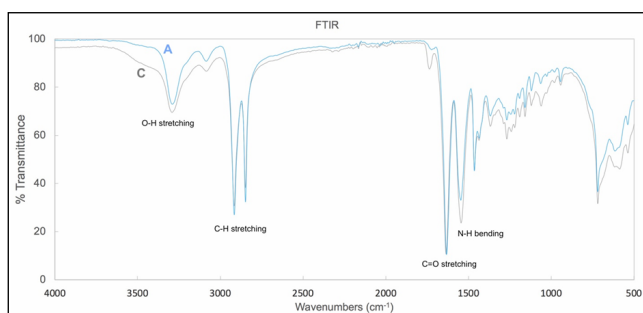


Figure 3. (a) Control and 5% Acetic acid

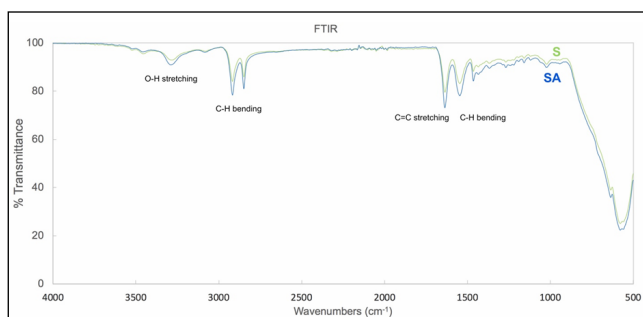


Figure 3. (b) Air abrasion and air abrasion followed by 5% Acetic acid.

Discussion

Based on the results, the hypothesis that surface treatments had no effect on shear bond strength values between polyamide and PMMA resin was rejected. Groups S, SA, and SM had significantly increased SBS and surface roughness when compared to groups A, M and the control. It demonstrated that mechanical

treatment was necessary as part of surface modification approaches and that chemical treatment alone had minimal impact on SBS values. The SBS values increased when applying chemicals after mechanical treatment. The 4-META resin showed better outcome on SBS values than acetic acid since the polyamide treated with air abrasion and 4-META resin afterwards revealed the highest SBS values and the highest surface roughness in both non-thermocycling and thermocycling groups compared to the other treatment methods.

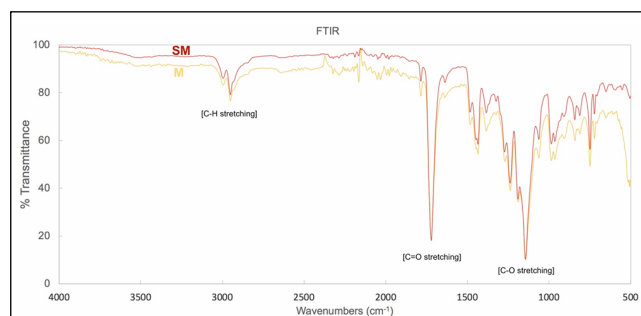


Figure 3. (c) 4-META and air abrasion followed by 4-META.

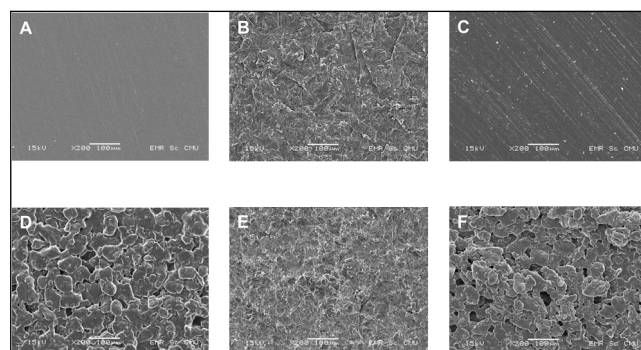


Figure 4. Scanning electron microscope image at 200x magnification of surface-treated polyamide before bonding with PMMA resin. (A) No treatment (B) Air abrasion with 110 micron (C) 5% Acetic acid in ethanol (D) 4-META (E) Air abrasion followed by 5% Acetic acid (F) Air abrasion followed by 4-META.

The adhesion of resin to substrate depends on both micromechanical interlocking and physiochemical bonding.¹¹ Especially when bonding to thermoplastic resin, a mechanical bond is necessary to achieve high bond strength.¹⁴ Air abrasion with aluminum oxide is one of the most effective approaches for micromechanical interlocking and is widely used for surface treatment in dentistry.¹⁵ Air abrasion

parameters including particle size, time, pressure, distance from nozzle and incidence angle have been studied for their effects on bond strength on various surfaces.^{16,17,18} Each material also requires different parameters for optimum outcome. Due to the limited studies of polyamide denture base resin, air abrasion protocol has still not been reported. Previous studies had used aluminum oxide 30 and 50 microns at a pressure range from 0.25 - 0.48 MPa at 10 or 15 seconds.^{5,8,10,11,12} The use of aluminum oxide 110 microns which was expected to increase surface roughness revealed a surface roughness of 1.33 microns. This contradicted previous studies tested under the same conditions that reported surface roughness of 0.53 and 0.27 microns from aluminum 30 and 50 microns, respectively.^{10,11} The sharp edge pattern of roughened surface was clearly seen in the SEM image.

