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The Effect of Chemical Surface Treatments on the Flexural Strength of Repaired Acrylic Denture Base Resin

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Keywords
Acrylic resin; flexural strength; methyl formate; methyl acetate; repair.

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This work was supported by the Thai Government Research Fund and the Chulalongkorn University Fund.

Accepted May 18, 2010

doi: 10.1111/j.1532-849X.2011.00688.x

Abstract

Purpose: To investigate the effect of the selected chemical surface treatment agents on the flexural strength of heat-polymerized acrylic resin repaired with autopolymerized acrylic resin.
Materials and Methods: Ninety heat-polymerized acrylic resin specimens (Meliodent) were prepared according to ISO1567 and randomly divided into nine groups: positive and negative control groups (groups I and II), and seven experimental groups (groups III to IX). Specimens in groups II to IX were cut in the middle and beveled 45°. Group III was then treated with methyl methacrylate (the liquid part of Unifast TRAD) for 180 seconds. Group IV was treated with Rebase II adhesive according to the manufacturer's instructions. Groups V to IX were treated with methyl formate, methyl acetate, and a mixture of methyl formate–methyl acetate at various concentrations (75:25, 50:50, 25:75% v/v, respectively) for 15 seconds. They were then repaired with autopolymerized acrylic resin (Unifast TRAD). A three-point loading test was performed using a universal testing machine. One-way ANOVA and post hoc Tukey's analysis at $p < 0.05$ were used for statistical comparison. Failure analysis was then recorded for each specimen. The morphological changes in untreated and treated specimens were observed by scanning electron microscopy.
Results: The flexural strengths of groups III to IX were significantly higher than that of group II ($p < 0.05$). The flexural strengths of groups IV to IX showed no significant difference among them ($p > 0.05$). All specimens in groups V to IX showed 100% cohesive failure, while groups II, III, and IV showed cohesive failure of 10%, 60%, and 60%, respectively. From scanning electron micrographs, the application of methyl formate, methyl acetate, and a mixture of methyl formate–methyl acetate solutions on heat-polymerized acrylic resin resulted in a 3D honeycomb appearance, while specimens treated with methyl methacrylate and Rebase II adhesive developed shallow pits and small crest patterns, respectively.
Conclusion: Treating surfaces with methyl formate, methyl acetate, and a mixture of methyl formate–methyl acetate solutions significantly enhanced the flexural strength of heat-polymerized acrylic denture base resin that had been repaired with autopolymerized acrylic resin.

Heat-polymerized acrylic resin is a major component material of denture base. Despite the physical and mechanical properties of denture base resin, denture bases sometimes fracture.[1-7] Without proper scheduling and financial planning, making a new denture may be impractical. Therefore, denture repair seems to be an alternative choice. Autopolymerized acrylic resin has been recommended as a first material of choice because of its fast polymerization and simple procedures.[7-9] Unfortunately, the repaired denture can refracture, especially at the junction between heat- and autopolymerized acrylic resins (adhesive failure) rather than within the autopolymerized acrylic resin (cohesive failure). That means the bond strength between heat- and autopolymerized acrylic resins is weaker than that of autopolymerized acrylic resin itself.[10]

To increase the bond strength between heat- and autopolymerized resins, chemical surface treatment on the fracture surface of heat-polymerized acrylic resin, prior to the repairing procedure, has been recommended. Many chemical surface treatment agents have been suggested, including chloroform[11] and methylene chloride;[12-14] however, due to their carcinogenic potential, alternative surface treatment agents such as acetone,[15,16] ethyl acetate,[17] methyl methacrylate,[18] methyl formate,[19] methyl acetate,[19] and a mixture of acetone and ethyl acetate (Rebase II adhesive)[20] have been introduced.

The data for each alternative surface treatment material have been obtained from individual studies. A comparative study of these materials has not yet been performed. The purpose of this study was to evaluate the effects of selected chemical surface treatment agents—methyl methacrylate, Rebase II adhesive, methyl formate, methyl acetate, and a mixture of methyl formate–methyl acetate on the flexural strength of heat-polymerized acrylic resin repaired with autopolymerized acrylic resin.

Materials and methods

The following materials were used: heat-polymerized acrylic resin (Meliodent, lot no. 08DP0017, Heraeus Kulzer, Senden, Germany); autopolymerized acrylic resin (Unifast TRAD, lot no. 0710151, GC Dental Products Corp, Tokyo, Japan); Rebase II adhesive (lot no. X75117, Tokuyama Dental Corp., Tokyo, Japan); methyl formate (lot no. 1239211, Fluka & Riedel-de Haen, Buchs, Switzerland); and methyl acetate (lot no. A0259676, Acros Organics, Geel, Belgium).

