

Residual monomer: effect on tensile bond strength of silicone resilient liners

Monômero residual: o efeito na resistência de união de reembasadores resilientes de silicone

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ABSTRACT

Adhesion failure between silicone resilient liner materials and denture base resin is a common problem found in clinical practice. Bond failure results in localized unhygienic conditions at the debonded regions and causes functional failure of the prosthesis. The aim of this study was to evaluate the tensile bond strength of 2 resilient liners (auto-polymerized silicone - Permafix[®] and heat-polymerized silicone - Permaflex[®]) under the influence of a residual monomer methylmethacrylate ($[MMA]_R$) concentration. Two polymethyl methacrylate (PMMA) specimens were prepared by implementing brass dies by means of a 3 mm thick spacer in a denture flask. Specimens (20 X 10 X 3 mm) were made by processing the resilient liners against the polymerized PMMA blocks. After polymerization, the brass spacer was removed from the mold, the PMMA blocks were trimmed, and the bonding surfaces were smoothed. The PMMA blocks were placed back into the molds and resilient liners were packed into the space provided by the brass spacer, followed by trial packing and polymerization according to manufacturer instructions. Twenty specimens were prepared and divided into 2 Groups (n=10) for each material: Group I (acrylic resin blocks were bonded to the resilient material immediately after processing), and Group II (blocks were bonded to the resilient material after storage in distilled water for 21 days at 37°C, aimed at decreasing the residual MMA). Tensile bond strength was measured in a universal testing machine at a crosshead speed of 5 mm/min. Two-way ANOVA and Tukey tests were used to analyze the data ($\alpha=0.05$). The results indicated that the materials tested showed a decrease in bond strength values (Group II). The silicone-based Permafix[®] had significantly ($p\leq 0.05$) low mean values. Within the limitations of this in-vitro study, storage of acrylic resin-based liners in water before bonding with specimens of resilient liner Permafix[®] may not provide long-term clinical success.

Uniterms: Denture liners. Acrylic resins. Tensile strength. Methylmethacrylate.

INTRODUCTION

Resilient denture liner materials are applied to the intaglio surface of dentures to achieve more equal force distribution, reduce localized pressure, and improve denture retention by engaging undercuts. Ideal properties of resilient liners include resiliency, which is desired over a long period of time, and a good bond to the denture base¹.

The resilient denture liners can be divided into 2 Groups: acrylic resin (which generally includes methacrylate polymers and copolymers, along with a liquid containing methacrylate monomer and plasticizers) and silicone (polydimethyl siloxane). Both groups are available in auto-polymerized or heat-

polymerized forms². It has been suggested that the initial softness of the plasticized acrylic resins results from the large amount of plasticizer (ethyl alcohol and/or phthalate) in the liquid, which would be responsible for maintaining the material softness^{2,3}. When immersed, these resilient liners undergo 2 processes: leaching out of plasticizers and other soluble materials and sorption in water and saliva, promoting the hardening of the material within a given period of time^{4,5}. On the other hand, the silicone resilient liners need no plasticizer to produce a softening effect². The silicone liner resiliency at mouth temperature is an intrinsic property of this type of polymer, thus the resiliency is retained for a

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longer period of use⁵. Unfortunately, silicone liners present a weak adherence to the PMMA from the acrylic denture base. The bond between the acrylic denture base and silicone liners is aided by the use of a silicone polymer (such as methyl siloxane) in a volatile solvent or by the use of alkylsilane bonding agents. Therefore the bond strength of the silicone denture base liners depends on the tensile strength of the materials and the adhesive used⁵.

It is likely that the bond between silicone resilient liner materials and acrylic denture bases depends on the presence of the free unpolymerized monomer within the denture base to produce chemical bonding to the bonding agent supplied by the manufacturer^{6,7}. However, it has been demonstrated that free radicals remain within the polymerized resins, which can lead to a continued polymerization, which in turn consumes the residual monomer upon time⁸. Therefore, the time elapsed between the polymerization of the acrylic resin and the lining procedure may well influence the bond strength among the different materials⁶.

The importance of measuring the levels of residual methylmethacrylate ($[MMA]_R$) in acrylic resins for prosthesis bases is reported in a number of studies, since these levels can damage the fibromucosa, acting as a disturbing agent as well as causing deleterious effects on the polymer properties⁹⁻¹⁵. It is known that the amount of residual MMA depends not only on the amount of monomer in the liquid/powder ratio, but also on the polymerization method of the acrylic resins. The purpose of this study was to evaluate the tensile bond strength of two silicone-based materials under the influence of a residual monomer. The hypothesis proposed was intended to prove a decrease in the concentration of residual monomer effect on the bond strength of silicone resilient liners.

