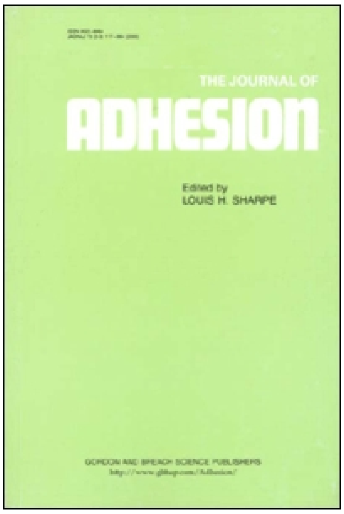

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Bond Strength of a Silicone Soft Lining Material to Poly(methyl methacrylate) Resin Treated with Maleic Anhydride and its Terpolymers

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Bond Strength of a Silicone Soft Lining Material to Poly(methyl methacrylate) Resin Treated with Maleic Anhydride and its Terpolymers

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This study investigated the effectiveness of surface treatment of Poly (methyl methacrylate) (PMMA) denture base resin on tensile bond strength between PMMA/silicone-based soft liner. A total of 25 specimens were fabricated and assigned into five groups ($n = 5$). The surfaces of PMMA were treated with maleic anhydride, maleic anhydride-styrene-vinyl-acetate, n-butylmaleate-styrene-vinyl-acetate, or n-pentamaleate-styrene-vinyl-acetate prior to Primo adhesive primer application and silicone liner placement. The Primo adhesive primer on applied group untreated dentuse base resin served as control. The tensile test was performed using a universal testing machine. Fractured surfaces were observed under Scanning Electron Microscopy (SEM) and spectroscopic interpretation of the interfaces was done by Fourier Transform Infrared (FTIR). Test results showed that surface treatment increased interfacial strength giving the highest value for n-butylmaleate-styrene-vinyl acetate treated group. SEM micrographs revealed that the specimens

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with n-butylmaleate-styrene-vinyl-acetate and n-penta maleate-styrene-vinyl-acetate terpolymers underwent cohesive failure. FTIR analysis indicated secondary interactions such as hydrogen bonding, possibly on acrylic resin surfaces, caused by the use of maleic anhydride and its terpolymers, and the adhesive.

Keywords: Infrared spectroscopy; Maleic anhydride; Poly (methyl methacrylate); Silicone-based soft liner; Surface treatment; Tensile bond strength; Terpolymers

INTRODUCTION

Acrylic resins, especially poly (methyl methacrylate) (PMMA), have been widely used as denture base resins in dentistry over the last five decades. These resins have a number of advantages, including ease of application and repair, esthetic appearance with addition of colorant, and low cost. However, in over-sensitive mucosal cases, patients are unable to tolerate such a hard denture base and must be provided with a permanent soft cushion on the fitting surface of the denture. The clinical benefits of soft denture liners have been recognized in prosthodontic practice for many years [1]. The development of polyvinylsiloxanes allows simple application procedures to be used [2]. They act as stress absorbers, enabling uniform distribution of pressure on denture bearing tissues, and reduce discomfort for patients with sharp or severely resorbed alveolar ridges and sensitive mucosa [1,3].

Soft denture liners have several problems associated with their long-term use such as the loss of softness, staining, porosity, poor tear strength, and colonization by *Candida albicans* [4,5]. Adhesion failure between the soft liner and the PMMA is one of the serious problems encountered in clinical practice. The bond failure may create a potential surface for bacterial growth, plaque, and calculus formation [3,6,7].

Bonding properties of soft lining materials have been evaluated by several investigators using tensile, tear, shear, and peeling tests [8–13]. McCabe *et al.* [5] using two adhesive systems, employed two different test methods (tensile and peel) to measure the bond strength between soft liner and acrylic resin, and concluded that both test regimes were relevant and suitable for gaining insight into bonding and debonding characteristics of soft liners bonded to an acrylic resin. The tensile properties are regarded as a general guide to the quality of rubbers [14]. In general, because silicone-based soft liners have lower tear strengths than other types of soft liners [15], the adhesive strength of such materials would best be characterized by use of a tensile bond test [16].

