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Effect of surface preparation using ethyl acetate on the repair strength of denture base resin

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Abstract

Objective. The objective of this study was to evaluate the effect of surface preparation using ethyl acetate on the repair strength of a denture base resin. ***Material and Methods***. Bar specimens were fabricated with a heat-processed denture base resin and cut in half. The repair surfaces of the specimens were treated with ethyl acetate for varying amounts of time before the autopolymerizing repair resin was applied. The specimens were then immersed in 37°C distilled water for 2 days. A three-point bending test was used to determine the transverse strength of the test specimens. Ten specimens prepared using a 120-s application of ethyl acetate and 10 specimens prepared using a 5-s application of dichloromethane were thermocycled at 10,000 cycles (at 5°C and 55°C) with a 60-s dwell time. The morphological changes in the repair surfaces after preparation were observed by scanning electron microscopy. ***Results***. The repair strength of the denture base resin prepared using ethyl acetate for 120 s (30.6 MPa) was the highest among the results for the various amounts of time tested ($p < 0.05$). There were no significant differences between the repair bond strength both before and after thermocycling of the denture base resin prepared using ethyl acetate for 120 s and that of the denture base resin prepared with dichloromethane for 5 s ($p > 0.05$). ***Conclusion***. Within the limitations of the current study, a 120-s application of ethyl acetate was as effective as a 5-s application of dichloromethane at preparing the surfaces of a denture base resin.

Key Words: *Acrylic resin, denture base, dichloromethane, ethyl acetate, repair*

Introduction

Acrylic denture base fracture is an infrequent accidental complication for denture wearers but, when it occurs, repair of the fracture can be performed in the clinic. Recently, autopolymerizing acrylic repair resin has often been utilized as a repair material. However, it is not always easy to gain high bond strength between a heat-processed denture base resin and an autopolymerizing acrylic repair resin [1,2]. To improve the bond strength between these two types of acrylic resin or between denture base resin and acrylic denture teeth, surface treatment using methyl methacrylate [3,4] and dichloromethane [5–8] has been reported. Reinforcement of repaired acrylic denture base resin with glass fibers and dichloromethane pretreatment produced high transverse strength and modulus of elasticity [9].

Dichloromethane has been widely used in industrial processes, food preparation, and agriculture. However, it has also been one of the subjects of recent toxicological and carcinogenesis studies [10,11]. There is evidence that dichloromethane is carcinogenic, as shown by the increased incidence of cancer in some internal organs [10–15]. Therefore, a safer surface preparation than the application of dichloromethane is strongly desired.

Ethyl acetate is an organic and non-polymerizable solvent with the potential to swell the surface and permit the diffusion of the polymerizable material. A method of extracting residual monomer from acrylic resin was reported in order to determine the concentration of the residual monomer by gas chromatography using several kinds of organic solvents, including ethyl acetate, that were selected according to their physicochemical properties [16]. Ethyl acetate was an effective cleaning agent when a silane-coated alloy surface previously exposed to gypsum processing was bonded to composite resin [17]. Adhesives containing ethyl acetate solvents produced stronger bond strengths between polyvi-

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nylsiloxane denture soft liners and a heat-processed acrylic resin denture base [18]. Little information, however, is available about the effect of ethyl acetate as an alternative to dichloromethane for denture base repair.

In this study, it was assumed that the denture base resin surface was dissolved by ethyl acetate. The purpose of the study was to evaluate the effect of surface preparation using ethyl acetate on the repair bond strength of an acrylic denture base resin material and to compare this method with the conventional method using dichloromethane.

