The effect of plasma treatment on the bonding of soft denture liners to heat cured acrylic resin denture base material and on some surface properties of acrylic resin polymer

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ABSTRACT

Background: Acrylic resin polymers used in dentistry, are usually with problems in bonding, especially failure of the bond with soft denture lining materials. The aim of this study is to investigate the effect of plasma treatment on tensile bond strength, wettability and on physical surface changes for acrylic resin polymer.

Materials and methods: Heat cured acrylic resin specimens with dimensions 8×10×30 mm were prepared for tensile bond strength test, in which each two acrylic specimens were joined by a 3-mm thick soft liner (Vertex Soft, Molloplast-B). Another heat curd acrylic resin specimens were prepared with dimensions 2×8×30 mm for wettability test and physical surface analysis. For each test done in this study, the specimens were grouped as control, oxygen plasma treated and argon plasma treated acrylic specimens.

Results: Plasma treatment increased the tensile bond strength for both Vertex and Molloplast-B soft lining materials, also induced a decrease in water contact angle values (i.e., increase in wettability) for oxygen and argon plasma treated groups compared with control group, with highly significant difference (P <0.01) among groups. AFM images showed a collection of new distinct nanograins and numerous grooves (pitlike-structures) after oxygen and argon plasma treatment with argon plasma treatment showed more new nanograins, deepest grooves and highest protuberances which increased the surface-roughness (i.e. nano-roughness) when compared with control and oxygen plasma treated groups.

Conclusion: Plasma treatment was an effective method for increasing tensile bond strength, wettebility, and induced physical topographical surface changes that increased the surface roughness(mainly after argon plasma treatment) for plasma treated heat cured acrylic resin specimens.

Key words: plasma treatment, tensile bond strength, wettability, AFM analysis. (J Bagh Coll Dentistry 2012;24(3):29-35).

INTRODUCTION

Polymer surfaces usually present problems in bonding and finishing due to their low hydrophilicity [(1)]. Soft polymers (Denture Liners) have been used for almost 40 years as lining materials for dentures in the short-term prosthodontic management of denture-supporting mucosa. In general, the most common drawbacks with regard to the use of soft liners are poor adhesion to the denture base and the loss of softness over time [(2)]. Many studies have revealed improved adhesion of polymers by plasma treatment [(3)]. Plasma is a partially or wholly ionized gas with a roughly equal number of positively and negatively charged particles [(4)]. With plasma treatment, the surfaces of polymers can be improved in terms of hydrophilicity by forming oxygen-containing functional groups, such as C=O and –OH, [(5)]. These effects result in acid-base interactions and covalent linkages. Where some of these effects overlap, bonding enhancement is thus successfully achieved through plasma treatment [(6)].

MATERIALS AND METHODS

Heat cured acrylic resin (PMMA) specimens were prepared for each test done in this study.

These specimens were prepared from SR Triplex hot, heat-cured acrylic denture base material (Ivoclar Vivadent, Germany).For each test done in this study, the specimens were grouped as control plasma untreated, oxygen plasma treated and argon plasma treated acrylic specimens.

Plasma treatment

In this study a plasma apparatus with parameters: 800 V, 75 mA, power 60 W, with 2 minutes exposure time**,** with the plasma source was kept 4cm above the test specimens, were used for all tests of this study with the application of two types of plasma treatments (oxygen and argon plasma treatments).

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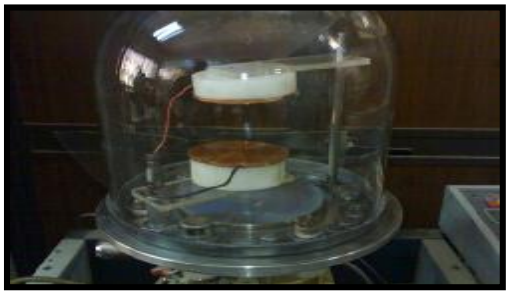

Figure 1: Plasma apparatus.

Tensile bond strength test: Two hundred and forty rectangular heat cured acrylic resin specimens with dimensions 8mm×10mm×30mm as width, height, and length respectively, were prepared, in which each (2) specimens were joined by a 3-mm thick soft liner disk **(7)**, to finally reproduce (120) specimens which were grouped as: 40 control specimens without plasma treatment, 40 oxygen plasma treated specimens, and 40 argon plasma treated specimens. each 40 specimens for each group was subdivided into 20 specimens with application of Molloplast-B soft liner and 20 specimens with application of Vertex Soft liner.