In this study, only the groups with air abrasion as part of the surface treatment completed the thermocycling and achieved significantly higher SBS values and surface roughness than the control and chemically-treated groups. The large increase in SBS values after air abrasion corresponded with a study in 3 commercial polyamides treated with aluminum oxide 50 microns.¹⁰ However, some studies found no significant difference or even revealed lower bond strength than no treatment.^{5,8,9}

The 4-META is a functional monomer that contains two carboxylic groups as a functional monomer and a vinyl group as a polymerizable group. The 4-META resin composes of a PMMA powder and a liquid containing the catalyst, MMA monomers and 4-META. The 4-META resin was found to improve adhesion between dentin and metal prosthesis. It is also highly compatible with PMMA due to the similarity of their main composition. Recent studies found that 4-META resin improves bond strength between polyamide and PMMA resin.^{5,8,9} Likewise, this study also discovered that the application of 4-META resin with and without air abrasion increased SBS values. However, the bond mechanism between 4-META and polyamide has not been reported.

Whereas a previous study from Hamanaka showed that polyamide treated with 4-META had higher SBS than aluminum oxide 50 microns, in the present study group M yielded lower SBS values than group S. It is possible that the larger particle size in this study might have caused more roughness on the polyamide

surface. As a result, mechanical treatment appears to have a greater impact on SBS values than chemical treatment. However, both studies agreed that polyamide treated with air abrasion followed by 4-META significantly increased SBS in both thermocycling and non-thermocycling groups. This implies that mechanical treatment is required for treating polyamide surfaces and, when combined with proper chemical application, this would effectively improve SBS values.

The SEM images of groups M and SM showed a similar pattern of resin cement layer. Since the application of 4-META resin covered the entire abraded surface in group SM, the resin layer was the only factor affecting surface roughness of groups M and SM. The brush-dip technique was used as recommended by the manufacturer for denture repair; however, it was a sensitive technique due to the difficulty in controlling the powder/liquid ratio.⁹ This might have caused uneven distribution of the cement layer on large surface and affected the surface roughness values.¹² Although the surface roughness of group M was as high as group SM, its SBS value was statistically different due to the lack of micromechanical interlocking effect from air abrasion.

The FTIR of groups M and SM showed C=O stretching at 1,730-1,715 cm⁻¹ of the carboxylic group which was the functional group of 4-META. The combination of micromechanical interlocking and proper chemical treatment on polyamide surface resulted in remarkable SBS values of group SM which corresponded to previous studies that used the aluminum oxide 50 microns followed by 4-META and witnessed the improvement in bond strength between polyamide and autopolymerized resin.^{5,8,9} Besides, altering the monomer and catalyst ratio from 4:1 to 8:1 reported no significant difference in bond strength; nevertheless, the PMMA polymer powder in 4-META resin was essential in bonding between polyamide and autopolymerized resin.⁹

Apart from 4-META, another functional monomer widely used in dentistry is 10-MDP, a crucial part of primers or resin cement products for bonding zirconia to teeth. This functional monomer phosphate group can bond with calcium ion, hydroxy apatite, metal oxides, or Zirconium ion (Zr⁴⁺) on one side, and another polymerizable group can polymerize with adhesive or resin composite. However, no

studies have used 10-MDP with polyamide, probably because the polyamide surface is mostly carbon, with no metal oxide or metal ion, causing it to be incapable of chemically bonding with the phosphate group.¹⁹

Acetic acid is a colorless, small weak organic acid that has been used as a denture disinfectant and surface treatment agent for ceramics. The previous study hypothesized that weak organic acid caused acid-swollen polyamide polymer which led to increasing diffusion of MMA monomer.¹² They reported that surface treatment of polyamide with 5% acetic acid had highly improved bond strength to autopolymerizing resin comparable to tribochemical-silica coating system.¹² On the contrary, this study found that 5% acetic acid-treated group yielded very low SBS and was not significantly different from no treatment group. However, bond strength values cannot be directly compared when experimental designs are different. Additionally, although the surface roughness, SEM images, and FTIR graph of group A were similar to the control, both SBS values and surface roughness increased significantly when treated with acetic acid together with air abrasion.

This in vitro study demonstrated that air abrasion with aluminum oxide 110 microns improved SBS of polyamide and PMMA resin significantly. Within the limitation of in vitro study, further experiments on newly launched materials with various methods are recommended and intraoral investigation is also necessary.

Conclusions

The shear bond strength between polyamide and autopolymerizing resin was affected by surface treatment methods on the polyamide surface. Within the limitation of this study, the most effective method was air abrasion with aluminum oxide 110 microns at 0.28 MPa pressure for 15 seconds at a distance of 10 mm, followed by the application of 4-META/MMA-TBB resin.

Air abrasion with aluminum oxide 110 microns was proved to significantly increase bond strength of polyamide and PMMA resin.

The application of 5% acetic acid in ethanol had no effect on bond strength and surface roughness of polyamide.

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Declaration of Interest

The authors report no conflict of interest.

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