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Shear bond strength of an autopolymerizing repair resin to injection-molded thermoplastic denture base resins

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Abstract

Objective. This study investigated the shear bond strength of an autopolymerizing repair resin to injection-molded thermoplastic denture base resins. ***Materials and methods.*** Four injection-molded thermoplastic resins (two polyamides, a polyethylene terephthalate copolymer and a polycarbonate) were used in this study. The specimens were divided into eight groups according to the type of surface treatment given: (1) no treatment, (2) air abrasion with alumina, (3) dichloromethane, (4) ethyl acetate, (5) 4-META/MMA-TBB resin, (6) alumina and 4-META/MMA-TBB resin, (7) tribochemical silica coating or (8) tribochemical silica coating and 4-META/MMA-TBB resin. Half of the specimens in groups 1, 5, 6 and 8 were thermocycled for 10,000 cycles in water between 5–55°C with a dwell time of 1 min at each temperature. The shear bond strengths were determined. ***Results.*** The shear bond strengths to the two polyamides treated with alumina, dichloromethane and ethyl acetate and no treatment were very low. The greatest post-thermocycling bond strengths to polyamides were recorded for the specimens treated with tribochemical silica coating and 4-META/MMA-TBB resin (PA12: 16.4 MPa, PACM12: 17.5 MPa). The greatest post-thermocycling bond strengths to polyethylene terephthalate copolymer and polycarbonate were recorded for the treatment with alumina and 4-META/MMA-TBB resin (22.7 MPa, 20.8 MPa). ***Conclusion.*** Polyamide was exceedingly difficult to bond to an autopolymerizing repair resin; the shear bond strength improved using tribochemical silica coating followed by the application of 4-META/MMA-TBB resin. Both polyethylene terephthalate copolymer and polycarbonate were originally easy to bond to an autopolymerizing repair resin. However, with 4-META/MMA-TBB resin, the bond was more secure.

Key Words: *injection-molded thermoplastic denture base resin, polyamide, polyethylene terephthalate copolymer, polycarbonate, shear bond strength*

Introduction

In recent years, removable partial dentures (RPDs) without metal clasps have been used in dental practice [1,2] because the metal clasps of conventional RPDs have poor esthetics and metal allergies can occur in some situations [3]. RPDs without metal clasps have been made with injection-molded thermoplastic resins (polyamides, polyethylene terephthalate copolymer and polycarbonate) [4–6]. It was proved in our previous studies [5,6] that one kind of polyamide and of polycarbonate had high impact strengths, but the impact strengths decreased after thermocycling. Injection-molded thermoplastic resins with low impact strength may fracture due to impact force. It appears that RPDs without metal clasps fracture easily and fail due to the debonding of the denture teeth.

Autopolymerizing resin is often clinically used as a repair material for denture base resin made from PMMA. However, high bond strength between the denture base resin and autopolymerizing acrylic resin is not always predictable [7,8]. Surface treatments are necessary to enhance the bond between the denture base resin and the autopolymerizing repair resin. Many researchers have reported on the surface treatments used on acrylic resins [7–16], but little study has been done on bonding injection-molded thermoplastic resins to an autopolymerizing repair resin. Katsumata et al. [3] found that one kind of polyamide denture base polymer (PACM12) and an autopolymerizing repair resin did not bond to each other, but the surface treatment with a tribochemical silica coating system enhanced the bond strength. However, little attention has been focused on the effect of the

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surface treatment to PA12, which is one of the polyamides for dental use, as well as polyethylene terephthalate copolymer and polycarbonate.

The purpose of the present study was to improve the bond strength of an autopolymerizing repair resin to injection-molded thermoplastic resins using the most effective surface treatment. The null hypothesis was that neither the surface treatments nor the thermocycling would affect the bond strength between an autopolymerizing repair resin and injection-molded thermoplastic resins.