Ninety heat-polymerized acrylic resin specimens ($3.3 \times 10 \times 64$ mm^3) were prepared according to ISO 1567, and then randomly divided equally into nine groups (Table 1). Except for the positive control group (group I), each specimen was cut lengthwise in the middle to create a 3-mm gap, then beveled at 45°.[10,18,21] Autopolymerized acrylic resin was prepared and used to fill up the space. After complete polymerization, the repaired areas were polished with 600 and 1000 silicon carbide papers, consecutively. All specimens were stored in distilled water at 37°C for 48 hours before testing.

To reduce experimental variability, all experimental procedures were performed by one operator. Additionally, in each experimental group, the procedures on the specimens (cut and bevel, apply the surface treatment agents, fill up with autopolymerized acrylic resin, and polish the repaired area) were performed in 1 day.

Flexural strength testing

Flexural strength was determined using a three-point bending testing device (Universal Testing Machine 8872, Instron, High Wycombe, UK) with a cross-head speed of 5 mm/min, a span of 50 mm, and 1000 N load cell. Specimens were loaded until fracture occurred. Flexural strength was calculated using the following equation:[22]

$$\delta = 3FI/2bh^2$$

where δ = flexural strength (MPa), F = maximum load (N), I = span length between the supports (mm), b = width of specimen (mm), and h = height of specimen (mm).

To determine the type of fracture failure as either cohesive or adhesive, all fracture surfaces were examined using an ML9300 stereo microscope (Meiji Techno, Saitama, Japan) at 7 × magnification. Specimens with an entire layer of autopolymerized acrylic resin on both repaired surfaces were judged to have failed cohesively.[18]

Scanning electron microscope (SEM) evaluation

To determine the morphological changes on the surfaces after surface treatment, a few extra specimens were sputter-coated with gold particles. SEM examination was performed at 15 kV and a sample tilt angle of 0° on a JEOL-5410 (JEOL Inc., Tokyo, Japan). The untreated surface was used as a negative control.

Statistical analysis

All statistical computations were performed by SPSS software version 11.5 (SPSS Inc., Chicago, IL). Data obtained from the three-point bending test were presented as mean and standard deviation, and analyzed by one-way ANOVA and Tukey's multiple comparison. Values of $p < 0.05$ were considered as statistically significant. SigmaStat software version 2.0 (SPSS Inc.) was used to calculate the statistical power.

Table 1 Experimental group classification according to surface treatment

Group	Cut and beveled	Surface treatment	Filled with autopolymerized acrylic resin
I	–	No*	No
II	+	No**	Yes
III	+	Methyl methacrylate (liquid part of Unifast TRAD), 180 sec	Yes
IV	+	Rebase II adhesive	Yes
V	+	Methyl formate, 15 sec	Yes
VI	+	Mixture of methyl formate–methyl acetate solution (75:25 v/v), 15 sec	Yes
VII	+	Mixture of methyl formate–methyl acetate solution (50:50 v/v), 15 sec	Yes
VIII	+	Mixture of methyl formate–methyl acetate solution (25:75 v/v), 15 sec	Yes
IX	+	Methyl acetate, 15 sec	Yes

*Intact heat-polymerized acrylic resin specimen (positive control).

**Untreated repaired surface (negative control).

Table 2 Mean flexural strength (MPa) with standard deviation. The number and percentage of cohesive and adhesive failure types after measurement of fracture load of test specimens; n(%)

		Failure types (%)	
Group	Flexural strength (MPa) mean (SD)*	Cohesive	Adhesive
I	71.9 (3.4)[d]	–	–
II	47.8 (4.2)[a]	1 (10)	9 (90)
III	58.8 (2.8)[b]	6 (60)	4 (40)
IV	60.6 (4.4)[bc]	6 (60)	4 (40)
V	65.1 (3.9)[c]	10 (100)	0 (0)
VI	62.7 (4.3)[bc]	10 (100)	0 (0)
VII	61.7 (4.0)[bc]	10 (100)	0 (0)
VIII	65.5 (3.7)[c]	10 (100)	0 (0)
IX	60.2 (4.1)[bc]	10 (100)	0 (0)

*No significant difference ($p > 0.05$) within groups denoted by the same superscript letter.
One-way ANOVA test, followed by post hoc Tukey's multiple comparison test.

Results

The flexural strengths of all experimental groups are presented in Table 2. The intact group (group I, positive control) had the highest flexural strength, while the untreated surface group (group II, negative control) had the lowest. Chemical treatment of fracture surfaces (groups III to IX) significantly increased the flexural strength, compared to the untreated surface group ($p < 0.05$). Among these designed treatments, the application of methyl methacrylate revealed the lowest flexural strength. Treatment with methyl formate and a mixture of methyl formate–methyl acetate (25:75 v/v) significantly increased the flexural strength of the repaired denture, compared to treatment with methyl methacrylate ($p < 0.05$). The statistical power of this study was 71.2%

To determine the type of fracture failure, the fractured surface of each specimen was investigated under a stereomicroscope. Methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate resulted in 100% cohesive failure, while methyl methacrylate and Rebase II adhesive resulted in 60% cohesive failure (Table 2).

