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Research Article

The Effect of Incorporating Gold and Silver Nanoparticles in Orthodontic Adhesive System on Bond Strength of Orthodontic Bracket

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Received: April 05, 2017; **Published:** June 13, 2017

Abstract

Aim of the study: Increase the bond strength of orthodontic composite to reduce its clinical failure.

Methods: Silver nanoparticles (Ag NPs) and gold nanoparticles (Au NPs) were prepared using microwave assisted method by reduction of ($AgNO_3$) and ($HAuCl_4.3H_2O$) separately in ethanolic solution of polyvinyl pyrrolidone (PVP). The nanoparticles were added to the primer of orthodontic adhesive system. Three adhesive groups were used: group 1 (control), group 2 (10 µg/ml silver), group 3 (100 µg/ml gold). Thirsty six sheep's teeth were used in this study. The bonded brackets were subjected to shear loading until failure occurred. The data were analyzed using One-way ANOVA test. The primer–enamel surfaces were surveyed by environmental scanning electronic microscope ESEM.

Results: Group 1 showed the highest shear bond strength value (7.8 ± 2.8), while group 2 showed the lowest value (7.4 ± 1.96 MPa), group 3 shear bond strength was (7.7 ± 2.54 MPa). There was no significant difference in shear bond strength among the studied groups. The ESEM photomicrographs revealed same patterns of the primer infiltrated into pores of etched enamel surface for all groups.

Conclusions: Modification of two-steps etch and rinse orthodontic adhesive system with silver and gold nano-fillers separately did not affect the bond strength or the primer ability to wet enamel surface.

Keywords: *Nano Gold; Nano Silver; Primer; Scanning- Bond Strength Modification*

Introduction

Decades since their introduction into the field of orthodontics, composite resin adhesives undoubtly remain the first choice of most orthodontists for bonding brackets [2]. However, despite their popularity, some of failure rate still occurs.

Modifying the adhesion materials then investigates its effect is a successful and popular method to improve these materials. Recently different types of nanoparticles have been used in the formulation of restorative composite systems and dental adhesives [29]. Hydroxyapatite nanoparticles were added to dental adhesive, as a major component of inorganic tooth material; it might be a promising material for the preparation of new dental adhesives with improved mechanical and biological properties [29]. Adding titanium oxide (TiO_2) [28] and amorphous calcium phosphate [19] nanoparticles to orthodontic composite considered one of the procedures to improve its mechanical characteristics. A study of adding quaternary ammonium polyethylenimine nanoparticles indicated that these nanoparticles

immobilized in resin-based materials have a strong antibacterial activity upon contact without compromise in mechanical properties [6]. It has also been reported that an experimental dental composite material containing nanoparticles of copper is suitable to enhance the adhesive clinical performance [5].

Silver and Gold nanoparticles (NPs) have special characteristics that make them possible choice to be used as fillers for dental nanocomposite. They could stay in nano scale in presence of suitable stabilizer which means little aggregation or clustering and uniformly distributed particles [25]. They have high chemical stability and photo stability [10,11] makes them easy to be synthesized and manipulated. Biocompatibility makes them nontoxic for organism [20,30,33].

It was suggested that nanofillers can improve adhesion at the interface between the restorative material and the tooth structure through increasing mechanical strength of the adhesive layer and providing structural reinforcement [2]. The nanofillers are stress absorbing and have the role of an elastic layer between dental composite and enamel [2]. Others considered the presence of nano particles could deflect the micro-crack and effectively increase the resistance to the applied force [31]. Mechanical, electrical and magnetic adhesive behaviors were expected to be altered [15]. Interparticle forces such as van der Waals and electrostatic forces, as well as magnetic attraction, become stronger [15]. The Effect of adding gold NPs and silver NPs on enamel surface energy by increasing minor galvanic current inside the material also was suggested [32]. The presence of nanoparticles also improved the coefficient of thermal expansion and provided more dimensional stability [5].