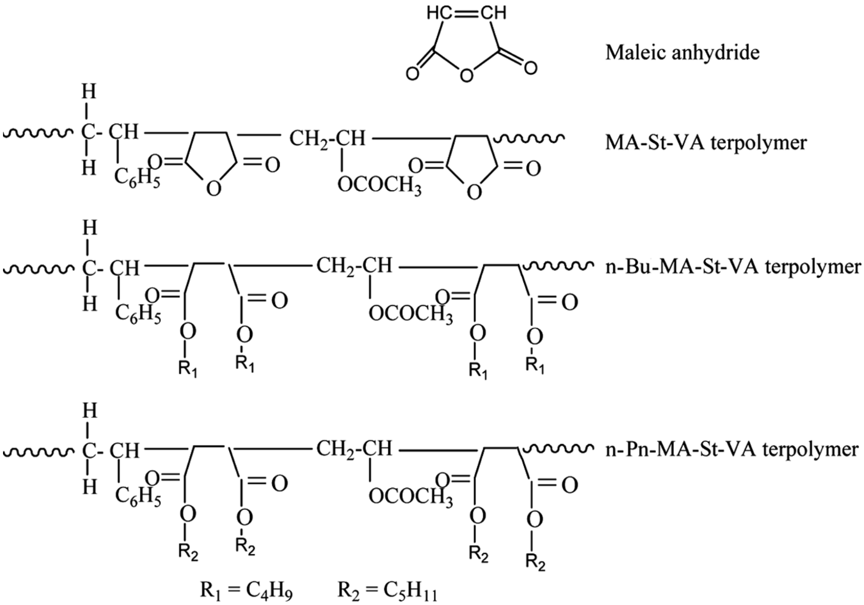
Silicone soft lining materials are a dimethyl siloxane polymer which is a viscous liquid that can be cross-linked to form a rubber with good elastic properties [17]. Since silicone has a different structural chemistry when compared with PMMA denture base resin, little or no chemical bond occurs between them [3,4,17,18]. Thus, the bond between the PMMA denture base and silicone soft liners depends on the effectiveness of the adhesive supplied. It is speculated that adhesive primers may consist of an organic solvent and adhesive monomer which react with both silicone and resin materials [18].

Researchers have attempted to develop other methods in order to improve the PMMA/soft liner bond [19–22]. Some studies reported that sand-blasting or laser treatment of the PMMA denture base resin surface preceding placement of a soft liner had provided mechanical locking for the soft material, thereby increasing the interfacial strength in varying degrees [19,20]. Recently, the effect of different reactive interfacial agents on interfacial strength has been studied [21,22]. Maleic anhydride (MA) is a reactive monomer that contains an unsaturated double bond and acid anhydride group. The presence of these groups leads to a variety of chemical reactions [23–25]. The product of simultaneous polymerization of two monomers with MA in the main chain forms a terpolymer structure. Different terpolymers of MA could increase adhesion between resin and lining materials. In a previous study [22], we have investigated the effect of surface treatment with maleic anhydride-styrene-vinyl acetate (MA-St-VA) terpolymer and some of its ester derivatives on the tensile bond strength of a silicone soft liner without using its adhesive primer. It has been found that the use of such agents could be effective on the bonds between the two materials. In the present study, MA and some of its ester derivatives, together with adhesive primer, were used and the effect of these agents on the tensile strength of silicone soft liner and acrylic resin interface were investigated. Spectroscopic interpretation of the interfaces was done by a Fourier Transform Infrared (FTIR) Spectrometer equipped with an Attenuated Total Reflectance (ATR) unit and also the type of failure was observed by use of a scanning electron microscope (SEM).

Materials and Methods

The soft liner used in this study was a silicone-based material (Molloplast-B, Detax, Ettlingen, Germany) and the denture base material was a heat-cured polymerized acrylic resin (Meliodent, Bayer Dental, Newbury, UK). Acrylic resin surfaces were treated with MA terpolymer or some of its ester derivatives such as MA-St-VA, n-butylmaleate-styrene-vinyl acetate (n-Bu-MA-St-VA), and n-pentamaleate-styrene-vinyl acetate (n-Pn-MA-St-VA) terpolymers, respectively. MA (Sigma Aldrich Inc., St.Louis, MO, USA) was recrystallizated in benzene by sublimation under vacuum and the terpolymers were synthesized and characterized as in our earlier work [22] The chemical structures of these terpolymers and MA are presented in Scheme 1.

