Effect of Surface Preparation Using Ethyl Acetate on the Shear Bond Strength of Repair Resin to Denture Base Resin

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Keywords
Acrylic denture base resins; autopolymerizing acrylic repair resins; dichloromethane; ethyl acetate; repair strength; surface preparation agent.

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Abstract

Purpose: This study evaluated the effect of using ethyl acetate as a surface preparation agent on the shear bond strength of repair resin to denture base resin.
Materials and Methods: The flat surfaces of a heat-processed denture base resin were prepared with one of the following: (1) without preparation, (2) 60-second application of ethyl acetate, (3) 120-second application of ethyl acetate, (4) 180-second application of ethyl acetate, and (5) 5-second application of dichloromethane. An autopolymerizing repair resin was applied. The specimens were then immersed in 37°C distilled water for 24 hours. The specimens in groups 1, 3, and 5 were thermocycled up to 10,000 times in water between 5 and 55°C with a 1-minute dwell time at each temperature. The shear bond strengths were determined at a crosshead speed of 1.0 mm/min (n = 10). The morphological changes in the repair surfaces after preparation were observed with a scanning electron microscope.
Results: The shear bond strengths of groups 3 and 5 were significantly higher than the other groups before thermocycling ($p < 0.05$). The shear bond strengths of group 3 were significantly lower than those of group 5 after thermocycling ($p < 0.05$). The scanning electron microscope (SEM) views showed that the dissolution progressed deeper with the preparation duration.
Conclusions: The 120-second surface application of ethyl acetate enhanced the shear bond strength between the repair resin and the denture base resin, although the bond durability was inferior to that of the conventional surface preparation.

Autopolymerizing acrylic repair resin has long been used as a repair material when acrylic denture bases fracture. Dichloromethane is a surface preparation agent for denture base resin that enhances the bond between the denture base resin and the autopolymerizing acrylic resin;[1-4] however, there is medical evidence that dichloromethane may be carcinogenic to humans (e.g., the incidence of cancer in some internal organs).[5-11] Therefore, ethyl acetate, which was considered to be a safer surface preparation agent, was tested as an alternative to dichloromethane in a previous study.[12] It was learned that ethyl acetate can cause the surface to swell, which allows the repair resin to diffuse into the denture base; a three-point bending test indicated that the bond strength after a 120-second application of ethyl acetate may be nearly equivalent to that of the conventional method using a 5-second application of dichloromethane. Almost no information, however, is available about the effect of ethyl acetate for denture base repair except for our previous study.[12]

The purpose of the current study was to evaluate the initial effect and the durability of surface preparation using ethyl acetate on the shear bond strength of repair resin to denture base resin.

Materials and methods

A heat-processed acrylic denture base resin and an autopolymerizing acrylic repair resin were selected for this study (Table 1). Eighty 1-cm cubes of heat-processed denture base resin were prepared according to the manufacturer's instructions. Poly(methyl methacrylate) powder (24 g) and liquid (12 ml) were mixed and packed into stone molds according to conventional laboratory procedures for denture processing. After processing, each cube was embedded in an autopolymerizing resin material with an acryl ring. The surfaces of the specimens were abraded under running water with 100-grit silicon

Table 1 Materials used

Materials	Batch number	Manufacturer
Heat-processed denture base resin		
Acron clear	Powder 0403231, Liquid 0402202	GC Corp., Tokyo, Japan
Autopolymerizing acrylic repair resin		
Unifast II pink	Powder 0401062, Liquid 0404161	GC Corp.
Surface preparation agent		
Ethyl acetate	KLN1346	Wako Pure Chemical Industries, Ltd., Osaka, Japan
Dichloromethane	KLR7743	Wako Pure Chemical Industries, Ltd.

carbide paper. All specimens were immersed in 37˚C distilled water for 2 weeks.

