Original Article

Effect of Methyl Formate-Methyl Acetate Treatment on Flexural Strength of Relined Denture Base

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Abstract

The purpose of this study was to evaluate the effect of methyl formate-methyl acetate (MF-MA) surface treatment on flexural strength between denture base and hard reline materials. One hundred heat-cured acrylic denture base (Meliodent®) specimens were prepared according to ISO 20795-1 (2013) and divided into ten groups. Groups I-III: relined with Unifast Trad®, Group IV-VI: relined with Kooliner® and Group VII-X: relined with Tokuyama® Rebase II Fast. Groups I, IV and VII were untreated surface (control groups), Groups II, V and VIII were surface treated with methyl methacrylate (MMA) for 180 s and Groups III, VI and IX were surface treated with methyl formate-methyl acetate (MF-MA) solution for 15 s, Group X were surface treated with the provided adhesive per the manufacturer's instructions. Flexural strength was measured using a Universal Testing Machine. The data were analyzed using two-way ANOVA (group I-IX) and one-way ANOVA (group I-X) where significant differences in the groups were found. The group means were compared using Tukey's test at a 95 % confidence level. The reline material type and surface treatments significantly affected on the flexural strength ($p<0.05$). For each reline material, the flexural strength of the MF-MA treated group was significantly higher compared with the other groups ($p<0.05$). For the same surface treatment, the flexural strength of Unifast Trad® was significantly higher compared with Kooliner® ($p<0.05$). The flexural strength of Kooliner® was higher than that of Tokuyama® Rebase II Fast ($p<0.05$). This study suggests the application of MF-MA solutions for 15 s before relining procedure can increase the flexural strength between the denture base and hard reline materials.

Keywords: Acrylic denture base, Flexural strength, Hard reline materials, Methyl formate-methyl acetate, MMA

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Introduction

Alveolar ridge, supported prosthesis, are continuously resorbed[1], resulting in loss of stability and tissue pain under prosthesis. Patients need to have their denture reline to restore good stability and retention.[2-4] The two methods for relining a denture base are direct and indirect relining. The indirect technique uses a heat-polymerizing resin in a laboratory, while the direct technique uses self-cured hard reline materials and is performed chairside. The direct technique is quick, easy and does not require laboratory procedures. Patients can use their prosthesis immediately after the relining is completed. However, the disadvantages of this method include reline odor and an unpleasant taste. This method can also cause tissue irritation under the denture base due to residual monomers and higher temperatures during polymerization.[5] Chairside hard reline procedures use self-cured hard reline materials to support increased tissue stability and retention. The classification of hard reline materials, based on the main component in the liquid, are MMA-based and non-MMA-based. MMA-based reline materials include Unifast Trad® (GC Corp., Tokyo, Japan), Probase Cold® (Ivoclar, Liechtenstein), and Palapress Vario® (Heraeus Kulzer, Wehrheim, Germany). Examples of non-MMA-based reline materials are Kooliner® (Coe Laboratories, Chicago, USA), Ufi gel hard® (Voco, Cuxhaven, Germany), and Tokuso Rebase II® (Tokuyama Dental Corp, Tsukuba, Japan). The non-MMA-based reline material monomers are higher molecular weight molecules that cause less tissue irritation. The MMA-based reline materials adapt well to the denture base; however, oral irritation can occur due to the residual monomer.[6-8]

Adhesion failure between the reline material and the denture base also causes the accumulation of bacteria and color change.[5,9,10] Adhesion failure also reduces the strength of the denture base.[5,9,11,12] There have been many techniques employed to increase the bond strength of the reline materials and denture base, such as grinding the denture base surface[13], using particles to create surface abrasion[14], and applying various chemical agents such as MMA[15-18], methylene chloride[15,19], chloroform[17], acetone[14,17], ethyl acetate[20], MF and MA[21,22]. However, chloroform and methylene chloride are carcinogens.[17] In addition, methyl methacrylate is irritating and can cause an allergic reaction.[23]

Vallittu *et al.,* 1994 concluded that MMA wetting time of 180 s was recommended to strengthen repaired acrylic resin.[18] Asmussen *et al.,* 2000 found that MF and MA surface treatment improved the shear bond strength between hard reline materials and denture base when using methylene chloride and compared to using ethyl acetate.[19] Thunyakitpisal *et al.,* 2011 found that the application of an MF-MA solution on the denture base surface for 15 s before doing repair work significantly increased flexural strength.[21] In addition, Osathananda and Wiwatwarrapan, 2016 also found that applying an MF-MA solution increased the shear strength between hard reline and denture base compared with using the adhesive recommended by the manufacturer.[22] A comparative study of the effect of the MF-MA surface treatment on flexural strength of the relined denture base has not yet been reported.