Material and methods

Test specimen preparation

A heat-processed denture base resin (Acron, GC Corp., Tokyo, Japan) and an autopolymerizing acrylic repair resin (Unifast II, GC Corp.) were selected for this study (Table I). A total of 80 bar specimens of the heat-processed denture base resin (approximately $3.0 \times 10.5 \times 68.5$ mm) were prepared in accordance with the manufacturer's instructions. Poly(methyl methacrylate) (PMMA) powder (24 g) and liquid (12 ml) were mixed. The time for the dough to reach sufficient plasticity for packing was approximately 15 min. The procedures for mixing and packing the resin in stone molds followed conventional laboratory procedures for denture processing. After processing, the specimens were abraded under running water with 100-grit silicon carbide paper to make the final dimensions of $2.5 \times 10.0 \times 68.0$ mm. The specimens were stored in 37°C distilled water for 2 days and then cut in half with a band saw under running water guided by a standardized positional jig. The surfaces were cut parallel to each other and perpendicular to the long axis of the specimens by abrading under water with 100 grit silicon carbide paper to simulate roughening of the repair surface of the denture with laboratory burs. The abraded surfaces were divided into five groups: untreated, and treated with ethyl acetate for 5, 30, 60, and 120 s. For the three-point bending test, the parallel halves of the specimens were placed in open-ended stone molds having the same dimensions as the original specimens. These molds were used with room allowed for a 3 mm bar butt joint gap between the ends to be repaired. The gap was then filled with the autopolymerizing acrylic repair resin mixed at a ratio (powder to liquid) of 2:1 (w/w). The free-flowing mix was poured into the joint space to allow for a slight excess to ensure a complete joint. After the polymerization process was completed at 23°C to mimic the most basic clinical conditions, the repaired specimens were gently trimmed to their original dimensions (±0.03 mm) and kept in distilled water at 37°C for 1 day. Twenty specimens with their surfaces prepared using dichloromethane for 5 s were also prepared. Ten of these 20 specimens and the extra 10 specimens with surfaces prepared using ethyl acetate for 120 s were thermocycled up to 10,000 cycles in water between 5°C and 55°C with a 1-min dwell time at each temperature using a Thermal Shock Tester TTS-1 (Thomas Kagaku Co., Ltd., Tokyo, Japan).

Three-point bending test

A three-point bending test was performed using a universal testing machine (Autograph AGS-J, Shimadzu Corp., Kyoto, Japan) with a distance of 50 mm between the supports and a crosshead speed of 5 mm/min. The load at fracture was converted to transverse strength (S) according to the formula $S = 3PL/2bd^2$, where P is the breaking load, L is the length between the supports, b is the width of the specimen, and d is the thickness of the specimen. All testing was performed under uniform atmospheric conditions of 23°C and 50% relative humidity. The fracture surfaces of the specimens treated with the 120-s application of ethyl acetate and the 5-s surface application of dichloromethane were observed through an optical microscope (92052, Nikon, Tokyo, Japan) at ×30 magnification.

Statistical analyses

The data were analyzed statistically using a one-way analysis of variance (ANOVA), and the Newman-Keuls post-hoc comparison and contrast evaluation were applied when appropriate (95% confidence level). The computer program STATISTICA Standard 03J (StatSoft, Inc., Tulsa, Okla., USA) was used for all statistical analyses.

Table I. Materials used

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

Table II. Transverse strengths of the repaired denture base material for each group

	Transverse strength (MPa)		
Application duration (s)	Mean	SD	Newman-Keuls grouping
0	17.8	2.4	a
5	20.8	4.9	a, b
30	22.4	2.0	b
60	19.3	2.1	a, b
120	30.6	2.1	c

$n = 10$; SD: standard deviation. Identical letters indicate that the values are not statistically different ($p > 0.05$).

SEM observation

To determine the morphological changes on the surfaces after preparation, a few extra specimens were gold sputter-coated and observed with a scanning electron microscope (SEM, JSM-T 6330 F, JEOL Inc., Tokyo, Japan) operating at 5 kV.

Results

The one-way ANOVA and Newman-Keuls post-hoc comparison indicated that the surface preparation using ethyl acetate for 120 s produced higher strength than the other preparation durations and the untreated group ($p < 0.05$). There were no significant differences in transverse strength among the untreated group, 5-s application and 60-s application ($p > 0.05$); these specimens had the lowest strength. There were no significant differences in transverse strength among the 5-s, 30-s, and 60-s applications ($p > 0.05$). Contrast evaluation revealed that there were no significant differences in transverse strength between the 120-s application with ethyl acetate and the 5-s application with dichloromethane for both thermocycle 0 and thermocycle 10,000 ($p > 0.05$). The average strengths, standard deviations, and statistical categories of the transverse strengths are summarized in Tables II and III. The modes of failure of the specimens prepared using the 120-s application with ethyl acetate and the 5-s surface application with dichloromethane for both thermocycle 0 and thermocycle 10,000 are presented in Table IV.