For tensile bond strength testing of specimens, gypsum (Moldabaster S, Heraeus Kulzer GmBH, Hanau, Germany) molds were prepared with dumbbell-shaped brass patterns, 75 mm in length, 12 mm in diameter at the thickest section, and 7 mm at the thinnest section. Denture base resin was polymerized in the sealed molds keeping them in water at 70°C for 1 hour followed by boiling in a water bath for 30 min. Then the specimens were removed from the molds and 3 mm of the material were cut off from the thin midsection using a water-cooled diamond edge saw (Model No. 11-1280-250, Buhler Ltd., Lake Bluff, IL, USA). The surfaces to be bonded with soft liner were smoothed using 240-grit silicone carbide paper, cleaned, and dried. Fifty similar acrylic resin blocks corresponding to twenty-five acrylic resin specimens were thus obtained.



SCHEME 1 The chemical formula of the substances used.

The specimens were randomly assigned into five groups ($n = 5$) and their bonding surfaces were treated as follows: Group 1 was served as control and only Primo Primer was applied onto the surface; the resin surfaces of the specimens in the other groups 2, 3, 4, and 5 were treated with the solutions of the MA; MA-St-VA; n-Bu-MA-St-VA; and n-Pn-MA-St-VA together with Primo Primer, respectively. The solutions (100 mg/ml) of terpolymers were prepared separately in 5 ml tetrahydrofuran (Sigma Aldrich Inc., St. Louis, MO, USA) and applied immediately onto the surfaces of the acrylic resin with a brush in the other experimental groups. After applying the MA solutions and evaporation of solvent, the Primo Primer (Detax, Ettlingen, Germany) was also brushed onto the surfaces of all the specimens including the controls. In order to standardize the coating thickness for each application, the same brush was used by the same person. After waiting for one hour, the specimens (each including two trimmed acrylic blocks) were then secured back into the gypsum (Moldabaster S, Heraeus Kulzer GmBH, Hanau, Germany) molds, and Molloplast-B was applied between the acrylic resin blocks and then polymerized. This process was carried out according to manufacturer's instruction (for 2 h in boiling water). The processed molds were left to cool at room temperature for 20 min, and were then placed under running tap water for 10 min.

All the specimens were stored dry for 24 hours, and experiments were carried out at room temperature. Tensile bond strength tests were performed on a universal testing machine (Lloyd NK 5, Lloyd Instruments Ltd., Fareham, Hampshire, UK), using a crosshead speed of 50 mm/min in the vertical direction.

Tensile bond strength was calculated using the formula:

$$S = \frac{F}{D},$$

where S is tensile bond strength (MPa), F is the force (N), and D is the adhesion surface area (mm^2). After the collection of data, mean values and standard deviations were calculated by using a SPSS statistical software program (version 10.0, SPSS Inc., Chicago, IL, USA). Data obtained were then analyzed by Kruskall-Wallis and *post hoc* Tukey tests for pairwise comparisons of the groups at the 0.05 level significance.

After the specimens were tested and removed from the testing apparatus, the nature of the bond failure was viewed optically and categorized into adhesive, cohesive, or mixed. *Adhesive failure* refers to total separation at the interface between the soft liner and acrylic resin; *cohesive failure* refers to tearing within the soft liner material, and *mixed failure* refers to both. The fractured surfaces were examined by a low-angle SEM (Jeol JSM 6400, Noran Instrument, Tokyo, Japan) after gold-coating. Representative specimens were photographed at 16× magnification.

The fractured surface of one specimen from each group was also investigated spectroscopically, in order to evaluate chemical interactions between the materials after relining process, by a FTIR Spectrometer (Bruker, Vertex 70, Bruker Optics Inc., Ettlingen, Germany). The FTIR spectrometer was used with a diamond crystal PIkeMIRacle ATR unit. Fifty scans were obtained and averaged to a resolution of $4\,\mathrm{cm}^{-1}$.