The objective of this study was to evaluate the effect of MF-MA surface treatment on flexural strength of relined denture base. The first null hypothesis was that the flexural strength of relined denture base groups with various chemical surface treatments were not significantly different from that of the untreated surface group. The second null hypothesis was that the flexural strength of relined denture base groups with various hard reline materials were not significantly different from each other. The third null hypothesis was that there was no significant difference in flexural strength between the relined denture base groups with various chemical surface treatments.

Materials and methods

The heat-cured acrylic denture resin, hard reline materials, and chemical agents used in this study are shown in Table 1. One hundred specimens of heat-cured acrylic denture base (Meliodent®) (64x10x2 mm) were prepared in a denture flask (Fig.1(a)) as recommended in ISO 20795-1 (2013).[24] The specimens were finished with 500-grit silicon carbide paper (TOA, Thailand) using an automatic grinding and polishing unit (Minitech 233, France) and then placed in a split metal mold (64x10x3.3 mm, Fig. 1(b)) and relined with their relining material (Fig. 1(c)).

The specimens were randomly divided into ten groups: Groups I, II and III were relined with Unifast Trad®; Groups IV, V, and VI were relined with Kooliner®; Groups VII, VIII, IX and X were relined with Tokuyama® Rebase II Fast. Groups I, IV and VII were the untreated surface control groups, Groups II, V and VIII were surface treated with Unifast Trad® (MMA) liquid for 180 s (by brush every five seconds) and then wait for 30 seconds to evaporate; Group III, VI and IX were surface treated with MF-MA solution (25:75 by volume) for 15 s (by brush every five seconds) and then wait for 30 seconds to evaporate; and Group X was surface treated with Tokuyama® Rebase II Fast adhesive following the manufacturer instructions.

The reline side of specimens were finished with a 500-grit new silicon carbide paper using an automatic grinding and polishing unit (Minitech 233, France) and stored in water at 37±1°C for 48±2 h. The flexural strength was measured by a universal testing machine (SHIMADZU, EZ-S 500N model, Japan) at a crosshead speed of 5 mm/min (Fig. 1 (d)). The flexural strength (MPa) was calculated using the following equation:

$$\delta = \frac{3Fl}{2bh^2}$$

Where δ = flexural strength (MPa)
F = the load (N) at fracture
l = the distance between supports (mm)
b = mean of specimen width (mm)
h = mean of specimen height (mm)

Table 1 Types of materials and their manufacturers were used in this study

Product name	composition	Manufacturer
Heat cured denture base		
Meliodent®	Powder:PMMA Liquid: MMA	Kulzer, German
Hard reline resins		GC America, USA
-MMA based	Powder:PMMA	
Unifast Trad®	Liquid: MMA	
-non-MMA based		
Kooliner®	Powder:PEMA Liquid:IBM	GC America, USA
Tokuyama® Rebase II Fast	Powder:PEMA Liquid: AAEMA, 1,9-NDMA	Tokuyama Dental Corp, Japan
Adhesive	ethyl acetate& acetone	
Chemical solvent		
Methyl formate		Merck Schuchardt OHG, German
Methyl acetate		Merck KGaA, German

PMMA, Poly(methyl methacrylate); MMA, Methyl methacrylate; PEMA, Poly(ethyl methacrylate); IBM, Isobutyl metacrylate; AAEMA, 2-(Acetoacetoxy) ethyl methacrylate; 1,9-NDMA, 1,9 Nonanediol dimethacrylate.