MATERIALS AND METHODS

The heat-polymerized acrylic resin and two silicone resilient liners tested in this study are show in Table 1.

Table 1 - Materials, type, and manufacturer information for materials tested

MATERIALS	TYPE	LOT N°.	MANUFACTURER
QC-20®	Heat-polymerized PMMA resin	541940	Dentsply, Petrópolis, Brazil
Permafix®	Auto-polymerized silicone (two-paste system)	050401	Kohler, Neuhausen, Germany
Permaflex®	Heat-polymerized silicone (one-paste system)	050301	Kohler, Neuhausen, Germany

Twenty specimens, measuring 3 mm thick, 10 mm wide, and 20 mm long, were prepared for each silicone resilient liner tested. Two PMMA specimens were prepared by implementing brass

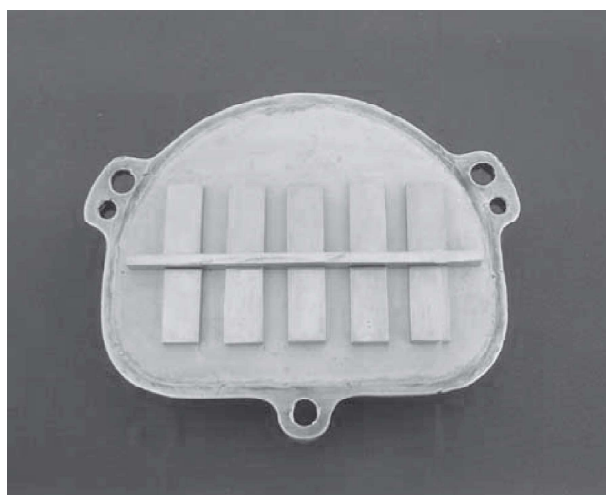


Figure 1 - Positioning of brass dies and spacer

dies by means of a 3 mm thick spacer in a conventional denture flask. The 3mm thickness in this experiment has been used in a variety of well-known studies^{2,5,16} and is considered ideal for resilient bases in clinical use. All dies and spacers were prepared using the same dimensions to standardize the shape of the denture base blocks and the thickness of the resilient denture liners. The dies and spacers were coated in a special laboratory silicone (Zetalabor – Zhermack, Badia, Polesine, Rovigo, Italy) to facilitate removal of the processed specimens from the flask (Figure 1).

Specimens were created by processing the resilient liners against polymerized PMMA blocks. The heat-polymerized acrylic resin was processed according to manufacturer instructions. After polymerization (immersion in boiling water, heat loss for 20 min, and further boiling water for another 20 min), PMMA resin specimens were removed from

the mold and trimmed. The surfaces to be bonded were smoothed with sandpaper and distilled water (number 240; Norton), cleaned, and dried. The PMMA blocks were placed back into the mold and the silicone resilient liner materials were packed into the space left by the brass spacers, trial packed, and polymerized according to manufacturer instructions. After polymerization, the specimens were removed from the flask and trimmed with a sharp blade. A total of 80 heat-polymerized PMMA resin blocks was processed. Half the blocks (n=40) were randomly selected and bonded to the resilient material immediately after processing. Under these conditions, 10 specimens were made for each resilient material and classified as Group I. The other 20 blocks were stored for 21 days in distilled water at 37°C in order to lower the concentration of the residual monomer. Storage water was replaced once a week. After this time, the silicone resilient liners were then bonded to the PMMA blocks. In this condition, 10 more specimens were made for each resilient material and classified as Group II. All specimens were placed under tension until failure in a universal testing machine (EMIC DL 500, São José dos Pinhais, Paraná, Brazil) at a crosshead speed of 5 mm/min (Figure 2).

The maximum tensile stress before failure was recorded for each specimen. Tensile bond strength values were calculated as the maximum load (N) divided by the cross-sectional area (mm²) of the specimen and recorded in megapascals (MPa). Results were tested by analysis of variance (ANOVA) and Tukey test. All data were analyzed at a 0.05 level of significance ($p \leq 0.05$).

