

The effect of hydrofluoric acid treatment on the repair strength of polyamide denture base materials: An in vitro study

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Abstract

Purpose: Although polymethylmethacrylate (PMMA) dentures can be repaired using autopolymerizing acrylic resin, achieving it using polyamides is difficult. This study aimed to achieve acceptable bond strength using autopolymerizing acrylic resin by applying surface treatments to the polyamide denture base material.

Materials and methods: Thirty-six disc-shaped samples (27 polyamide, 9 PMMA) were prepared. Based on the surface treatment applied, the polyamide samples were divided into three groups: No surface treatment ($n = 9$), tribochemical silica coating + silane coupling agent ($n = 9$), and 9% hydrofluoric acid + tribochemical silica coating + silane coupling agent ($n = 9$). PMMA specimens received no surface treatment. Polyamide and PMMA surfaces had auto-polymerizing acrylic resin bonded on them, and then a shear bond strength test was performed between them after aging. The Kruskal–Wallis test was used, and statistical significance was set at $p < 0.05$.

Results: PMMA had the highest shear bond strength, the untreated polyamide group had the lowest shear bond strength, and the difference was significant ($p < 0.05$). The group treated with 9% hydrofluoric acid, tribochemical silica coating, and silane coupling agent exhibited the highest shear bond strength of the polyamide groups, and the bond strength in this group was comparable to the PMMA specimens ($p > 0.05$).

Conclusions: The polyamide denture repair strength can be improved by 9% hydrofluoric acid, tribochemical silica coating, and silane coupling agent application to the polyamide surface.

KEYWORDS

autopolymerizing resin, denture repair, hydrofluoric acid, PMMA, polyamide

Polymethylmethacrylate (PMMA) has been widely used in denture fabrication since 1937. This material has some advantages, such as esthetic appearance, low water absorption, non-cytotoxicity, and ease of preparation and repair; however, it also has some disadvantages, such as low flexural and impact strength. These disadvantages cause failures due to chewing or when patients drop the denture. Thus, some reinforcing materials are added to the PMMA structure, or the chemical structure of PMMA is modified to eliminate these failures.¹

Polyamides (PAs), or nylon, are thermoplastic polymers formed through the condensation reaction between diamine and dibasic acid and can be used as denture base materials like PMMA.^{2,3} These resins are primarily advantageous as they reflect the color of the underlying gingival tissue, have low porosity, and do not cause discoloration or foul odor.

Additionally, they have lower rigidity than acrylic resins; however, they have stronger properties.⁴ Despite these advantages, one of the continuous disadvantages is the weak bond strength between PA and artificial teeth or autopolymerizing acrylic resin (AR).^{5,6} In PA, fixing a broken tooth or claps, repairing a fracture, or relining is difficult and expensive. Sometimes, a new denture fabrication may be a more appropriate approach than the old denture repair.² However, fabricating a new denture is costly and time-consuming for the patient and the dentist. Therefore, repairing the failed denture is an appropriate clinical step in case of mechanical failure.⁷ While repairing PMMA dentures with AR is feasible, it is challenging to repair PA.¹

Studies examining the repair strengths of PA are rare in the literature. This study aimed to assess the repair strengths of PA with AR by modifying their surface properties and

TABLE 1 The materials used in the study.

Material	Brand	Manufacturer
Polyamide denture base material	Deflex	Nuxen S.R.L Buenos Aries, Argentina
Heat polymerized PMMA	Vertex	Vertex-Dental B.V., Netherlands
Autopolymerized PMMA	Blau Cryl	Efes Dental Bursa, Turkey
Silane coupling agent	Clearfil-Primer	Kuraray, Osaka, Japan
Sandblasting material	Cojet Sand	3M ESPE, Seefeld, Germany
Hydrofluoric acid	Porcelain Etch	Ultradent Products, USA

TABLE 2 The study groups and surface treatments.

	Sample size	Surface treatment
Polyamide		
PA1	9	No
PA2	9	TSC + SC
PA3	9	HA + TSC + SC
PMMA	9	No

comparing them with the repair strength of PMMA. The null hypothesis was that surface treatments would not impact the bond strength between PA and AR.