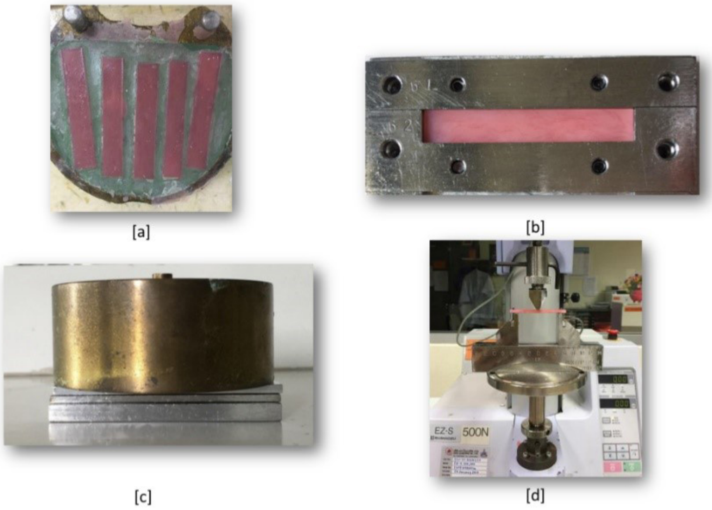

Figure 1 *(a) Heat-cured acrylic denture base (64x10x2 mm) specimens were prepared in a denture flask. (b) The specimens were placed in split metal mold (64x10x3.3 mm), applied with their respective surface treatment agent, and relined with a re lining material. (c) pressed lightly topped with 1 kg iron. (d) Flexural strength test.*

The data were analyzed using SPSS software version 22.0 (SPSS Inc., Chicago, IL, USA). The results were statistically analyzed by two-way ANOVA (group I-IX) and one-way ANOVA (group I-X) where significant differences in the groups in each row and each column were found, the group means were compared using Tukey's test at a 95% confidence level.

Result

The data were analyzed by using the Kolmogorov-Smirnov test to determine data distribution. The results showed that all data were normally distributed in all groups (p>0.05). The mean flexural strength and standard deviation of each group is presented in Table 2. The surface treatment and type of reline materials affected on the flexural strength (p<0.05) and the exact P-values are presented in Table 3 and Table 4.

For each material, the flexural strength of the surface treatment groups were significantly higher compared with the control group (p<0.05). The MF-MA treated group also had a significantly higher flexural strength compared with the MMA treated group for each hard reline material (p<0.05). However, in Tokuyama® Rebase II groups, there were no significant differences in the mean flexural strength between the groups treated with MMA or adhesive (p>0.05). For the same surface treatment, the flexural strength of Unifast® was significantly higher than that of Kooliner® (p<0.05), and the flexural strength of Kooliner® was significantly higher than that of Tokuyama® Rebase II (p<0.05).

Table 2 *The mean flexural strength with standard deviation of each reline material and surface treatment.*

Surface treatment	Reline materials		
	Unifast®	Kooliner®	Tokuyama® Rebase II
Control	$79.56 \pm 2.35^{a, A}$	$72.28 \pm 2.47^{a, B}$	$60.05 \pm 2.45^{a, C}$
MMA	$88.94 \pm 3.72^{b, A}$	$76.42 \pm 3.18^{b, B}$	$64.60 \pm 2.22^{b, C}$
MF-MA	$97.53 \pm 2.36^{c, A}$	$81.09 \pm 2.17^{c, B}$	$71.97 \pm 2.48^{c, C}$
Adhesive	-	-	65.95 ± 2.57^{b}

****Same uppercase letter indicates no significant difference between the group in each row (p>0.05)*
****Same lowercase letter indicates no significant difference between the group in each column (p>0.05)*

Table 3 *Two-way ANOVA analysis of the mean flexural strength.*

Source	Type III sum of squares	df	Mean square	F	*P*
Corrected model	10757.685[a]	8	1344.711	192.297	< 0.005
Intercept	532774.108	1	532774.108	76187.921	< 0.005
Surface treatment	2497.784	2	1248.892	178.594	< 0.005
Reline materials	8032.067	2	4016.034	574.302	< 0.005
Surface treatment*reline materials	227.833	4	56.958	8.145	< 0.005
Error	566.424	81	6.993		
Total	544098.217	90			
Corrected total	11324.110	89			

Table 4 *The exact p-value in this study.*

Materials	Group comparison	Sig.
Unifast ®		
	Control- MMA	0.000
	Control- MF-MA	0.000
	Control- Kooliner® control	0.000
	Control- Tokuyama® Rebase II control	0.000
	MMA- MF-MA	0.000
	MMA- Kooliner® MMA	0.000
	MMA- Tokuyama® Rebase II MMA	0.000
	MF-MA- Kooliner® MF-MA	0.000
	MF-MA- Tokuyama® Rebase II MF-MA	0.000
Kooliner®		
	Control- MMA	0.023
	Control- MF-MA	0.000
	Control- Tokuyama® Rebase II control	0.000
	MMA- MF-MA	0.005
	MMA- Tokuyama® Rebase II MMA	0.000
	MF-MA- Tokuyama® Rebase II MF-MA	0.000
Tokuyama® Rebase II		
	Control- MMA	0.008
	Control- MF-MA	0.000
	Control- Adhesive	0.000
	MMA- MF-MA	0.000
	MMA- Adhesive	0.978
	MF-MA- Adhesive	0.000