For tensile bond strength test the following procedures were done:

1. Preparation of acrylic resin blocks: A mold was made by investing a metal piece of dimensions 8×10 mm² cross-sectional area and 30 mm length, in hard but flexible silicone rubber (Addition silicone duplicating material). The obtained mold was then used to fabricate rectangular wax blocks, which in turn were used to produce the rectangular acrylic resin blocks. Proportioning and mixing of acrylic was done according to the manufacturer's instructions with ratio 2.25 gm (powder): 1 ml (liquid). The packing process was performed while the acrylic was in the dough stage. According to the manufacturer's instructions, polymerization was carried out by placing the clamped flasks in cold water, heat them up to 100 ºC, and let boil for 45 minutes. All the other acrylic blocks were prepared as the previously mentioned method. After that, the bonding surfaces of all the acrylic blocks were smoothened using 240-grit aluminum oxide paper. All specimens should be cleaned by means of ultrasonic cleanser machine, and dried. Only the 40 rectangular acrylic resin blocks for oxygen plasma treatment group and the 40 rectangular acrylic resin blocks for argon plasma treatment were exposed to plasma treatment.

2. Preparation of tensile bond strength test specimens: A second mold was made by investing a metal sample of 8×10 mm² cross-sectional area and 63 mm length. The 3 mm represent the spacer length between each two acrylic blocks for packing of soft liner material (Vertex Soft, Molloplast-B), in hard but flexible silicone rubber investment material. The obtained mold was used to fabricate the tensile bond strength test specimens by processing the soft liner against the two rectangular acrylic resin blocks, so each 2 acrylic blocks were placed back into the mold and the soft liner was packed into the space between two blocks, trial packed, and polymerized according to the manufacturer's instructions.

Figure 2: Rubber mould for preparation of tensile bond strength test specimens.

Figure 3: Tensile test specimen with Molloplast-B.

Soft Liner Materials polymerization procedure was done according to manufacturer's instructions for each material as illustrated in table (1).

3. Preparation of artificial saliva: An electrolyte composition similar to that of human saliva was used in this study **(8)** which includes: 1. [1 g] Sodium carboxy-methyl-cellulose. 2. [4.3 g] Sorbitol. 3. [0.1 g] Potassium chloride. 4. [0.1 g] Sodium chloride. 5. [0.02 mg] Sodium fluoride. 6. [5 mg] Magnesium chloride. 7. [5 mg] Calcium chloride. 8. [40 mg] Potassium phosphate. 9. [1 mg] Potassium thio-cyanate. 10. [100 ml] Distilled de-ionized water. Before tensile bond strength testing, all tensile bond strength specimens were stored in artificial saliva substitute **(9)** in an incubator at (37Cº) for two periods in which half the specimens were stored for 48h and the other were stored for 12 weeks.

4. Tensile bond strength test procedure: The rectangular tensile bond strength test specimens

were tested using Instron testing machine with a suitable grips for the test specimens. The specimen was subjected to tensile bond with crosshead speed 5 mm/min with maximum load capacity 1000 N. Force at failure was recorded in Newton. The value of tensile bond strength were calculated for each test specimen as the force at the de-bonding divided by a cross-section area of interface according to the following formula:

$$Bond\ strength = \frac{F(N)}{A(mm^2)}$$

Where: F= force at failure (N)

A= surface area of the cross section (mm^2)

Wettability test (water contact angle measurement): Three wax specimens were prepared with dimensions 2×8×30 mm, which in turn were used to prepare the (3) heat cured acrylic resin specimens. Immediately after preparation, the control specimen was measured for wettability test. The other two specimens were measured immediately after oxygen and argon plasma treatments. For wettability test, a versatile digital microscope was used. Each specimen was placed onto a glass microscope slide using double-sided tape to ensure a flat viewing surface. The glass slide was then placed onto a stage, where a 10-µL deionized water drop was dispersed from the pipette onto the surface. For each specimen, five measurements were taken immediately after plasma treatment. The values were averaged to obtain a final contact angle value.

Figure 4: Dino-Lite Digital Microscope.

Physical or Topography Surface Analysis (Atomic Force Microscopy or AFM Analysis): The surface topography/morphology of the untreated and plasma treated acrylic polymer specimens was analyzed and compared by atomic force microscopy. Also, the specimen dimensions' for (AFM) analysis were, 2×8×30 mm, as the same dimensions which were used for wettability test.

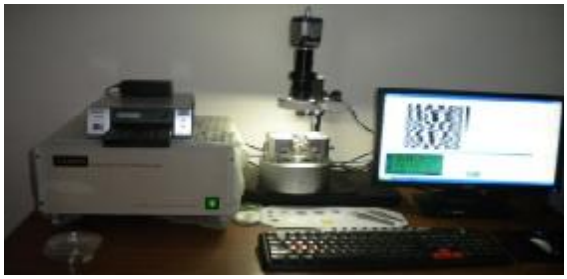

Figure 5: Atomic Force Microscope for AFM analysis.