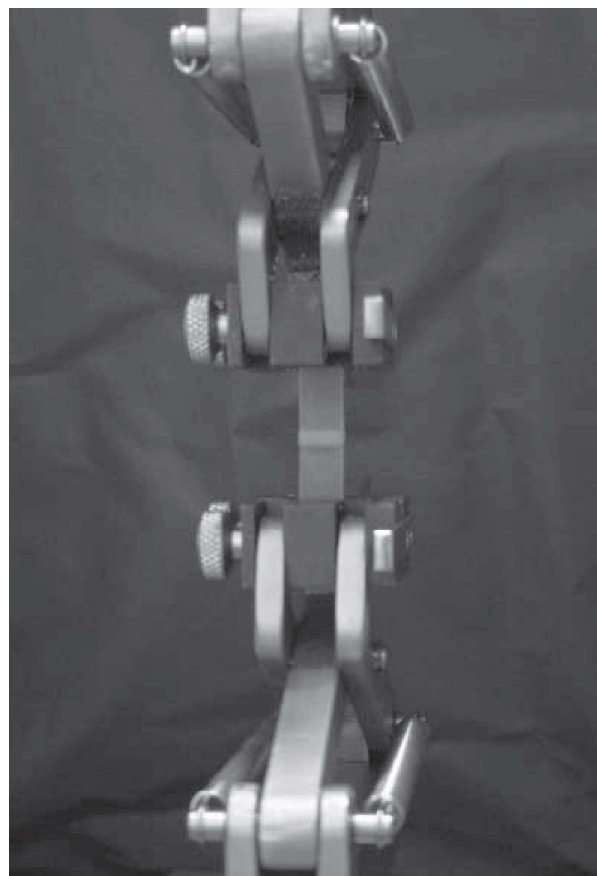


Figure 2 - Tensile specimen in universal testing machine

RESULTS

The two-way ANOVA results shown in Table 2 indicate that significant differences were found between the conditions of PMMA blocks (Group I and II) and materials.

Table 2 - Two-way ANOVA for comparison of bond strength values

SOURCE	SS	DF	MS	F	p
Groups (I and II)	4.67905	4	1.16976	13.74	0.000
Materials	3.31968	1	3.31968	39.01	0.000
Groups x materials	0.86691	4	0.21673	2.55	0.045
Error	7.65962	90	0.08511		
TOTAL	16.52526	99			

The mean and standard deviation (SD) values of tensile bond strength of specimens are

shown in Table 3.

Table 3 - Mean (SD) values of tensile bond strength (MPa) of resilient liner materials (n=10)

	BOND	STRENGTH	p
Group I	Permafix® 0.83 ^{Ab} (0.16)	Permaflex® 1.25 ^{Ab} (0.32)	ab (0.0201)
Group II	0.31 ^{Ba} (0.16)	1.11 ^{Ab} (0.33)	ab (<0.0001)
p	AB (0.0013)	AA (.9672)	

Different superscripted uppercase letters indicate statistically different means within each column ($p < 0.05$). Different superscripted lowercase letters indicate statistically different means within each row ($p < 0.05$).

The tensile bond strength of all resilient materials tested decreased after storage of the acrylic resin in distilled water. However, this phenomenon was statistically significant for auto-polymerized silicone Permafix® ($p=0.0013$). The mean bond strength of Permafix® varied from 0.83 to 0.31 MPa. Permaflex® (heat-polymerized silicone) presented the highest mean bond strength for the acrylic resin (QC-20®) in both Groups (1.25 MPa and 1.11 MPa, respectively).

DISCUSSION

There is a consensus in the literature that a decrease in residual MMA levels occurs after immersion in water for at least a 24-hour period¹¹. The storage of the acrylic resin should preferably be at 37°C¹⁴.

In the present study, the heat-polymerized silicone behaved as the best lining material for clinical use, which is in accordance with findings from Hekimoglu and Anil¹⁷ and from Kulak-Ozkan *et al.*⁵ who also tested the material Permaflex®, although under thermocycling ageing. These authors observed a variation in the bond strength from 0.83 MPa to 0.68 MPa. Nevertheless, this decrease was not statistically significant ($p=0.13$). Taking into consideration the heat-polymerized silicone performance, high bond strength values for the material Permaflex® were also found in reports from Sertgöz *et al.*¹⁸. The bond strength of the resilient liners tested (Group I) varied between 0.83 MPa and 1.25 MPa. These values (greater than 0.44 MPa) showed that the resilient liners presented a satisfactory bond strength for PMMA denture base resin^{5,19}. According to this finding, one may question whether or not heat-polymerizing is in fact more relevant than the concentration of a residual monomer.

As reported by Kulak-Ozkan *et al.*⁵, Permafix® also presented the lowest bond strength values for the acrylic resin in the present study. It is possible that the decrease in bonding capacity of some materials is also due to the difficulty to achieve homogeneous pressure over the entire bond surface, when packing a resilient liner against an acrylic resin surface¹⁸. It can therefore be concluded that the bonding of resilient materials with different chemical compositions to the rigid acrylic base is highly dependent on the processing method²⁰. This finding also indicates why the heat-polymerized silicone (Permaflex®) presented a better behavior in relation to the auto-polymerized silicone Permafix®.

