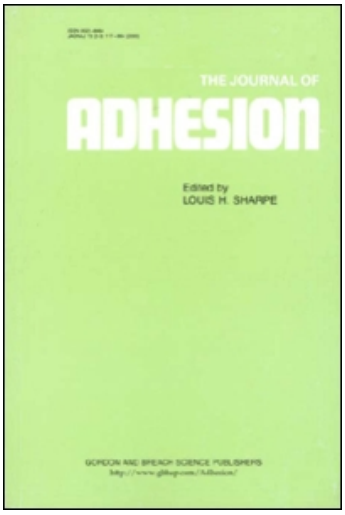

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Flexural and Bonding Properties of a Denture Base Polymer Treated with Nitric Acid or Ultraviolet Radiation Before Relining with Molloplast-B

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This study investigated adhesive forces and flexural strength of acrylic resin denture base relined with Molloplast-B soft lining material. To increase bonding between the two materials, the surface of the resin was modified with ultraviolet (UV) irradiation or nitric acid treatment. The peel strength greatly increased with nitric acid treatment because of the high polarity on the poly (methyl methacrylate) (PMMA) surface and the increase in the surface roughness, whereas low peel strength was seen with the UV treatment of the PMMA surface. Although both types of the surface pretreatment increased the flexural strength of PMMA-reline composites compared with the control and bulk PMMA groups, the increase in the UV-treated group was found to be higher than that of the nitric acid–treated group.

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Keywords: Flexural strength; Nitric acid treatment; Peel test; Poly (methyl methacrylate); Relining; Soft liner; Tensile strength; Ultraviolet irradiation

INTRODUCTION

Long-term soft denture liner materials are polymers used on the intaglio surface of dentures. Such materials are used for patients who cannot tolerate a hard-fitting surface of conventional denture base resin or to improve retention of the denture by engaging undercuts. The major requirements for long-term use of the soft lining materials are permanent resiliency, high dimensional stability (low water sorption and solubility), wettability by saliva, color stability, sufficient mechanical properties, good adhesion to the denture base, and compatibility with the oral tissues [1]. Among these, the load-bearing ability is critical to the clinical success of dentures lined with the soft materials. The vast majority of situations in which reline materials are applied call for both the reline material and the denture base to sustain masticatory load together. Therefore, information on the mechanical properties of the resilient liners and the denture base materials together is obviously clinically relevant in respect to strength of the relined denture rather than to the strength of bulk denture reline material alone [2,3].

Among desirable properties, physical requirements of resilient liners should include good adhesive properties and sufficient strength and elongation to breakage [4]. The typical mechanical test investigates the resistance to deformation or fracture of the bulk reline material under a flexural load [3]. In the previous studies examining flexural strength of specimens of denture base relined with hard liner materials, it was found that most of the hard liners exhibited moderately lower strength than bulk denture base specimens [3] and also that the flexural strength of relined denture base material was significantly higher than that of hard reline material alone [5]. Better bonding between base and liner materials has contributed to a higher flexural strength of the relined denture base [2,6,7]. So, it was important to investigate whether bulk denture base material could maintain its own flexural strength after relining with the silicone-based liner.

Clinically, the bond strength of the resin–base composite is especially important, because breakdown of the bond creates a potential surface for the microbial activity, plaque, and calculus formation [8–16]. Many of the studies have measured the bond strength between

the resilient liners and the denture base materials with peel [8,9,15,17–22], shear [8,15,17,23], and tensile [7,8,11,13–15,17,18] bond tests. The measured bond strength of resilient liners to poly (methyl methacrylate) (PMMA) is dependent on the nature of the test method used [8,18–20]. Braden *et al*. [9] and Wright [16] have reported that the adhesion of all resilient liners could be best characterized by a peel test.