SEM revealed that the untreated surface was quite smooth, with a few debris particles from grinding. The surface patterns after applying chemical surface treatment are shown in Figure 1. Specimens treated with methyl methacrylate showed shallow pits on the surface (Fig 1B), while those treated with Rebase II adhesive showed small crest patterns (Fig 1C). Specimens treated with methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate revealed a honeycomb appearance of differing severity (Fig 1D–H).

Discussion

In this study, the effects of various surface treatment agents on the flexural strength and surface morphological pattern of repaired acrylic denture resin were investigated. Flexural failure is one of the most common fracture types in repaired acrylic denture base resin. A three-point loading test was used to determine the repair strength of acrylic base resin. To reproduce the forces affecting a repaired denture, three different loads were applied to the repaired area and to both sides of the specimens.[15-18]

In this study, the various timings for each surface treatment agent were selected based on previous studies. Vallittu et al indicated that the best timing for applying methyl methacrylate on heat-polymerized acrylic resin is 180 seconds.[18] Rebase II adhesive was applied according to the manufacturer's instructions. Methyl formate and methyl acetate were applied for 15 seconds, following Asmussen and Peutzfeldt's experiment.[19]

The results of this study showed that the mean flexural strengths of the chemically surface-treated groups were higher than that of the untreated group. That corresponds with previous studies showing that the chemical surface treatment of repaired acrylic denture augments the bonding strength, compared to untreated denture.[11,16-19] Among the chemical agents used, methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate had higher bond strengths than methyl methacrylate. In addition, specimens treated with methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate showed 100% cohesive failure. From SEM data, methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate created 3D pores of various diameter and depth, while methyl methacrylate and Rebase II adhesive created shallow pits and small crest patterns. These 3D pores should allow greater penetration of the autopolymerized acrylic resin (and hence, increased surface contact and mechanical interlocking bonds between heat- and autopolymerized acrylic resins), in comparison to the shallow pits and small crests. That should explain the better bond strength between heat- and autopolymerized acrylic resins after treatment with methyl formate, methyl acetate, and the mixtures of methyl formate–methyl acetate.

Still, the precise action of chemical surface treatment agents is unclear. Many researchers have suggested that these chemical agents may dissolve and soften heat-polymerized acrylic resin.[13,15,17,18] Based on the softening theory, a liquid could act as a plasticizer of a polymeric solid when the solubility parameters and polarities between the liquid and the polymeric solid are close to each other.[19] The solubility parameter of poly(methyl methacrylate) is 18.3 MPa$^{1/2}$, while those of methyl methacrylate, methyl formate, methyl acetate, ethyl acetate, and acetone (the main component in Rebase II adhesive) are around 18 to 20.9 MPa$^{1/2}$.[23] In addition, methyl methacrylate, methyl formate, and methyl acetate all have the same methyl ester group, while ethyl acetate has an ethyl ester group, suggesting that the difference in polarity between the methyl ester and ethyl ester groups would affect the ability of these chemical agents to soften poly(methyl methacrylate). Another possibility is the influence of their molecular structure and size.

Methyl formate, with a molecular weight (MW) of 60.05, and methyl acetate (MW: 74.08) have much smaller molecules than methyl methacrylate (MW: 100.12). That allows methyl formate and methyl acetate to penetrate more easily between the poly(methyl methacrylate) chains. Evchuk et al reported that the greater the molecular weight of the solvent, the less its ability to dissolve poly(methyl methacrylate).[24] That corresponds with our SEM data, which show deep holes in the surfaces of