RESULTS AND DISCUSSION

In this study, a tensile test method was preferred, because it applies a simple tensile load to the joint and allows for comparison among different materials [26]. It provides a fracture surface that can offer information about the structure of the boundary layers and the location of failure. The statistical results of the tensile bond strength measurements of the groups were summarized in Table 1. The highest tensile bond strength was obtained with n-Bu-MA-St-VA (4.84 ± 0.69 MPa); the control group yielded the lowest value (1.57 ± 0.54 MPa) among all the groups tested. The tensile bond strength values of the groups appeared to be different when they were compared by using Kruskall Wallis ($p < 0.05$). The pairwise comparisons of the groups showed no difference between the groups 2 and 3; and also between the groups 4 and 5 ($p > 0.05$), respectively. The difference of the other groups was found to be statistically significant ($p < 0.05$). These findings were in agreement with those of our previous study [22], in which

TABLE 1 Mean and Standard Deviation for Tensile Bond Strength of Each PMMA/Soft Liner Material According to Surface Treatment Type in MPa

Group	Treatment type	Tensile bond strength
1	Primo Primer (control)	1.57 ± 0.54
2	MA + Primo Primer	3.30 ± 0.97^{a}
3	MA-St-VA + Primo Primer	3.02 ± 0.65^{a}
4	n-Bu-MA-St-VA + Primo Primer	4.84 ± 0.69^{b}
5	n-Pn-MA-St-VA + Primo Primer	4.61 ± 0.56^{b}
Kruskall-Wallis test value 18.57		

$n = 5$.

The groups with the same superscripted letters shows no statistical difference by the Tukey test $p > 0.05$; other groups not superscripted are statistically different at $p = 0.001$, $p < 0.05$ significance level by the Tukey test.

n-Bu-MA-St-VA and n-MA-St-VA treated groups yielded higher tensile bond strength values (2.11 ± 0.21 MPa, 1.88 ± 0.11 MPa), compared with those of the untreated specimens without Primo Primer (0.74 ± 0.10 MPa), and with Primo Primer (0.88 ± 0.11 MPa), respectively. In the present study, the use of the MA and its derivatives together with Primo adhesive further improved the bond between PMMA/soft liner. This could be because of the better interaction of this adhesive with the terpolymers.

Denture soft liner material was polymerized on dry, freshly heat-cured PMMA denture base polymer and tested after 24 hours under dry conditions. The bond strength results obtained from this study were higher than those reported previously [27]. According to Kawano *et al.* [27], the values found for tensile bond strength between the soft liner and heat cured acrylic base might vary from 0.94 to 2.56 MPa when the lining materials are processed to polymerized PMMA. The higher values obtained in this study may be attributed to the surface treatment of PMMA preceeding placement of the liner. However, the water contents of polymers and the humidity of the testing environment may have an influence on the results. The effect of aging in water on the bond strength of soft lining materials has been discussed. While some studies have reported that aging in water does not have any effect on the bond strength of a heat-cured silicone soft liner to the denture base materials [28], others have suggested that longer immersion of specimens in water at 37°C or thermocycling of specimens at 5–55°C led to a marked reduction in bond strength [15,28]. Therefore, there is a need for further investigation including the effect of aging on bond strength between soft liner and PMMA treated with MA or some of its ester terpolymers.

The FTIR technique has been widely used to identify the types of specific interactions between different bonds that occur in various polymer systems [29]. In order to analyze chemical interactions between the materials, FTIR-ATR spectra of all sample surfaces, MA solutions, and the Primo Primer were determined (Figure 1).

The bond strength of silicone liners relies on the effectiveness of the adhesive, without the adhesive silicone denture base liners have little or no chemical adhesion onto PMMA resins. In an earlier study investigating the structure-property relationship of a soft denture liner [30], FTIR analysis and ^{1}H and ^{13}C Nuclear Magnetic Resonance(NMR) spectra have showed that Primo Primer was in the nature of 3-methacryloxypropyltrimethoxy silane. The methacrylate end of the adhesive bound chemically to PMMA resin (denture base material), while the silicone end bound to the soft lining material. PMMA, which has a double bond terminated by disproportionation