Bonding to the denture base surface is a significant problem for resilient liner, especially for silicone-based ones; because of the differences in chemical composition between them and PMMA, chemical reaction does not occur [9,13,14,19,23]. Therefore, most of them are supplied with a primer, which acts as an adhesive between the two materials. Molloplast-B (Detax, Ettliugen, Germany) is widely used for relining and includes a curing agent, which reacts with reactive groups of the polymer, leaving methacrylate groups available to bond with PMMA [9,14,19,24–27]. Kutay [18] has shown that Molloplast-B failed adhesively when subjected to a peel test at low rates of separation. Wright [16] has found much higher peel values and stated that adhesion of Molloplast-B liner to PMMA was unreliable. To improve bonding between the silicone liner and PMMA, researchers have tried to alter the PMMA surface mechanically before applying a resilient material. However, data from these attempts is controversial. Some of the studies [28,29] have reported that bond strength to the roughened surface was higher compared with that of the smooth surface, because of the irregularities of the surface, which provide mechanical retention for the lining materials. Others [17,22,23] have reported that mechanical surface preparation with an acrylic bur, sandblasting and laser applications had an adverse effect on bonding between the two materials and could not be recommended. Thus, it is of interest to observe the modifications on PMMA surface with ultraviolet (UV) irradiation or nitric acid (HNO_3) treatments and also their effects on the flexural strength and bond properties of denture base material relined with Molloplast-B.

In this work, the surface of PMMA was treated by UV irradiation or HNO_3 application. After binding Molloplast-B, mechanical property changes were investigated by flexural and peel strength tests. Another concern was whether PMMA and resilient liner bulk materials could maintain their own strengths subsequent to the relining procedure. So, the flexural strength of bulk PMMA specimens was also determined. The null hyphotesis under this study is that PMMA denture base resin specimens treated with UV or HNO_3 before lining would give higher flexural and peel strength values compared with untreated PMMA specimens.

MATERIALS AND METHODS

The resilient denture lining material used in this study was Molloplast-B (Detax, Ettlingen, Germany) and the heat-cured denture base, poly (methyl methacrylate) (PMMA) resin, was Meliodent (Bayer Dental, Leverkuseu, Germany). For the determination of peel and flexural strengths, specimens were made according to test requirements.

For the peel tests, 15 specimens were prepared by packing and processing denture base resin into a rectangular mold of dimensions $75 \times 25 \times 2$ mm according to the manufacturer's instructions. Acrylic resin was mixed thoroughly at a powder/liquid ratio of 2.34 g/ml. It was packed in the space created by the wax pattern of the same size and polymerized in a conventional manner in dental flasks. Subsequent to polymerization, they were deflasked, and excess material was trimmed away with a scalpel. Acrylic specimens associated with the fresh wax patterns of the same dimensions were reflasked to create for a space for resilient lining material. After removing the wax, samples were divided into three groups of five specimens each. The surfaces of the samples were then treated with UV radiation or nitric acid: (1) UV irradiation at 245 nm and 750 W (Beckman Instruments GmbH, Munich, Germany) at 10 cm for 30 min (2) 1-M HNO_3 treatment (Sigma Aldrich Inc., St.Louis, MO, USA) for 1 min (these samples were then washed with distilled water to remove residual material left on the prepared surfaces); and (3) The untreated group saved as control samples. During the application of Molloplast-B, the denture base surface of all specimens was covered with a piece of tinfoil so that a specimen was produced in which 25 mm of the lining material was bonded and the remaining 50 mm remained unattached. Primer adhesive (Primo, Detax, Ettlingen, Germany) was used as the bonding agent for all reline–base composite specimens. This agent was applied onto the surface of PMMA to be bonded with Molloplast-B and held for 1 h, and the lining material was packed and processed using the recommended procedure (*i.e.*, 2 h in water at 100°C). The processed flasks were left to cool at room temperature for 20 min and were then put under running tap water for 10 min.