The SEM views of the denture base resin material treated with ethyl acetate for the varying preparation durations are found in Figure 1. It is apparent that the dissolution progressed deeper in proportion to the preparation duration. The SEM views of the denture base resin treated for 30 s and 60 s with ethyl acetate show almost homogeneous surfaces with pores less than 1 μm in diameter. The views of the denture base resin treated with ethyl acetate for 120 s show a dissolved surface with no pores, which is different from the views for the 30 s and 60 s preparation times.

Discussion

It was reported that the shear bond strength test is not more appropriate than the tensile strength test for evaluating the adhesive capabilities of resin composite to ceramics because the shear bond strength test inherently measures the strength of the base material rather than the strength of the adhesive interface [19]. It seems that this finding can also be applied to testing the strength of a denture base resin and an autopolymerizing acrylic repair resin [20]. However, the tensile strength test requires a precise load direction to the specimen in order to gain correct results, and this factor considerably affects the values and is very difficult to control [21]. On the other hand, the validity of the three-point bending test closely correlated with the failure mode of the specimens [8]. Therefore, the three-point bending test was performed for the current study.

It is not always easy to gain high bond strength between a heat-processed denture base resin and an autopolymerizing acrylic repair resin [1,2]. Since the bonding mechanism of the autopolymerizing acrylic resin to the surface of the dissolved PMMA is based on monomer interdiffusion and the swelling and formation of an interpenetrating polymer network during polymerization, proper wetting of the repair surface with methyl methacrylate contributes to the strength of the repaired acrylic resin [3]. It has been

Table III. Transverse strengths of the repaired denture base material before and after thermal cycling

	Transverse strength (MPa)					
	0 cycles			10, 000 cycles		
Thermocycles Surface preparation	Mean	SD	Category	Mean	SD	Category
Ethyl acetate 120 s	30.6	2.1	a	29.0	4.4	b
Dichloromethane 5 s	33.3	3.6	a	26.5	5.3	b

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

Table IV. Mode of failure

Thermocycles Surface preparation	0 cycles	10, 000 cycles
Ethyl acetate 120 s	M M M M M M M M A A	M M A A A A A A A A
Dichloromethane 5 s	M M M M M M M M M M	M M M M M A A A A A

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

suggested that the methyl methacrylate diffuses more easily into autopolymerized poly(methyl methacrylate) than into heat-processed poly(methyl methacrylate) during the repair of denture base polymer [4]. Surface preparation with dichloromethane also causes the surface to swell and permits diffusion of the polymerizable material. Such preparation can create surface pores approximately 1 μm in diameter on acrylic resin teeth [5,6] or an acrylic denture base resin [7–9]. Therefore, the application of dicholoromethane is beneficial for the surface structure of denture teeth prior to denture base processing or on the denture base resin prior to repair. However, dichloromethane is currently not recommended for use in dental practice because of indications of carcinogenicity [10,11], as shown by the increased incidence of cancer of the mammary gland and alveoli/bronchia [10], liver