Concerning the processing method, studies by Kawano *et al.*²¹ and Kutay *et al.*²² compared the bond strength of resilient materials when processed

in conjunction with acrylic resins. It is important to note, however, that the difference in results from the work of Kutay *et al.*²² as compared to the present study was influenced, among other factors, by the use of an adhesive that increases bonding between silicones and the prosthesis acrylic base, considering that the solvent chemical composition is the main factor responsible for the bonding. The adhesives supplied by the manufacturers of silicone resilient liners are important bonding agents for the PMMA of the prosthesis base^{5,19}. Nevertheless, in this study, Permaflex® presented a solid bonding strength when attached to the rigid base of the prosthesis, without the need for any kind of adhesive.

The direct relationship of non-polymerized residual MMA from the acrylic base of the prosthesis in the bonding between the silicone liners and the acrylic resins⁸ was responsible for the choice of the acrylic resin QC-20®, taking into consideration the polymerization cycle suggested by the manufacturer. It is known that the conversion of monomer into polymer is a slow process. When done quickly, in a hot water bath, at a high initial temperature, an increase in residual MMA levels is expected due to a probable incomplete cure. Austin and Basker²³ observed a seven-fold increase in residual MMA levels in acrylic resin specimens under a short cycle (immersion in boiling water, heat loss for 20 min, and further boiling water for another 10 min). This cycle was similar to that used in this study and in the study by Bartoloni *et al.*¹², who found a lower level of residual MMA when converting the monomer into the Accelar20 resin (polymerization in boiling water for 20 min). Smith and Bains² highlighted the correlation between a greater amount of residual MMA, present in the polymerized acrylic resin, and the mechanical strength, whereas Woelfel²⁴ reported a potentially damaging effect of $[MMA]_R$ on mouth tissues. The concentration of the residual monomer is, therefore, strongly dependent on the efficiency of the polymerization process. Furthermore, the fact that the residual MMA continues to be consumed by the free radicals present in the polymerized resin⁸ provides further evidence to support that proposed by Machado, Breeding, and Puckett⁶, who found that the time elapsed between the making of the prosthesis and the resilient material fitting may well influence the coherence of bond strength.

Resilient liners, when correctly indicated, are highly valuable clinical materials. The durability of these lining materials may significantly vary due to handling techniques and the polymerization process.

CONCLUSION

Within the limitations of this study, the heat-

polymerized silicone (Permaflex[®]) was the material which presented the best performance regarding bond strength. The auto-polymerized silicone (Permafix[®]) demonstrated a significant decrease in bond strength values.

RESUMO

Falha na união entre reembasadores resilientes de silicone e base acrílica da prótese é um problema encontrado na prática clínica. A falha na união resulta em condições anti-higiênicas localizadas em regiões que apresentam descolamento, além de causar perda de função das próteses. O objetivo deste trabalho foi avaliar a resistência de união de 2 reembasadores resilientes de silicone (autopolimerizável - Permafix[®] and termopolimerizável - Permaflex[®]) sob a influência da concentração do monômero residual metilmetacrilato ($[MMA]_R$). Duas amostras de polimetilmetacrilato (PMMA) foram obtidas por meio da inclusão de matrizes metálicas separadas por um espaçador com 3mm de espessura em mufla. As amostras (20 X 10 X 3 mm) foram obtidas processando o material resiliente contra os blocos de PMMA polimerizados. Após a polimerização, removeu-se o espaçador, submeteram-se os blocos ao processo de acabamento, sendo as superfícies de união alisadas. Os blocos foram recolocados no molde e o material resiliente condensado no local ocupado pelo espaçador, de acordo com as instruções dos fabricantes. Foram preparadas 20 amostras (divididas em 2 Grupos / n=10) para cada material: Grupo I (blocos de resina acrílica unidos ao material resiliente imediatamente após o processamento), e Grupo II (blocos unidos ao material resiliente após armazenamento em água destilada por 21 dias (37°C), com o objetivo de diminuir a $[MMA]_R$). Os valores de resistência de união foram registrados numa máquina de ensaio universal com velocidade de carregamento de 5 mm/min. ANOVA e teste de Tukey foram utilizados na análise dos dados ($\alpha=0.05$). Os resultados indicaram que os materiais testados mostraram uma diminuição nos valores de resistência de união (Grupo II). O silicone Permafix[®] teve significativamente a menor média ($p \leq 0.05$). Dentro das limitações deste estudo *in vitro*, o armazenamento da resina acrílica em água, antes da união ao material resiliente Permafix[®], pode não prover longo tempo de sucesso clínico.

Descritores: Reembasadores de dentadura. Resinas acrílicas. Resistência de união. Metilmetacrilato.

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