Fifty specimens were divided into five groups (n = 10) according to the type of surface treatment given: (1) without preparation, (2) 60-second application of ethyl acetate (Wako Pure Chemical Industries, Ltd., Osaka, Japan), (3) 120-second application of ethyl acetate, (4) 180-second application of ethyl acetate, and (5) 5-second application of dichloromethane (Wako Pure Chemical Industries, Ltd.). 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. An autopolymerizing repair resin was mixed and applied inside the Teflon ring. After polymerization, the sticky tape and Teflon ring were gently removed, and then all the specimens were immersed in water at 37°C for 24 hours. The extra ten specimens in groups 1, 3, and 5 were placed in a thermocycling apparatus (Thermal Shock Tester TTS 1, Thomas Kagaku Co., Ltd., Tokyo, Japan) and cycled in water between 5 and 55°C with a dwell time of 1 minute at each temperature for 10,000 cycles. The shear bond strengths were determined using a universal testing machine (Autograph AGS-J, Shimadzu Corp., Kyoto, Japan) at a crosshead speed of 1.0 mm/min. After shear bond strength testing, the interfaces of the specimens where failure occurred in groups 1, 3, and 5 both before and after thermocycling were observed through an optical microscope (Nikon 92052, Nikon Corp., Tokyo, Japan) at 30× magnification for all specimens.

The means and standard deviations for the shear bond strengths (n = 10) were calculated and statistically analyzed with a one-way analysis of variance (ANOVA) before and after thermocycling. After one-way ANOVA, the Newman-Keuls post hoc comparisons test was performed at the 0.05 level of significance. The statistical analyses were performed using STATISTICA Standard 03J (StatSoft, Inc., Tulsa, OK).

To determine the morphological changes to the surfaces after preparation, a few extra specimens were prepared according to the original protocol. They were gold sputtered-coated and observed at a magnification of 3500× with a scanning electron microscope (SEM) (JSM-T 330, JEOL, Inc., Tokyo, Japan) operating at 5 kV.

Results

The one-way ANOVA and Newman-Keuls post hoc comparisons test showed that there were significant differences in shear bond strength before thermocycling ($p < 0.05$). The shear bond strengths of groups 3 and 5 were significantly higher than those of groups 1, 2, and 4 ($p < 0.05$). There were no significant differences between groups 3 and 5 and among groups 1, 2, and 4 ($p > 0.05$). After thermocycling, the one-way ANOVA and Newman-Keuls post hoc comparison test indicated that there were significant differences in shear bond strength among the three groups ($p < 0.05$). The shear bond strength of group 5 was significantly higher than that of group 3 ($p < 0.05$), and the shear bond strength of group 3 was significantly higher than that of group 1 ($p < 0.05$). The average shear bond strengths, standard deviations, and statistically significant categories are summarized in Table 2. The mode of failure of each specimen in groups 1, 3, and 5 both before and after thermocycling is presented in Table 3.

Table 2 Shear bond strength of an autopolymerizing repair resin to denture base resin

Thermocycles	0 cycles			10, 000 cycles		
Group*	Mean (MPa)	SD (MPa)	Significance	Mean (MPa)	SD (MPa)	Significance
1	20.2	5.6	b	17.3	4.7	c
2	22.9	7.6	b			
3	35.2	6.9	a	26.0	2.2	b
4	23.7	2.4	b			
5	36.2	1.9	a	41.6	5.3	a

SD = standard deviation.

Identical letters indicate that the values are not statistically different ($p > 0.05$).

*Groups: 1: without preparation; 2: 60-second application of ethyl acetate; 3: 120-second application of ethyl acetate; 4: 180-second application of ethyl acetate; 5: 5-second application of dichloromethane.

Table 3 Mode of failure of an autopolymerizing repair resin bonded to denture base resin with and without thermocycling

Thermocycles	0 cycles	10,000 cycles
Group*		
1	AAAAAAAAAA	AAAAAAAAAA
3	MMMMMMMMAA	MMMAAAAAAA
5	MMMMMMMMMM	MMMMMMMMAA

A = adhesive failure at the denture base resin/repair resin interface; M = mixture of cohesive and adhesive failure within the repair resin. Each letter corresponds to a separate specimen.

*Groups: 1: without preparation; 3: 120-second application of ethyl acetate; 5: 5-second application of dichloromethane.