MATERIALS AND METHODS

The sample size for this study was determined at a 95% confidence level using G.Power-3.1.9.2. The analysis yielded a standardized effect size of $\eta^2 = 0.456$, with 0.96 power based on a previous study.⁹ The minimum sample size required was calculated at 7 per group and a minimum of 28 samples. However, for this study, the sample size was 9 per group and a total of 36 samples. The list of materials used in the study is shown in Table 1. In the study, 27 disc-shaped PA (Deflex, Nuxen SRL, Argentina) and 9 disc-shaped heat polymerized PMMA (Vertex, Vertex-Dental B.V, Netherlands) specimens (10 mm diameter, 2 mm thickness) were fabricated. All specimens were fixed in cylindrical plastic tubes (inner diameter 17 mm, outer diameter 25 mm, and height 30 mm) using PMMA-based auto-polymerizing resin (BLAU CRYL, Efes Dental, BURSA). The fixed samples were polished using #600, #800, and #1200 silicon carbide papers and then kept in an ultrasonic cleaner (VEVOR, China) at 25°C for 10 min.

Table 2 shows the study groups and surface treatments applied. Based on the surface treatments, the PA samples were divided into the following three groups: PA1: No surface treatment, PA2: Tribochemical silica coating (TSC)+silane coupling agent (SC) ($n = 9$), and PA3: 9% hydrofluoric acid (HA) + TSC + SC ($n = 9$). No surface treatment was applied to the heat-polymerized PMMA.

An intraoral sandblaster (Prophy-neo Partner, Liang ya Dental, China) with 30 μm Al₂O₃ particles containing silica was used to perform TSC at a distance of 10 mm for 15 s at 4.2 psi pressure. The sandblasted specimens were placed in

an ultrasonic bath at 25°C for 5 min. SC was performed using a silane containing 3-trimethoxysilyl propyl methacrylate-10-methacryloyloxydecyl dihydrogen phosphate based on the manufacturer's instructions (Clearfil-Primer, Kuraray, Osaka, Japan). For acid application, 9% HA (Porcelain Etch, Ultradent Products, Inc, South Jordan, UT, USA) was applied to the specimens for 60 s, then washed and dried.

A cylindrical transparent tube (4 mm inner diameter, 2 mm height) was placed in the center of the PA and PMMA specimens, and PMMA-based AR was placed into this transparent tube using a brush. After polymerization, the transparent tube around the AP was cut vertically using a scalpel and removed.

All samples were kept in distilled water at 37°C for 24 h, then were subjected to thermocycling (1000 cycles, 5–55°C, 20 s dwell time); after thermocycling, the samples were again kept in distilled water at 37°C for 24 h.

For the shear bond strength (SBS) test, the specimens were fixed to the test apparatus, and the knife-edged chisel tangent was fixed at right angles to the junction of the PA or PMMA specimens and the AR. SBS was measured using a universal tester (Mod dental, Ankara) at a 0.5 mm/min approach speed. When separation occurred, the test automatically stopped, and the computer calculated the results in MPa.

After the separation process, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) analysis were performed to examine a specific sample from each group in detail. Additionally, a stereomicroscope was used to examine the failure mode of all samples at 15 \times magnification. Failures in which the AR separated from the PA were considered an adhesive failure, ruptures of the AR or PA in itself were considered a cohesive failure, and these two conditions were seen together were considered a mixed failure.

Descriptive statistics of the continuous variables were presented with mean and standard deviation values. The normality of continuous variables was tested using the Shapiro–Wilk test. The Kruskal–Wallis test was used to compare continuous variables, and $p < 0.05$ was set as the level of statistical significance.

RESULTS

The mean and standard deviation values of the groups and the statistical relationship between the groups are shown in Table 3. The highest and lowest SBS were found in the

TABLE 3 Mean values and standard deviations (MPa) for shear bond strength.

	Mean ± SD		<i>p</i>
PA1	1.61 ± 1.45		
		PA1-PA2	0.587
		PA1-PA3	<0.001 ^a
		PA1-PMMA	<0.001 ^a
PA2	5.08 ± 2.07		
		PA2-PA3	0.264
		PA2-PMMA	0.005 ^a
PA3	10.15 ± 2.76		
		PA3-PMMA	1.000
PMMA	13.80 ± 1.93		

^aAccording to the Kruskal–Wallis test, the statistical significance value between the groups is $p < 0.05$, significant values had been adjusted by the Bonferroni correction.