For the flexural test, 20 PMMA resin samples without treatment were constructed in the same manner with a dimension of $65 \times 10 \times 2$ mm, and they were randomly divided into four groups, each containing five specimens. Fifteen of them were used for reline–base composites. One group was subjected to UV irradiation, the second one was treated with HNO_3, and the third one received no treatment and served as a control. PMMA resin surfaces were treated with the UV or HNO_3 as mentioned in the peel test except for that the whole

surface of the PMMA resin to be bonded with liner was included. After application of the primer bonding agent, resilient lining material of the same dimension as the PMMA specimens was packed onto the acrylic surface for fabricating reline–base composites. The Fourth group, including the other five specimens of PMMA denture base resin, were used to determine flexural strength of the bulk material.

All specimens were stored dry for 24 h, and experiments were done at room temperature. Mechanical tests were performed on a universal testing machine (Lloyd NK 5, Lloyd Instruments Ltd., Fareham, Hampshire, UK). Peel specimens were tested at a constant cross-head speed of 10 mm/min. Peel strength was calculated using the following equation, where the peeling angle was considered 180° [16,17]:

$$\text{Peel Strength } (\text{Nmm}^{-1}) \frac{F}{d}\left(\frac{1+\lambda}{2}+1\right)$$

where F is applied force, d is width of the specimen in the peeling area, and λ is extension ratio of the liner (the ratio of stretched to unstretched length).

Flexural strength was measured by a three-point bending test, and the surface of the denture base material was placed face down for each specimen. A vertical load was applied at the midpoint of each specimen at a constant cross-head speed of 50 mm/min. The load and deflection curves of the specimens were recorded on a chart recorder. The flexural strength was calculated with the following formula [5]:

$$S = \frac{3FL}{2bd^2}$$

where S is flexural strength (MPa), F is applied load (N), L is span distance (mm), b is width of the specimen (mm), and d is thickness (mm) of specimen.

Data obtained from all tests were analyzed statistically by one-way variance analysis (ANOVA), and the Tukey-Least Significant Difference test (Tukey's LSD) test was used to make a pairwise comparison within the groups. The SPSS 12.0 (SPSS, Inc., Chicago, USA) software was used.

RESULTS

The peel test results for the mean values and standard deviations of three groups are tabulated in Table 1. The results showed that the peel strength was the highest when the specimen surface was treated with HNO_3 ($0.49 \pm 0.07\,\text{Nmm}^{-1}$), and this group revealed statistically significant differences from those of the control group

TABLE 1 Mean Values of the Peel Strength of Each Group (Nmm^{-1})

Groups	Mean ± SD
UV treated	$0.19 \pm 0.06^{b,c}$
HNO_3 treated	$0.49 \pm 0.07^{a,c}$
Control	$0.35 \pm 0.07^{a,b}$

Notes. $n = 5$. The groups with the same superscripted letters are statistically significant by the Tukey HSD test at the 5% level.

($0.35 \pm 0.07\,Nmm^{-1}$) and the UV-treated group ($0.19 \pm 0.06\,Nmm^{-1}$) ($p < .05$), respectively. The lowest peel strength among the group tested was recorded for the UV-treated group, which was statistically significantly different from the others ($p < .05$). Upon examining the mode of failure of treated specimens, it appeared generally that the HNO_3-treated specimens failed cohesively, with remnants of the Molloplast-B liner adhering to the PMMA denture base polymer, whereas UV-irradiated specimens showed adhesive failure in which no visible trace of material adhered on its counterpart.

The flexural strength results of the mean values and standard deviations for specimens of (a) Molloplast-B-bonded PMMA pretreated with UV, (b) the Molloplast-B-bonded PMMA pretreated with HNO_3, (c) control group, and (d) PMMA bulk material are tabulated in Table 2. The highest value was recorded for the UV-treated group with a value of 8.20 ± 1.09 MPa among the others. The ANOVA revealed that the mean values of the groups tested were different from each other. Tukey HSD test results showed that the flexural strength of the UV-irradiated group was statistically significantly different

TABLE 2 Mean Values of the Flexural Strength of Each Group (MPa)

Groups	Mean ± SD
UV treated	$8.20 \pm 1.09^{d,e}$
HNO_3 treated	7.03 ± 0.75
Control	5.94 ± 0.90^{d}
Bulk PMMA	5.74 ± 0.99^{e}

Notes. $n = 5$. The groups with the same superscripted letters are statistically significant by the Tukey HSD test at the 5% level.

from those of the control group (5.94 ± 0.90 MPa) and the bulk PMMA group (5.74 ± 0.99 MPa) ($p < .05$), respectively. However, there was no significant difference from the HNO_3-treated group (7.03 ± 0.75 MPa) ($p > .05$). On the other hand, HNO_3-treated-, control, and also bulk PMMA specimens were not found to be statistically different from each other with respect to this property ($p > .05$).