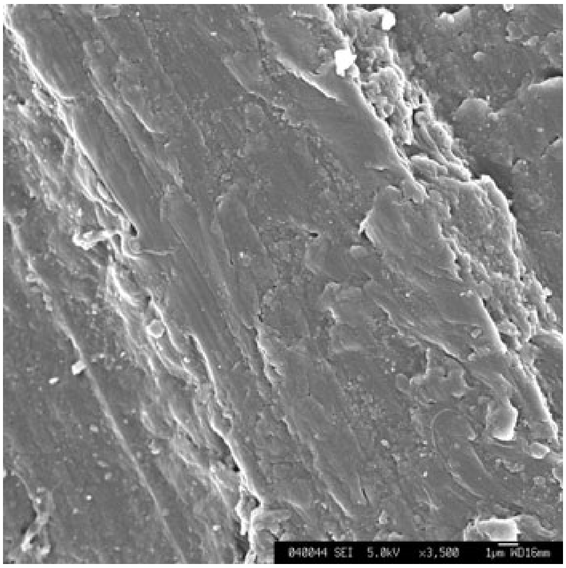

Figure 1 SEM of the denture base resin material abraded with 100-grit silicon carbide paper (without preparation) at a magnification of 3500×. Uniform parallel scratches are evident.

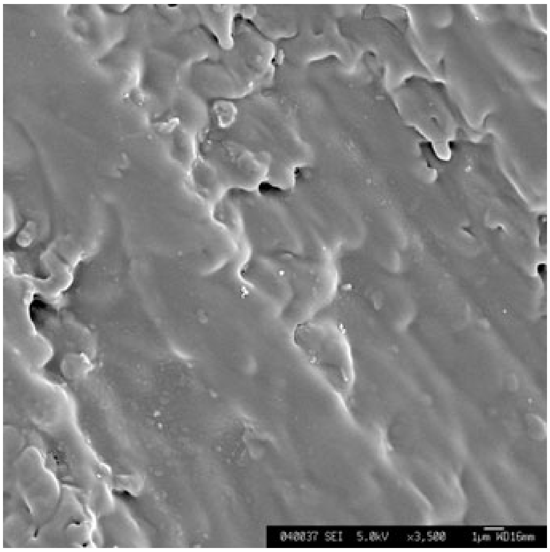

Figure 3 SEM of the denture base resin material prepared with 180-second application of ethyl acetate (3500×). The surface has a flatter and smoother appearance than in Figure 2.

The SEM views of the denture base resin material prepared with ethyl acetate for 120 and 180 seconds, as well as the specimens without preparation and with a 5-second application of dichloromethane, are found in Figures 1-4. The view of the denture base resin surface without preparation shows many uniform parallel scratches formed during the abrasion with silicon carbide paper. The denture base resin surface prepared with ethyl acetate for 120 seconds shows a dissolved surface with a few pores. The denture base resin surface prepared with ethyl acetate for 180 seconds has a flatter and smoother appearance than the surfaces prepared with a 120-second application. It seems that the dissolution progressed deeper in proportion to the preparation duration.

Discussion

Vallittu et al[13] reported that the monomers of denture base resin diffuse into acrylic resin teeth, and the interface between heat-processed acrylic denture base resin polymer and the resin teeth

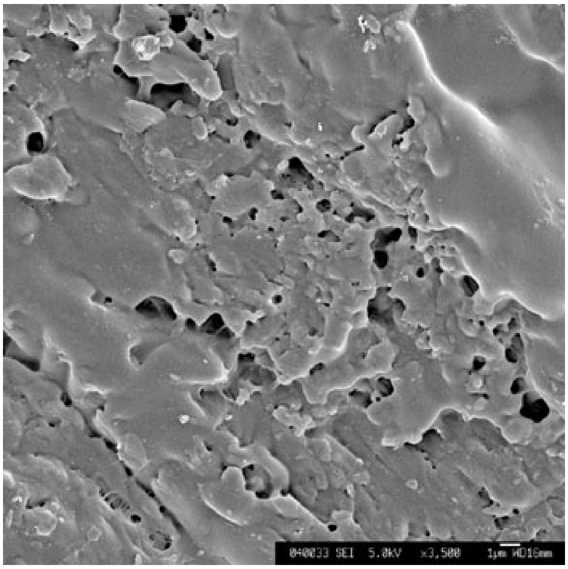

Figure 2 SEM of the denture base resin material prepared with a 120-second application of ethyl acetate (3500×). This view shows a dissolved surface with a few pores.