Materials and methods

Test specimen preparation

Four injection-molded thermoplastic resins were selected for this study (Table I). Each kind was polymerized according to the manufacturer's instructions. A total of 120 block specimens (10.0 × 10.0 × 3.0 mm) of each resin were prepared. Each specimen was embedded in an autopolymerizing resin material with an acryl ring and the surfaces of the injection-molded thermoplastic resins or a polymethyl methacrylate (PMMA) were abraded under running water with up to 400-grit silicon carbide paper. The specimens were divided into eight groups according to the type of surface treatment given ($n = 10$):

(1) No treatment (controls);
(2) Alumina air abrasion with 50 μm alumina (0.28 MPa, 10 s) (air abrasion);
(3) A 5-s application of dichloromethane (Wako Pure Chemical Industries, Ltd., Osaka, Japan, lot ALG5624) (dichloromethane);
(4) A 120-s application of ethyl acetate (Wako Pure Chemical Industries, Ltd., lot KLH2672) (ethyl acetate);
(5) Application of 4-META/MMA-TBB resin (Super-Bond C&B, Sun Medical., Moriyama, Japan, lot SX1) (4-META/MMA-TBB);
(6) Alumina with 50 μm alumina followed by application of 4-META/MMA-TBB resin (air abrasion + 4-META/MMA-TBB);
(7) Tribochemical silica coating (Rocatec® Plus and ESPE Sil, 3M ESPE AG., Seefeld, Germany, lot 344141 lot, 339017) (0.28 MPa, 13 s) (silica coating); and
(8) Tribochemical silica coating followed by application of 4-META/MMA-TBB resin (silica coating + 4-META/MMA-TBB).

In groups 5, 6 and 8, chemically-activated 4-META monomer was produced with a 4:1 (drop/drop) mixing ratio of liquid to catalyst. The activated monomer and powder were then applied using the brush-dip technique. To define the bonding area, sticky tape with a 6-mm diameter hole and a Teflon ring (1 mm thick) with a circular hole (5.0-mm inner diameter, 6.0-mm outer diameter) were placed on the surface to be bonded on each specimen. The powder and liquid of an autopolymerizing repair resin (Unifast III live pink, GC, Tokyo Japan, Lot number: liquid 1006281, powder 1005173) were mixed and applied inside the Teflon ring. The mixing ratio of powder-to-liquid was 2:1 (w/w). After polymerization, the sticky tape and Teflon ring were gently removed and then all the specimens were immersed in distilled water at 37°C for 24 h. Half of the specimens in four groups: (1) no treatment (controls), (2) 4-META/MMA-TBB, (3) air abrasion + 4-META/MMA-TBB and (4) silica coating + 4-META/MMA-TBB were placed in a thermocycling apparatus (Thermal Shock Tester TTS 1, Thomas Kagaku Co., Ltd., Tokyo, Japan) and cycled in water between 5–55°C with a dwell time of 1 min at each temperature for 10,000 cycles.

Measurement of shear bond strength

The shear bond strengths were determined using a universal testing machine (Autograph AGS-J, Shimadzu Corp., Kyoto, Japan) at a cross-head speed of 0.5 mm/min. All testing was performed under uniform atmospheric conditions of 23.0 ± 1°C and 50 ± 1% relative humidity. The means and standard deviations (SD) for the shear bond strength were calculated and statistically analyzed with a one-way analysis of variance (ANOVA) and the Student-Newman-Keuls post-hoc comparisons test at a significance level of $p = 0.05$. The type of bond failure was determined after shear bond testing when the

Table I. Injection-molded thermoplastic denture base resins tested.

Constituent	Material	Manufacturer	Processing method	Lot number
Polyamide (PA12)	Valplast	Valplast International Corp., NY	Injection molding technique; heat processed at 215°C for 20 min	091142
Polyamide (PACM12)	Lucitone FRS	DENTSPLY International Inc., PA	Injection molding technique; heat processed at 300°C for 17 min	100323A
Polyethylene terephthalate copolymer	EstheShot	i-Cast Co. Ltd., Kyoto, Japan	Injection molding technique; heat processed at 230°C for 20 min	JGA
Polycarbonate	Reigning	Toushinyoukou Co. Ltd., Niigata, Japan	Injection molding technique; heat processed at 320°C for 30 min	DMY29T

Table II. Mean and standard deviation (SD) of shear bond strength (MPa) of an autopolymerizing repair resin to polyamide (Valplast).