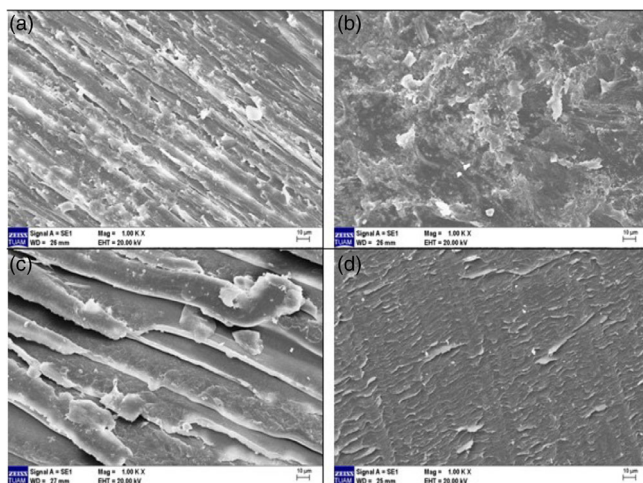


FIGURE 1 Scanning electron microscopy (SEM) images (1.00 K.X magnification) of polyamide and polymethylmethacrylate (PMMA) denture base materials after the shear bond test. (a) PA1, (b) PA2, (c) PA3, and (d) PMMA.

PMMA and PA1 groups, respectively, and the difference was significant ($p < 0.05$); in addition, there was a significant difference between the PA2 and PMMA groups ($p < 0.05$). The bond strengths increased in the surface-treated PA groups compared to PA1, while when SC was applied after TSC, this increase was not significant in the PA2 group ($p < 0.05$); moreover, it was statistically significant in the PA3 group, where HA, TSC, and SC were applied ($p < 0.05$). SBS of the PMMA group was significantly higher ($p < 0.05$) than other PA groups except PA3 ($p > 0.05$).

After the bond strength test, SEM images of one specimen from each group were presented. After the SBS test, the failure mode was investigated, and all specimens demonstrated adhesive failure (Figure 1). The weight ratio of the elements as a result of the EDX analysis is shown in Table 4. The major components in all samples were C and O. Si was observed in the samples belonging to the groups where TSC was applied,

TABLE 4 The amount (Weight %) of the elements in the samples of each group.

	C	O	Si	Cl	Ca	Al	N	Na	K
PA1	58.00	31.97	–	0.67	1.77	–	5.74	1.84	–
PA2	63.81	34.14	0.37	0.57	–	–	–	1.11	–
PA3	62.78	31.96	1.56	1.00	0.37	–	–	1.90	0.44
PMMA	49.51	50.49	–	–	–	–	–	–	–

while not in the other groups. The proportion of Si was higher in the PA3 group than in the PA2 group.

DISCUSSION

This study assessed the SBS between PA and AR after different surface treatments. It was concluded that the surface treatments influenced SBS; therefore, the null hypothesis established at the beginning of the study was rejected.

AR has an acceptable repair application in PMMA-based dentures; however, it is not PA.^{1,8} PAs are highly chemical-resistant materials owing to their crystalline nature, making their reaction with AR difficult.^{6,9} There are several studies where various surface treatments have been applied to PA to increase the bond strength with AR.^{6,9–11}