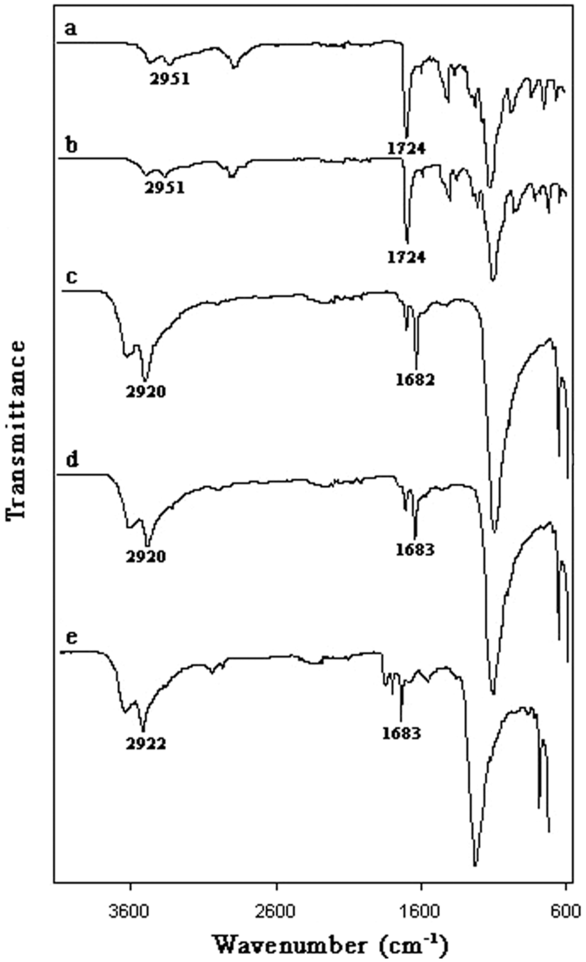


FIGURE 1 FTIR-ATR spectra of PMMA surfaces are of (a) Primo Primed sample (control); (b) MA and Primo Primer; (c) MA-St-VA and Primo Primer; (d) n-Bu-MA-St-VA and Primo Primer; and (e) n-Pn-MA-St-VA and Primo Primer.

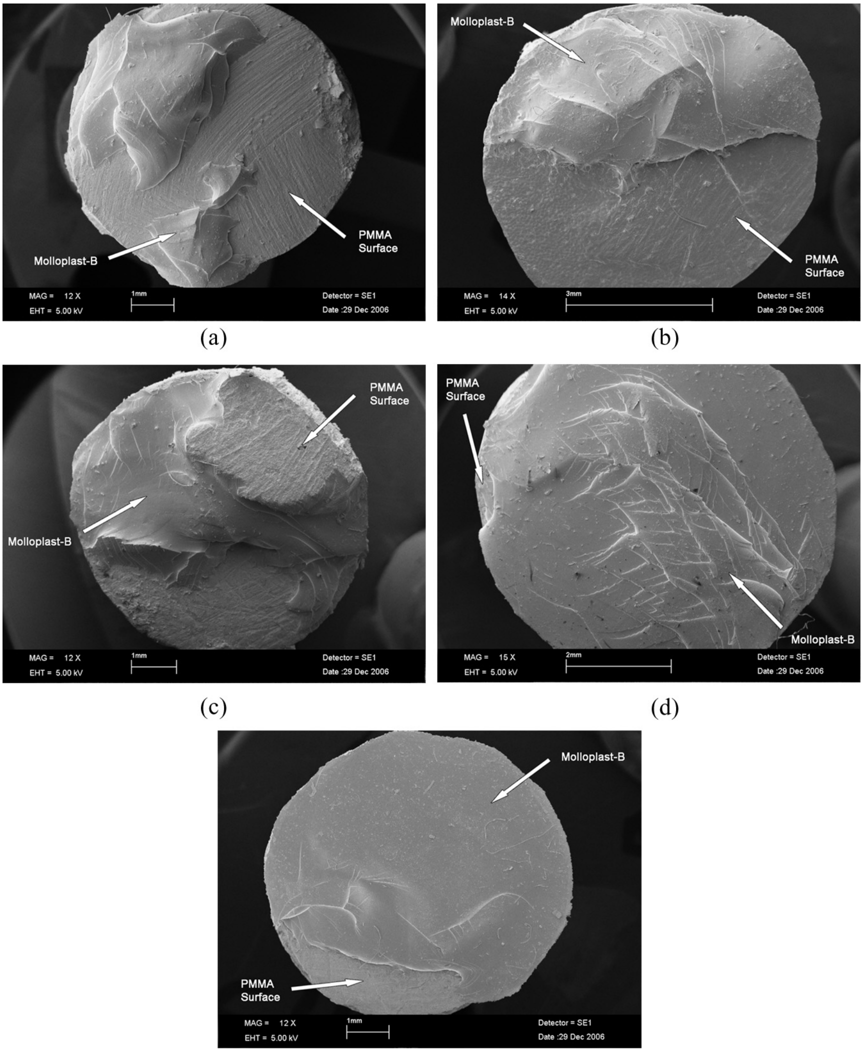
and other active centers, was compatible with the methacrylate end of the adhesive. As such, there would be both an additional reaction through vinyl groups and physical forces between similar groups (methacrylates). On the other hand, Si groups from the silicone soft lining material reacted with the methoxy-Si groups from silane. As a result, the adhesive bonded strongly to the soft lining material [30].