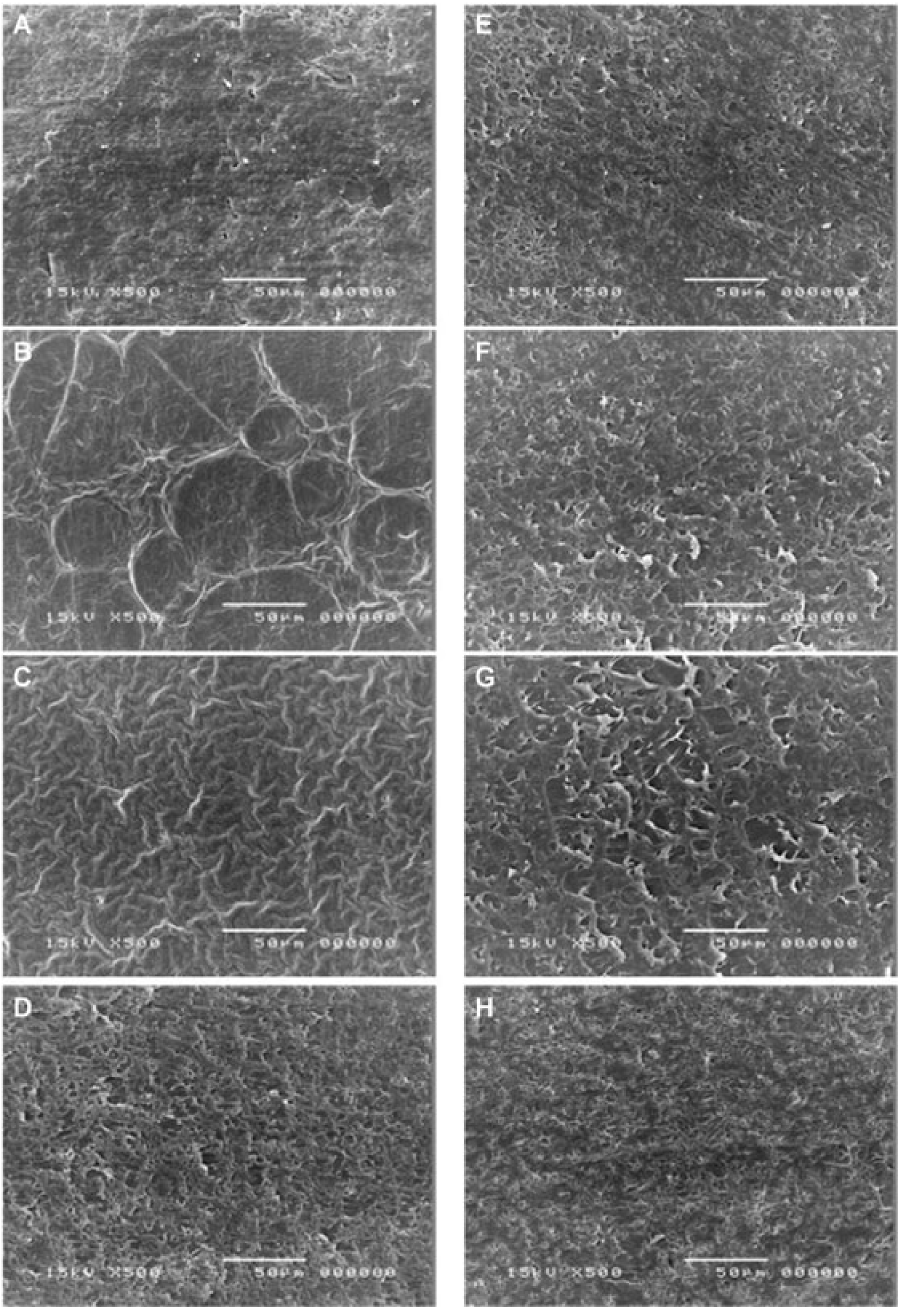

Figure 1 SEM morphology micrographs of untreated and treated surfaces of heat-polymerized acrylic resin. (A) untreated; (B) treated with methyl methacrylate for 180 seconds; (C) treated with Rebase II adhesive; (D) treated with methyl formate; (E) treated with methyl formate–methyl acetate solution (75:25 v/v); (F) treated with methyl formate–methyl acetate solution (50:50 v/v); (G) treated with methyl formate–methyl acetate solution (25:75 v/v); and (H) treated with methyl acetate.

acrylic resin treated with methyl formate and methyl acetate, while shallow craters appear on surfaces treated with methyl methacrylate. According to the American Conference of Governmental Industrial Hygienists,[25-27] the workplace airborne exposure limits for 8 hours to methyl methacrylate, methyl formate, and methyl acetate are 50, 100, and 200 ppm, respectively. That suggests that methyl formate and methyl acetate are not only good solvents, but are also safer than methyl methacrylate.

Even though the statistical power in this study was around 72%, it should be noted that this was a preliminary in vitro study, and the sample size was designed to limit the experimental errors. Therefore, further clinical research with a larger sample size and statistical power is required to confirm the effect of methyl formate, methyl acetate, and mixtures of methyl formate–methyl acetate on the bonding of repaired acrylic denture base resin.

Conclusions

Within the limitations of this study, the following conclusions were drawn:

(1) Surfaces treated with chemical agents showed significantly higher flexural strength than those of untreated surfaces.
(2) Treating surfaces with methyl formate, methyl acetate, and mixtures of methyl formate–methyl acetate at various concentrations for 15 seconds diminished adhesive failure in all repaired test specimens, as compared with methyl methacrylate and Rebase II adhesive.

Acknowledgments

We would like to thank Professor Sitichai Koontongkaew and Miss Paipun Phitayanon for statistical consultation; and Miss Sani Boonyagul and Miss Dusida Sahawat for their valuable suggestions.

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