DISCUSSION

Failure of the bond between PMMA denture base resin and lining materials has been a significant reason for the limited use of the soft lined dentures. In this study, to increase the adhesion between them, the surface of the base material was modified with HNO_3 or UV irradiation. The lowest mean peel strength was recorded for the UV-treated specimens compared with HNO_3-treated and untreated specimens ($p < .05$). This result could be because in the case of UV irradiation, the polymer chains are cross-linked after a series of reactions such as hydrogen removal, radical production, hydroperoxide formation, branching and cross-linking and some others [30,31]. The surface hardness of the material caused by cross-linking can make the flow of soft lining material into the PMMA surface difficult, causing poor adhesion between the two materials, as in this case.

The reactions between HNO_3 and hydrocarbons have been well documented [32]. After HNO_3 treatment, some nitro groups ($-NO_2$) formed on the chain introduce high polarity on the PMMA surface. This polarity greatly increases adhesion and therefore the peel strength. In addition, nitration of hydrocarbons also breaks down long molecules. It is possible that nitrated polymer chains on the surface are broken into smaller chains. The decrease of entanglement increases the adhesion force on the surface. Moreover, some of the bonds that are broken by nitro groups may pick up oxygen groups from air and may change them into carboxyl groups, which are also polar. The treatment by nitric acid introduces surface roughness at the molecular level also. In addition to polarity, the surface roughness also improves adhesion. The former exhibits dipole interactions, whereas the latter introduces mechanical locking [22]. Such changes induced by HNO_3 treatment may explain why the peel strength of the HNO_3-treated group was the highest among the others ($p < .05$).

Flexural test results revealed that there was no significant difference in flexural strengths of the control reline–base composites and the bulk PMMA specimens ($p > .05$). This finding is not in agreement with those of previous studies [3,6]. Takahashi *et al*. [3] tested four different polymerized denture bases relined with four hard liner

materials in terms of flexural strength at the proportional limit and showed that all the relined denture bases had significantly lower flexural strengths than the bulk denture bases. However, Chai *et al.* [6] demonstrated that the relining procedure significantly increased the flexural strength of a heat-processed denture base resin as compared with that of the bulk of the denture base alone. The difference of our finding in this respect may be due to the types of lining materials used, as well as different test conditions. Chai *et al.* [6] tested a light-cured resin-based liner that is well known to have good adhesion with PMMA resin because of similar chemical composition [2,3]. Accordingly, they proposed that the denture base surface should not be unnecessarily altered during the reline procedure and that the bulk of the denture base should be preserved for optimum strength. In our case, the mean flexural strengths of the UV- or HNO,-treated specimens were found to be higher than those of the control and the bulk PMMA groups; however, only UV treatment had a significant effect on the flexural strength of the specimens with respect to those of the control and the PMMA bulk groups. This may be expected because the surface irradiation made an improvement on the overall elasticity of the PMMA as a result of cross-linking. From these results, the treatment of PMMA surface before lining may be useful in terms of flexural strength of reline–base composites.

CONCLUSION

The effects of two surface pretreatments were investigated in terms of flexural and peel strengths, and over research hypothesis was partly confirmed, because HNO_3 treatment significantly increased the peel strength of relined denture base, whereas UV irradiation of the PMMA surface decreased peel adhesion; however it provided a significant increase in flexural strength of the whole structure. Further experimental work including other bond strength tests is warranted to confirm the usefulness of these application methods.

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