TC	Surface treatment	Mean (SD)	Failure mode C/M/A
0	no treatment	2.53 (0.54)^{a}	0/0/10
0	air abrasion	3.56 (0.68)^{a}	0/0/10
0	dichloromethane	2.77 (0.66)^{a}	0/0/10
0	ethyl acetate	2.31 (0.52)^{a}	0/0/10
0	4-META/MMA-TBB	7.30 (1.67)	0/1/9
0	air abrasion + 4-META/MMA-TBB	10.92 (1.80)	0/0/10
0	silica coating	13.41 (1.74)	0/0/10
0	silica coating + 4-META/MMA-TBB	16.45 (1.98)^{b}	0/0/10
10,000	no treatment	0.44 (0.63)^{c}	0/0/10
10,000	4-META/MMA-TBB	1.05 (1.10)^{c}	0/0/10
10,000	air abrasion + 4-META/MMA-TBB	3.18 (1.44)^{a}	0/0/10
10,000	silica coating + 4-META/MMA-TBB	16.44 (1.99)^{b}	0/0/10

a, *b* or *c* denotes no significant differences ($p > 0.05$).
Failure mode: Cohesive/Mixture of cohesive and adhesive/Adhesive.

fractured surfaces of the specimens were examined using an optical microscope (SZ61 OLYMPUS) at 30× magnification. Failure was evaluated in this study as A (adhesive failure at the denture base resin/autopolymerizing repair resin interface), M (mixture of cohesive failure within the denture base resin or the autopolymerizing repair resin and adhesive failure) or C (cohesive failure within the denture base resin or the autopolymerizing repair resin).

Results

The shear bond strengths of the autopolymerizing repair resin to polyamide (Valplast) and the failure modes are given in Table II. Before thermocycling, the shear bond strengths of the specimens treated with air abrasion, dichloromethane and ethyl acetate were very low, in addition to controls; there were no significant differences among them. The shear bond strengths of the specimens treated with silica coating + 4-META/MMA-TBB were significantly higher than for those receiving the other surface treatments. After thermocycling, the shear bond strengths of the specimens with no treatment and those treated with 4-META/MMA-TBB were extremely low and were significantly lower than the strengths before thermocycling. The shear bond strength of the treatment condition with silica coating + 4-META/MMA-TBB was the highest among the four treatments. There were no significant differences in the shear bond strengths of the specimens treated with silica coating + 4-META/MMA-TBB before and after thermocycling. The modes of failure were mostly adhesive.

The shear bond strength of an autopolymerizing repair resin to polyamide (Lucitone FRS) and the failure modes are given in Table III. Before thermocycling, the shear bond strengths of the dichloromethane and ethyl acetate treatments were very low, as well as controls. The shear bond strengths for silica coating + 4-META/MMA-TBB were significantly higher than those of the other treatments. After thermocycling, the shear bond strength of the no treatment condition was extremely low and, in fact, was significantly lower than that found before thermocycling. The shear bond strengths of the specimens treated with silica coating + 4-META/MMA-TBB were the highest among the four treatments. There were no significant differences in the shear bond strengths of specimens treated with silica coating + 4-META/MMA-TBB between the before and after thermocycling conditions. The modes of failure were generally adhesive.

The shear bond strengths of an autopolymerizing repair resin to polyethylene terephthalate copolymer (EstheShot) and the failure modes are given in Table IV. Overall, the bond strengths were higher than those to polyamide. Before thermocycling, there were no significant differences among the shear bond strengths for specimens treated with air abrasion, dichloromethane, ethyl acetate and silica coating as well as controls. The shear bond strengths of

Table III. Mean and standard deviation (SD) of shear bond strength (MPa) of an autopolymerizing repair resin to polyamide (Lucitone FRS).