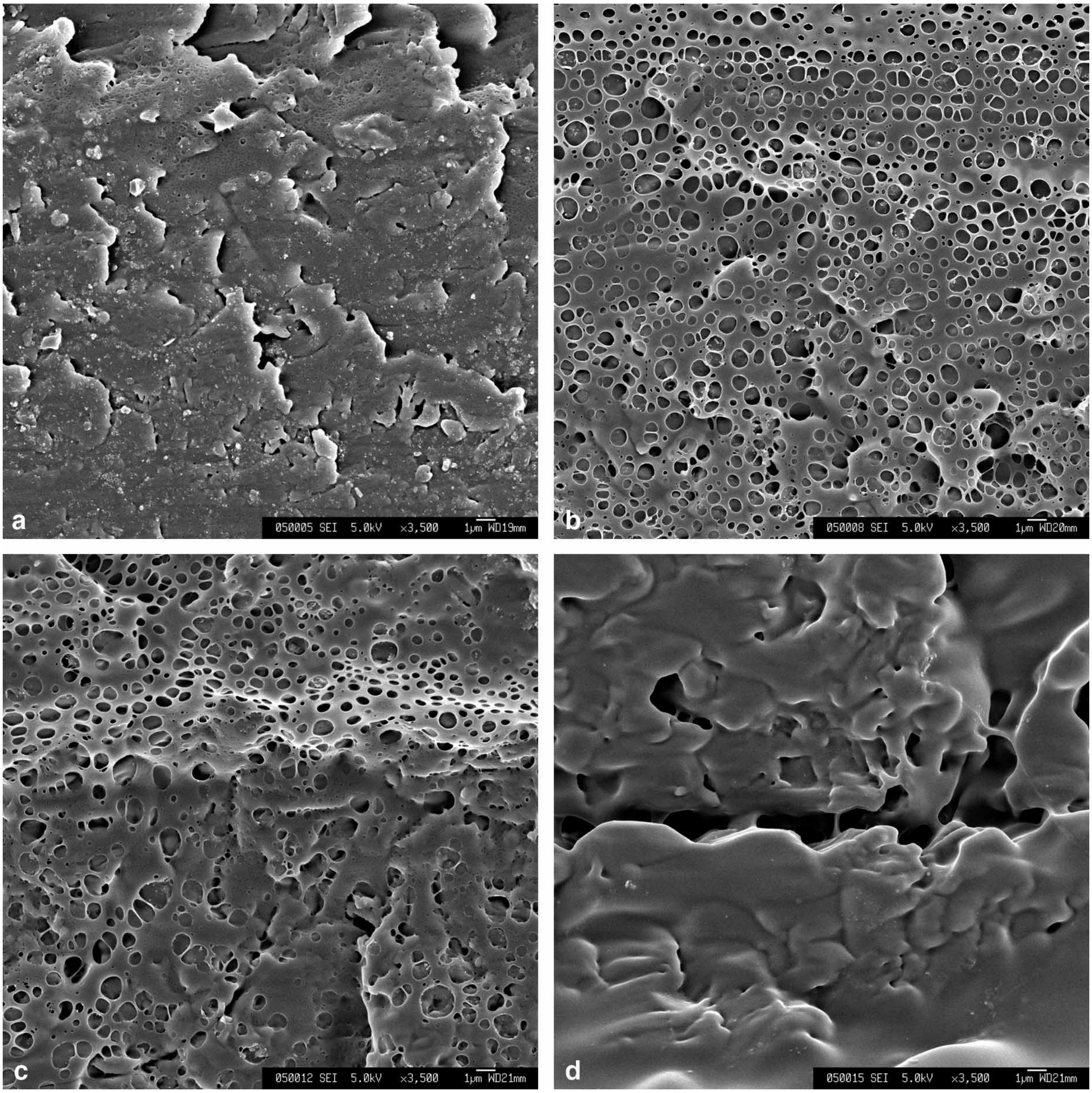

Figure 1. Scanning electron micrographs of the denture base resin material treated using ethyl acetate with various application durations (a: 5 s; b: 30 s; c: 60 s; d: 120 s).

[10,12,14,15] and lungs [13–15]. Thus, a safer surface preparation agent instead of dichloromethane is strongly desired.

The statistical analysis revealed that the 120-s surface preparation with ethyl acetate produced higher strength than did the other application durations and the untreated group ($p < 0.05$) and that there were no differences in the effect of surface preparation between the 120-s application with ethyl acetate and the 5-s surface application with dichloromethane. These findings can be explained not only by the swelling of the surface, which permits diffusion of the PMMA and creation of surface pores, but also in part by the exposure of the fresh denture base resin surface, an increase in the gross repair surface area, and the roughened structure of the autopolymerizing acrylic repair resin. The SEM views of the denture base resin surfaces treated with ethyl acetate demonstrated the tendency for dissolution to progress deeper in proportion to the application duration. The surfaces of the denture base resin treated with ethyl acetate for 30s and 60s looked almost the same as the surfaces treated with dichloromethane [5–8]. These observations indicate that ethyl acetate also has the ability to swell the surface and permit diffusion of the denture base resin material. The fact that the dissolution value of ethyl acetate (9.1) [22] is similar to that of PMMA (9.5) agrees with these observations. However, the SEM view of a surface treated with ethyl acetate for 120 s does not look like that treated with dichloromethane for 5 s. A comparison of the failure mode of the specimens also indicated the probability that 120-s surface preparation with ethyl acetate may not necessarily be more appropriate than 5-s preparation with dichloromethane. One thing to be noted is that when ethyl acetate is used clinically it must be applied repeatedly up to 120-s because of its high volatility.

This study concludes that ethyl acetate can cause the surface to swell, thus permitting diffusion of the denture base resin. The 120-s application of ethyl acetate yielded the highest bond strength among the four preparations tested and may be nearly equivalent to that of a conventional 5-s application of dichloromethane.

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