Surveying the literature, limited studies were conducted to assess the effect of incorporating gold nanoparticles on bond strength in orthodontics. Accordingly, it seemed to be valuable to study the effect of incorporating gold and silver NPs on the shear bond strength (SBS) of an orthodontic adhesive.

Materials and Methods

Modifying the commercial Primer solution

Colloidal silver NPs solution and colloidal gold NPs solution were synthesized at concentration of 107 µg/ml and 100µg/ml respectively. The colloidal solutions were diluted in Transbond™ primer (3M Orthodontic Products, USA) and mixed for preparing the modifying primer solution. The solutions were diluted as follows:

- Each 5 ml commercial Primer was mixed with 0.5 ml colloidal silver solution. The concentration of the resulted modified Primer was 10.7 µg/ml.
- Each 1 ml commercial primer was mixed with 1ml colloidal gold solution. The concentration of the resulted modified Primer was 100 µg/ml.
- The solutions of both nano gold and nano silver were mixed using a micropipette then further mixing was done by Vortex at low speed for 30 seconds.
- Three solutions were used as primer: unmodified solution as control, one modified by silver, and one modified by gold.

Transmission electron microscope TEM (JEOL Ltd, Japan) examination was performed on the modified solutions to detect size and shape of the NPs silver figure 1 and gold figure 2. Energy dispersive x-ray analysis (EDXA) was done to the modified material to confirm that the particles seen by TEM are silver figure 3 and gold figure 4. Table 1 and table 2 demonstrate mass percentage and atomic percentage of the different elements detected.

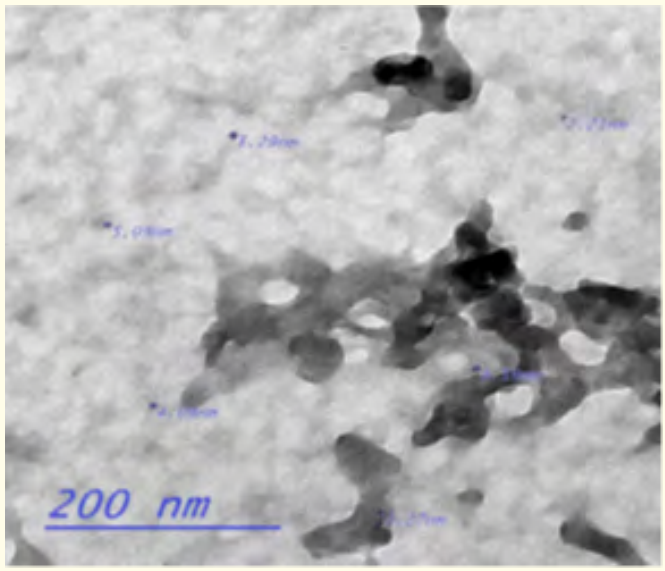


Figure 1: *TEM image showing the sizes of Silver particles incorporated in the primer.*

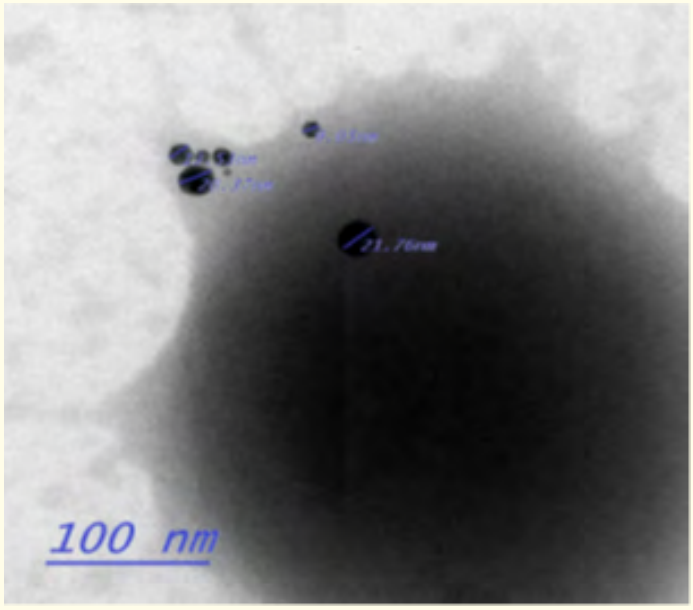


Figure 2: *TEM image showing the sizes of gold particles incorporated in the primer.*