RESULTS

Tensile bond strength test: The effect of oxygen and argon plasma treatments, on the tensile bond strength was tested and evaluated, as show in tables 2-9.

Wettability Test:

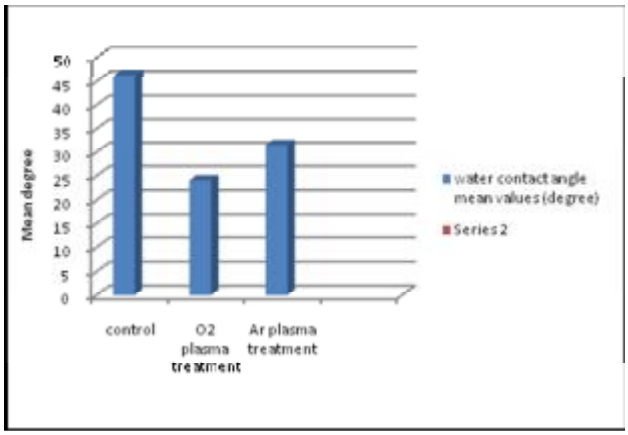

Figure 6: Polygon Illustrates the Mean Values of Water Contact Angles for Acrylic Polymer Specimens with Different Types of Surface Treatment.

AFM Analysis:

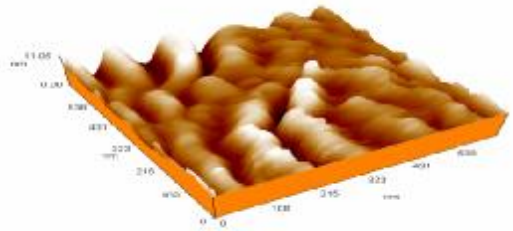

Figure 7: AFM Image for Control Acrylic Specimen: 3 Dimensions Image.

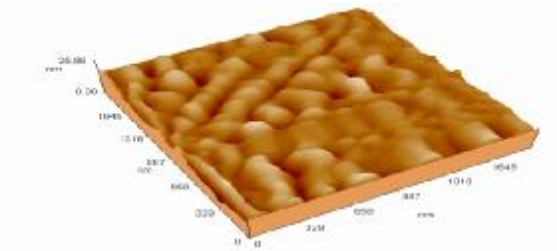

Figure 8: AFM Image for Oxygen Plasma Treated Acrylic Specimen: 3 Dimensions Image.

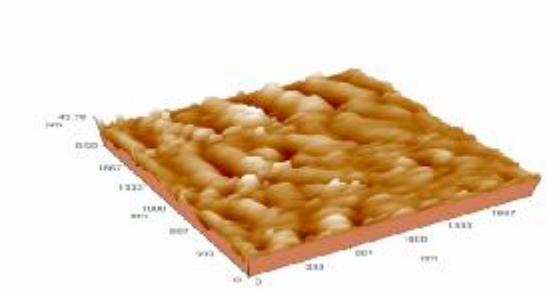

Figure 9: AFM Image for Argon Plasma Treated Acrylic Specimen: 3 Dimensions Image.

DISCUSSION

The Effect of Plasma Treatment on Tensile Bond Strength:

Based on the results obtained in this present study, both the oxygen and argon plasma treatments were increased and improved the tensile bond strength. As a discussion for these findings, for oxygen plasma treatment, these results might be due to the effects of chemical oxidation reactions and/or chemical etching process. During the oxidation reactions, plasma promotes adhesion by inducing further chemical reactions which generated new chemical functional groups on the O_2 plasma treated surface such as the hydroxyl group (-OH) which increased the hydrophilicity that enhanced the penetration of Vertex and Molloplast-B soft liners into the irregularities on the acrylic resin surface and contributed latter to the increase in the tensile bond strength that result after the oxygen plasma treatment, while during the chemical etching process, this process results in chemical removal of surface material that increased the effective surface area of the polymer (i.e., surface roughening). This roughening in turn promotes more intimate molecular contact between the plasma exposed polymer surface and the applied soft liner allowing for stronger bonds to occur. For argon plasma treatment, the increase in the tensile bond strength might be due to the effect of physical sputtering (i.e. physical removal of surface material) which increased the surface roughness that caused by the bombardment of highly energetic and high molecular weight argon particles that enhanced micromechanical interlocking between the Vertex or the Molloplast soft liners and the acrylic denture base material. These results were in agreement with the findings of study by [10] which showed that, argon and oxygen plasmas have also been shown to participate in surface sputtering in addition to modification, resulting in the physical removal of material from the surface, also in agreement with the findings of study by [11] which showed that, chemical etching process, physical sputtering occurs frequently as well when polymers are exposed to plasma. Also the results of this study were in agreement with the findings of studies by [12]; [13]; and [14] which revealed that, through the oxygen plasma treatment, oxygen-containing groups of C-O and C=O were effectively introduced onto the polymer surface due to the highly reactive property of oxygen plasma. The presence of oxygen-containing groups then improved the surface hydrophilicity of the plasma treated specimens.