Discussion

The present study compared the bond strength of relined denture base using different surface treatments and hard reline materials as demonstrated by flexural strength. Vallittu *et al.,* 1994 concluded that MMA wetting time of 180 s was recommended to strengthen repaired acrylic resin.[18] In addition, Thunyakitpisal *et al.,* (2011) found that applying an MF-MA solution on the denture base surface for 15 s before repair significantly increased its flexural strength.[21] Thus, the present study used surface treatments with MMA 180 s and MF-MA for 15 s to improve the bond strength between the hard reline and denture base materials. Unifast Trad® and Kooliner® do not have adhesive from the manufacturer, thus this study did not apply adhesive in this group.

For each hard reline material, the mean flexural strength of various solvent treated groups were significantly higher compared with the untreated group. The bonding mechanism of relined denture base occurs when the surface treatment solvents dissolves and swells the denture base surface and evaporates, causing swelling of the surface layers. The monomer in the reline material subsequently diffuses and penetrates into the pores of the denture base and polymerizes to form an interpenetrating polymer network.[27] Three solvents were used for the denture base surface treatment (MF-MA, MMA, and Tokuyama Rebase II adhesive (ethyl acetate and acetone)). The dissolution efficiency can be explained by the relative closeness of solubility parameters and polarities of PMMA and the solvents. The solubility parameters of various solvents are closed to acrylic denture base (PMMA, 18.3 MPa½). These solubility parameters of MMA, MF, MA, ethyl acetate, and acetone are 18.0, 20.9, 19.6, 18.2 and 19.7 MPa½, respectively. The first null hypothesis was rejected.

For each hard reline material, the mean flexural strength of the MF-MA treated group was significantly higher than that of the MMA treated group and the manufacturer adhesive treated group (for Tokuyama® Rebase II Fast). The MF, MA and MMA have similar polarities due to their methyl ester groups that enhance their ability to soften an acrylic denture base while the other solvents have different functional groups. Acetone has ketone group. Ethyl acetate is ethyl ester. The dissimilar polarity of ethyl acetate and acetone to PMMA is likely to bring these compounds out of the range of effective solubility. In addition, the molecular weight of the solvent has an effect on the softening efficacy in which lower molecular weight promotes the faster kinetics of diffusion. MF (60.05 Da), MA (74.08 Da), acetone (58.08 Da), and ethyl acetate (88.11 Da) have a lower molecular weight than MMA (100.12 Da) which promotes greater solubility to the denture base.[26]

The boiling point of solvents also affects the bonding process that lower boiling point of solvent causes easier evaporation and takes less chair-time. Methyl formate (31.8°C) has the lowest boiling point compared to the other solvents. Methyl acetate (56.9°C) and acetone (57°C) have a similar boiling point. Ethyl acetate and MMA have a higher boiling point of 77.1°C, 101°C, respectively. A higher molecular weight and boiling point of MMA might provide lower solubility to the acrylic denture base material compared to the MF-MA solution. Ethyl acetate and acetone (in Tokuyama® Rebase II Fast adhesive) has a similar solubility parameter compared to PMMA but they have different functional groups in their chemical structure. Besides, ethyl acetate has a higher molecular weight and boiling point compared to MF-MA solution and acetone. Acetone has many requirements to promote PMMA dissolution similar to MF-MA except the different functional groups in chemical structure. The second null hypothesis was rejected.

In the same surface treatment, the flexural strength of Unifast Trad® relined group was significantly higher compared with those of the Kooliner® and Tokuyama® Rebase II Fast relined groups. The monomer (in liquid part) with a lower molecular weight can diffuse and penetrate and form an interpenetrating polymer network better than that with high molecular weight. The Unifast Trad® liquid contains MMA (100.12 Da) that are lower in molecular weight compared with the IBMA (142.20 Da) in Kooliner, or AAEMA (214.21 Da) and 1,9 NDMA (296.40 Da) in Tokuyama® Rebase II Fast.[28] Thus, the third null hypothesis was also rejected.

Conclusion

Surface treatment with MF-MA solutions significantly increases the flexural strength of a relined denture base. This study suggests the application of MF-MA solutions for 15 s before the relining procedure to improve the flexural strength between the denture base and hard reline materials.

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