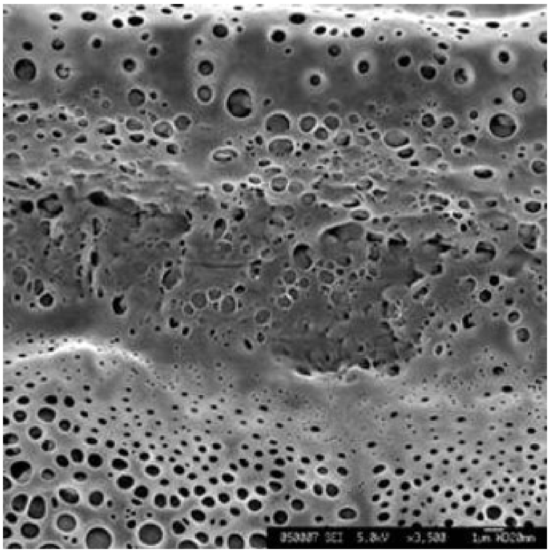

Figure 4 SEM of the denture base resin material prepared with a 5-second application of dichloromethane (3500×). Many pores can be seen.

appear diffused in the region of the interpenetrating polymer networks (IPN) and the matrix. This phenomenon increases the bond strength between the acrylic resin teeth and the denture base resin. Proper wetting of the repair surface makes an important contribution to the strength of repaired acrylic resin due to this mechanism.[14] Therefore, the bonding mechanism of the autopolymerizing repair resin to the surface of the dissolved denture base resin is based on monomer interdiffusion, the swelling, and the formation of IPN during polymerization.

Surface preparation with dichloromethane can cause the surface to swell, permitting the diffusion of the polymerizable material; this method is effective at changing the surface structure of the denture base resin prior to repair.[3-6] However, dichloromethane is currently not recommended for use in dental practice, because it may be carcinogenic to humans. There is sufficient evidence from animal experiments that dichloromethane is carcinogenic.[7] Ethyl acetate is a popular organic solvent that is not listed in the classification of the International Agency for Research on Cancer (IARC). Our hypothesis was that ethyl acetate would also dissolve the denture base resin surface and perform as well as dichloromethane. Therefore, in a previous study,[12] this solvent was selected as a safer surface preparation agent than dichloromethane; that study concluded that ethyl acetate causes the surface of a denture base resin to swell, thus promoting the formation of IPN. Additionally, a three-point bending test showed that the effect of a 120-second application may be nearly equivalent to that of a 5-second application of dichloromethane.

The statistical analysis in the present study indicated that there were no differences in the effect of surface preparation between the 120-second application with ethyl acetate and the 5-second surface application with dichloromethane before thermocycling ($p > 0.05$). This finding agrees with the conclusions of the previous study.[12] The 180-second surface preparation with ethyl acetate produced lower strength than the 120-second surface preparation ($p < 0.05$). In addition, there were no significant differences in the effect of the surface preparation among the 60-second application, the 180-second application, and without preparation ($p > 0.05$). This finding is partially explained by the SEM views, which show the tendency for dissolution to progress deeper with the application duration and indicate that the surface conditions are strongly linked with mechanical interlocking. The surfaces prepared with the 180-second application appear plastically deformed and look flatter and smoother than those prepared with the 120-second application, which indicates that ethyl acetate causes the surface to swell and that the 180-second application may be expected to provide little mechanical interlocking capability; however, the surfaces prepared with the 120-second application do not look like those treated with dichloromethane for 5 seconds.

The surfaces prepared with the 120-second application also show some of this deformation. A preparation of 180 seconds is too long to suitably swell the surface and permit the diffusion of the denture base resin. Statistical analysis revealed that after thermocycling, the shear bond strength of the specimens prepared with the 120-second application was significantly lower than the strength of specimens prepared with dichloromethane ($p < 0.05$). The t-test revealed that the strength of the 120-second surface preparation after thermocycling was significantly lower than before thermocycling ($p < 0.05$), whereas there were no significant differences in strength due to thermocycling in specimens prepared with dichloromethane and without any surface preparation ($p > 0.05$). These findings indicate that the bond durability of specimen surfaces prepared using ethyl acetate may be inferior to those prepared using dichloromethane. The reason for this inferiority may be due to the above-mentioned deformation.

The specimens prepared with ethyl acetate for 120 seconds underwent a greater number of adhesive failures than the specimens prepared with dichloromethane for 5 seconds, especially after thermocycling. This evaluation of the failure mode agrees with the results of the shear bond testing. Further in vitro studies and clinical research are necessary to investigate the effect of ethyl acetate on the bonding of repair resin to denture base resin.

Conclusions

The 120-second surface application of ethyl acetate enhanced the shear bond strength between the repair resin and the denture base resin; however, after thermocycling, this preparation was inferior to that of the conventional 5-second application of dichloromethane.

Acknowledgments

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