The Effect of Plasma Treatment on Wettability: Results of the present study showed that, there was a decrease in water contact angle mean values after the application of oxygen and argon plasma treatments when compared with the control group for the acrylic polymer specimens. This may be due to either surface texture changes or oxidation functionality surface changes. There can be benefits of such interactions, such as the modification of hydrophobic or hydrophilic properties of polymers due to chemical modification and texturing [15].

The Effect of Plasma Treatment on Physical Surface Morphology: AFM images for the surfaces of the acrylic (PMMA) specimens (control, oxygen and argon plasma treated specimens) showed a collection of grooves (pitlike-structures), ridges, peaks, crater-like features and surface irregularities. Our results are consistent with the findings of [16]. AFM images after argon plasma treatment in this study had produced more new, distinct nanograins with smaller diameters, deepest grooves, highest protuberances and more regularity in granularity normal distribution chart which increased the surface nano-roughness due to physical sputtering as compared with oxygen plasma treated and plasma untreated groups. Differences in the topological features of (PMMA) surfaces

specimens may be attributed to the differences in their physical and chemical properties. AFM analysis had proved that, plasma treatment produced nano-roughness on the plasma treated surface mainly after the argon plasma treatment, and such roughness was beneficial for enhancing the tensile strength by creating mechanical interlocks between the acrylic resin polymer and the two types of soft liners that were used in this study.

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Table 1: Polymerization of Soft liners.

Type of soft liner	Polymerization procedure
Vertex Soft	1.2 gr (powder): 1 ml (liquid) Polymerization was done by placing the flask in cold water and heat up to 70 ºC for 90 min, then boil up to 100 ºC and left at this temperature for 30 min, then cool down flask slowly.
Molloplast-B	Ready-to-use paste Before packing of Molloplast-B, Primo adhesive should be applied by brushing Primo adhesive 1-2 times onto the entire bonding surface of each specimen. Let Primo air-dry for 60 min. prior to applying Molloplast-B. Polymerization was done by placing the flask in cold water and heat up slowly to 100 ºC. Polymerization in boiling water at 100 ºC for approximately 2 hours, then cool down flask slowly.

Table 2: Descriptive statistics of tensile bond strength for Vertex Soft.

Type of Soft Liner	Vertex-soft					
Type of surface treatment	Control without plasma treatment		(O2) plasma treatment		Argon plasma treatment	
Time of storage	48 h	12 weeks	48h	12 weeks	48 h	12 weeks
Mean	1.594	1.394	2.217	1.876	1.875	1.799
SD	0.111	0.084	0.249	0.150	0.112	0.142

Table 3: Descriptive Statistics of Tensile Bond Strength for Molloplast-B.

Type of Soft Liner	Molloplast-B					
Type of surface treatment	Control without plasma treatment		(O2) plasma treatment		Argon plasma treatment	
Time of storage	48 h	12 weeks	48h	12 weeks	48 h	12 weeks
Mean	1.408	1.228	1.687	1.404	1.775	1.615
SD	0.120	0.115	0.169	0.142	0.160	0.230

Comparisons between groups:

Table 4: LSD for Vertex-soft after 48h.

Type of surface treatment	48h	
	P-value	Sig
Control and Oxygen	0.000	HS
Control and Argon	0.000	HS
Oxygen and Argon	0.002	HS

Table 5: LSD for Vertex after 12 Weeks.

Type of surface treatment	48h	
	P-value	Sig
Control and Oxygen	0.001	HS
Control and Argon	0.000	HS
Oxygen and Argon	0.251	NS

Table 6: LSD for Molloplast-B after 48h.

Type of surface treatment	48h	
	P-value	Sig
Control and Oxygen	0.001	HS
Control and Argon	0.000	HS
Oxygen and Argon	0.251	NS

Table 7: LSD for Molloplast-B after 12 Weeks.

Type of surface treatment	12 weeks	
	P-value	Sig
Control and Oxygen	0.008	HS
Control and Argon	0.000	HS
Oxygen and Argon	0.026	S

Table 8: Descriptive Statistics for Wettability Test.

Type of surface treatment	water contact angle mean values (degree)	SD
Control	46.161	2.201
Oxygen plasma treatment	24.03	2.87
Argon plasma treatment	31.499	2.024

Comparisons between groups:

Table 9: LSD between Groups of Acrylic Polymer.

Type of surface treatment	P-value	Sig.
Control and Oxygen plasma treatment	0.000	HS
Control and Argon plasma treatment	0.000	HS
Oxygen plasma treatment and Argon plasma treatment	0.002	HS