The FTIR spectra of the surface applied Primo Primer (Figure 1a) also showed chemical interactions such as hydrogen bondings between the PMMA resin and this adhesive.

The chemical structure of MA may not permit such kinds of interactions because sterically it is much less suitable. However, the tensile strength value of the specimens treated with MA (group 2) compared with that of control specimens may be attributed to the dipole-dipole interactions between the polar groups of MA and those of the Primo Primer and acrylic resin, respectively. The carbonyl bands in the FTIR-ATR spectra of the control and MA applied groups shifted from $1724\,\mathrm{cm}^{-1}$ to $1682\,\mathrm{cm}^{-1}$ and $1683\,\mathrm{cm}^{-1}$ in the samples PMMA/MA-St-VA, PMMA/n-Bu-MA-St-VA, and PMMA/n-Pn-MA-St-VA treated groups. This could be because of hydrogen bonding of the terpolymers with the carbonyl groups of the acrylic resin and Primo Primer (Figures 1 c, d, and e). The C-H bands of the control and MA applied groups shifted from $2951\,\mathrm{cm}^{-1}$ to $2920\,\mathrm{cm}^{-1}$ due to hydrogen bonding between the carbonyl of the terpolymers with the hydrogens of the acrylic resin and Primo Primer (Figures 1 a–e). Furthermore, it could also be suggested that there was a dipole-dipole interaction between the polar groups of MA terpolymers and those of Primo Primer or acrylic resin.

Based on tensile bond strength values, the chemical interaction of n-Bu-MA-St-VA terpolymer with acrylic resin seemed to be more effective than others because of the chemical structure of this terpolymer. As there are the least steric difficulties and the highest free volume in n-Bu-MA-St-VA ester derivatives obtained with butyl alcohol, strong interactions could occur between these two materials [22]. Similarly, n-Pn-MA-St-VA treated groups could also give more improvement in the bond strength compared with those of the others. From the representative SEM images (Figure 2), it can be clearly seen that while the n-Bu-MA-St-VA and n-Pn-MA-St-VA terpolymer treated specimens predominated in the cohesive failure category (Figures 2d and e), the others underwent a mixed type of failure (Figures 2 a–c).

Increased surface roughness and mechanical locking should theoretically enhance the bond site and result in stronger bonds [19]. In dentistry, it is well known that acid-etching techniques have been used to provide stronger bonds between different materials including polymers. Surface roughening of PMMA treated with some chemical agents may also help soft liner adhesive penetrate deeper into the acrylic surface, allowing a more intimate and stronger bond. MA and its terpolymers used in this study were acid anhydrides (Scheme 1). For this reason, it could be suggested that they might



(a) (b)

(c) (d)

(e)

FIGURE 2 SEM view of fractured surfaces is of (a) the Primo Primed sample (control); (b) MA and Primo Primer; (c) MA-St-VA and Primo Primer; (d) n-Bu-MA-St-VA and Primo Primer; and (e) n-Pn-MA-St-VA and Primo Primed samples.

increase roughness of the acrylic surface by helping Molloplast-B to better bind on the acrylic surface.

Although the tensile test used in the present study is an acceptable method, the test conditions may not simulate the clinical situation, as the test specimens had two adhesive surfaces and clinical cases have a single adhesive surface. Thus, this has, of course, some limitations. In addition, factors such as processing methods, immersion in water, and changes in bond strength in the harsh oral environment should require further investigations to predict which type of treatment will provide better clinical service.

CONCLUSIONS

The surface treatment of PMMA with MA and some of its terpolymers, together with an adhesive agent, increased the tensile bond strength between silicone soft liner and PMMA denture base materials. The FTIR-ATR results showed that chemical changes were induced by MA, MA-St-VA, n-Bu-MA-St-VA, and n-Pn-MA-St-VA on the acrylic surfaces. Representative SEM images indicated that pretreatment of the PMMA surface with n-Bu-MA-St-VA, and n-Pn-MA-St-VA led to predominantly cohesive failure of Molloplast-B from the acrylic resin surface.

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