TC	Surface treatment	Mean (SD)	Failure mode C/M/A
0	no treatment	3.30 (0.96)^{a}	0/0/10
0	air abrasion	5.52 (1.03)^{b}	0/0/10
0	dichloromethane	3.23 (0.88)^{a}	0/0/10
0	ethyl acetate	2.92 (0.58)^{a}	0/0/10
0	4-META/MMA-TBB	10.21 (1.94)	0/2/8
0	air abrasion + 4-META/MMA-TBB	13.46 (2.11)^{c}	0/0/10
0	silica coating	14.68 (2.71)^{c}	0/0/10
0	silica coating + 4-META/MMA-TBB	19.60 (2.14)	0/0/10
10,000	no treatment	0.73 (0.65)^{d}	0/0/10
10,000	4-META/MMA-TBB	1.83 (0.71)^{ad}	0/0/10
10,000	air abrasion + 4-META/MMA-TBB	6.15 (1.59)^{b}	0/0/10
10,000	silica coating + 4-META/MMA-TBB	17.46 (1.45)	0/0/10

a, *b*, *c* or *d* denote no significant differences ($p > 0.05$).
Failure mode: Cohesive/Mixture of cohesive and adhesive/Adhesive.

Table IV. Mean and standard deviation (SD) of shear bond strength (MPa) of an autopolymerizing repair resin to polyethylene terephthalate copolymer (EstheShot).

TC	Surface treatment	Mean (SD)	Failure mode C/M/A
0	no treatment	17.45 (1.48)	10/0/0
0	air abrasion	18.65 (0.79)	10/0/0
0	dichloromethane	20.36 (1.80)	10/0/0
0	ethyl acetate	17.30 (1.37)	10/0/0
0	4-META/MMA-TBB	23.66 (2.35)^{a}	10/0/0
0	air abrasion + 4-META/MMA-TBB	23.73 (1.28)^{a}	10/0/0
0	silica coating	19.07 (1.09)	10/0/0
0	silica coating + 4-META/MMA-TBB	23.49 (1.29)^{a}	10/0/0
10,000	no treatment	16.39 (1.47)	10/0/0
10,000	4-META/MMA-TBB	18.13 (1.47)	10/0/0
10,000	air abrasion + 4-META/MMA-TBB	22.74 (2.02)^{a}	10/0/0
10,000	silica coating + 4-META/MMA-TBB	22.45 (2.30)^{a}	10/0/0

a denotes no significant differences ($p > 0.05$).
Failure mode: Cohesive/Mixture of cohesive and adhesive/Adhesive.

specimens treated with 4-META/MMA-TBB, air abrasion + 4-META/MMA-TBB and silica coating + 4-META/MMA-TBB were the highest among the eight treatments. After thermocycling, the shear bond strengths of specimens receiving no treatment and 4-META/MMA-TBB were significantly lower than those for the air abrasion + 4-META/MMA-TBB and silica coating + 4-META/MMA-TBB conditions. There were no significant differences in the shear bond strengths in all four groups between before and after thermocycling. It was remarkable that the modes of failure were all cohesive within the polyethylene terephthalate copolymer bulk.

The shear bond strength of an autopolymerizing repair resin to polycarbonate (Reigning) and the failure modes are given in Table V. Overall, the bond strengths were higher than those to polyamide. Before thermocycling, the shear bond strengths for specimens treated with 4-META/MMA-TBB, air abrasion + 4-META/MMA-TBB and silica coating + 4-META/MMA-TBB were higher than those of the other treatments. After thermocycling, the shear bond strengths for air abrasion + 4-META/MMA-TBB treatment were higher than controls and 4-META/MMA-TBB. One important finding was that there was no significant difference in the shear bond strengths of the specimens with no treatment between the before and after thermocycling conditions. It was also remarkable that the modes of failure were all cohesive within the polycarbonate bulk as well as in the polyethylene terephthalate copolymer.