According to the study results, the lowest bond strength was observed in the PA1 group. This situation can be attributed to the difficulty of reacting with the stable structure of PA, which has not undergone any surface treatment.¹² TSC, also known as chemical bonding with mechanical energy, is one of the most commonly used techniques to ensure the surface roughness of dental materials. A silica-coated surface appears in the roughened area, and bonding can be achieved with SC.^{6,13,14} A study assessed the bond strength of PA with two different ARs when SC was applied to samples coated with TSC. The bond strength value was 4.99 and 3.27 MPa for two different resins.⁹ Katsumata et al. reported that the mean SBS was 13.18 MPa when TSC and SC were applied to PA.⁶ Hamanaka et al. also obtained a mean SBS of 13.41 MPa after TSC and SC; however, they determined the bond strength without applying the thermal cycling process.¹⁰ In this study, SC was applied to the PA2 group after TSC, and the mean SBS was 5.08 MPa. The difference in bond strength to similar studies in the literature may be owing to sandblasting, the type of silane used, or the thermal cycling process. Although PA is a chemically resistant material, the amide group in its structure enhances its susceptibility to absorbing water or various solvents. Additionally, the amide group can be more easily hydrolyzed under acidic conditions.¹⁵ In the present study, HA, TSC, and SC were used in the PA3 group, and the mean SBS was found to be 10.15 MPa. According to the manufacturer's technical documentation, the pH of the HA used in this study is less than 1, belonging to solid acids.¹⁶ HA was preferred owing to modifying the stable structure of PA materials with this strong acid. In a study that examined the bond strength

between PA with two different ARs, the most effective bond strength was obtained with the application of acetic acid, and the bond strengths for different ARs were found to be 18.02 and 33.20 MPa.¹⁵ Acetic acid is known to be a weak organic acid; however, the bond strengths in this study were extremely high compared to our study. Hocker et al. reported that weak acids are more effective in hydrolyzing PA at low concentrations; therefore, the difference in results could be attributed to this.¹⁷

The mean SBS for the PMMA group was found to be 13.80 MPa. A study reported that sufficient bond strength was formed at values extremely close to this strength.¹⁸ In the present study, after the application of HA, TSC, and SC, the repair strength of PA surfaces approached the acceptable bond strength, as the SBS obtained from samples belonging to the PA3 and PMMA groups did not show a statistically significant difference.

The long-term clinical behavior of bonded materials under in vitro conditions is often predicted using aging methods such as thermal cycling and water storage.¹⁹ ISO TR 11450 (1994) standards report that the thermal cycle applied with 500 cycles at a temperature of 5–55°C is suitable. The thermal cycling process has been shown to reduce the bond strength between the nylon polymer and AR; thus, the correct approach is the use of aging methods for the results' reliability.⁶ In the study by Hafezeqoran and Koodaryan, the bond strength between PA and AR was examined. The samples were kept in distilled water at a temperature of 37°C for 24 h, then were subjected to thermocycling (1000, 5–55°C, 15 s dwell time) after thermocycling; samples were again kept in distilled water at a 37°C for 24 h. This study applied a similar aging procedure to estimate the bond strength under clinical conditions.

The SBS test, which is frequently used to measure bond strength, is an in vitro test method created by applying force to the connection region at a certain speed until a fracture occurs. The SBS is calculated by dividing the maximum force applied by the connection area.^{20,21} This test has been frequently used in evaluating the bond strength between PA and autopolymerizing resins.^{6,10,11,15} The SBS test was conducted in our study using an approach speed of 0.5 mm/min as recommended in the literature. There are some limitations of this study. The disc-shaped specimens were used instead of complex denture shapes; the in vitro test did not stimulate the clinical conditions; the sample size per group was small; tribochemical silica coating was not applied with the device recommended by the company that produces silica-containing sand; however, the sandblasting pressure, duration, and distance were applied following the manufacturer's recommendations. Another limitation is that SEM and EDX analyses were applied after the shear bond test, not immediately after surface treatments. When the surface-treated PA samples were examined through EDX analysis, trace amounts of silica were found on them. Although a higher amount of silica was expected on the tribochemical silica-coated PA samples, the presence of trace amounts may be because the EDX analysis was performed after the bond

strength test rather than after the application of the surface treatments.

CONCLUSIONS

Surface treatments applied to polyamide bases can enhance their bond strength with autopolymerizing acrylic resins. However, the increase in bond strength was not significant if the polyamide bases were not treated with hydrofluoric acid. The most effective method to obtain the highest bond strength in polyamide groups was to apply 9% hydrofluoric acid, tribochemical silica coating, and a silane bonding agent. By following this method, the bond strength of polyamide denture base materials can be increased to the level of PMMA bonding to autopolymerized acrylic resin.

CONFLICT OF INTEREST STATEMENT

The authors have no conflicts of interest relevant to this article.

DISCLOSURE

The authors do not have any financial interest in the companies whose materials are included in this article.

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