Discussion

As shown in Tables II and III, it was found that the two kinds of polyamide tested were exceedingly difficult to bond to an autopolymerizing repair resin, which was supported by the observation that the failure mode was mostly adhesive. In the present study, the most effective surface treatment was the use of the tribochemical silica coating system followed by the application of 4-META/MMA-TBB resin. It was reported that the tribochemical silica coating system is effective for bonding an autopolymerizing repair resin to PACM12 and the durability of the silica coating on polyamide polymer may be good because all the fractures occurred at the interface between the silica layer and the resin [3]. Therefore, it can be presumed that the bond strength of an autopolymerizing repair resin to PACM12 is enhanced if the bonding of the autopolymerizing repair resin to silica layer is well done. The results of the present study indicated that chemically-activated 4-META/MMA-TBB resin may be effective to both the autopolymerizing repair resin and the silica layer. The method of applying air abrasion with 50 µm alumina followed by 4-META/MMA-TBB resin was effective before thermocycling. However, this method cannot be recommended to the polyamide due to the low bond durability when compared to the use of the tribochemical silica coating system. It is surmised that the flow of the 4-META/MMA-TBB resin is

Table V. Mean and standard deviation (SD) of shear bond strength (MPa) of an autopolymerizing repair resin to polycarbonate (Reigning).

TC	Surface treatment	Mean (SD)	Failure mode C/M/A
0	no treatment	12.33 (0.94)^{a}	10/0/0
0	air abrasion	14.38 (1.66)^{ab}	10/0/0
0	dichloromethane	16.36 (1.47)^{bc}	10/0/0
0	ethyl acetate	13.23 (3.04)^{a}	10/0/0
0	4-META/MMA-TBB	22.83 (3.15)^{de}	10/0/0
0	air abrasion + 4-META/MMA-TBB	22.19 (1.64)^{de}	10/0/0
0	silica coating	16.44 (0.86)^{bc}	10/0/0
0	silica coating + 4-META/MMA-TBB	24.08 (2.19)^{d}	10/0/0
10,000	no treatment	12.81 (1.08)^{a}	10/0/0
10,000	4-META/MMA-TBB	17.98 (3.17)^{cf}	10/0/0
10,000	air abrasion + 4-META/MMA-TBB	20.82 (1.79)^{eg}	10/0/0
10,000	silica coating + 4-META/MMA-TBB	19.41 (1.22)^{fg}	10/0/0

a, *b*, *c*, *d*, *e*, *f* or *g*: denote no significant differences ($p > 0.05$).
Failure mode: Cohesive/Mixture of cohesive and adhesive/Adhesive.

better than that of the autopolymerizing repair resin because the polymer particles of the 4-META/MMA-TBB resin are smaller than those of the repair resin. Consequently, it may be easy to obtain an effective combination of mechanical retention and chemical adhesion using the 4-META/MMA-TBB resin.

As shown in Tables IV and V, it was found that both the polyethylene terephthalate copolymer and polycarbonate are easily bonded to an autopolymerizing repair resin. This finding was supported by the observation that the failure mode was all cohesive with no exception, in contrast to the polyamide. The most effective way to enhance the bond strength and bond durability was by using 4-META/MMA-TBB resin, especially with the surface treatment of air abrasion with 50 μm alumina or the tribochemical silica coating system, followed by the application of 4-META/MMA-TBB resin. These results indicated the synergistic effect of the chemical bonding of 4-META/MMA-TBB resin and mechanical retention.

Therefore, the method of using a tribochemical silica coating system followed by application of 4-META/MMA-TBB resin is strongly recommended for polyamide, whereas polyethylene terephthalate copolymer and polycarbonate originally are prone to bond well to an autopolymerizing repair resin with no treatment. However, the bond is more secure by using the 4-META/MMA-TBB resin treatment.

Conclusions

This study compared the effect of various surface treatments on the bonding between four injection-molded thermoplastic denture base resins and an autopolymerizing repair resin. The following conclusions may be drawn:

(1) The two kinds of polyamide tested were exceedingly difficult to bond to an autopolymerizing repair resin without any treatment. The bond strength improved using a tribochemical silica coating system followed by application of 4-META/MMA-TBB resin; and

(2) Both the polyethylene terephthalate copolymer and polycarbonate were originally easy to bond to an autopolymerizing repair resin. However, with 4-META/MMA-TBB resin, the bond is more secure.

***Declaration of interest*:** The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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