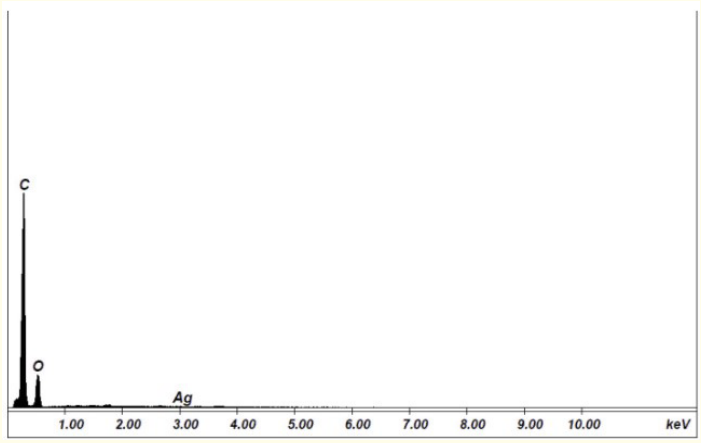


Figure 3: *Different elements found in the modified Silver primer.*

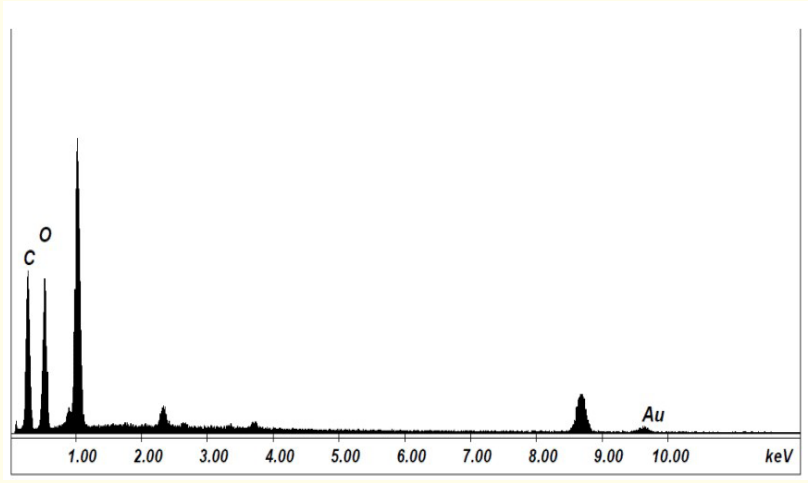


Figure 4: *Different elements found in the Gold group primer.*

Element	Mass %	Atomic %
Carbon	76.95	81.69
Oxygen	22.97	18.30
Silver	0.09	0.01
Total	100	100

Table 1: *Demonstrating the mass% and atomic% of the different materials detected with the energy dispersive x-ray analyzer in the silver modified primer at 10.7µg/ml.*

Element	Mass %	Atomic %
Carbon	50.46	59.03
Oxygen	46.39	40.74
Gold	3.15	0.22
Total	100	100

Table 2: *Demonstrating the mass % and atomic % of the different materials detected with the energy dispersive x-ray analyzer in the gold modified primer at 100 µg/ml.*

Shear Test

Thirty-six freshly extracted non-carious [7] sheep's incisors were cleaned to remove soft tissues and stored in distilled water. Each tooth was embedded in acrylic resin mold inside the 2.5 cm polypropylene pipe. The enamel of buccal surfaces of each tooth was polished using unflavored pumice and brushed at low speed.

The thirty-six teeth were grouped into three groups of 12 teeth, a stainless steel lower incisor orthodontic bracket were bonded to the flat buccal surface of each tooth, using control primer for the first group teeth, silver NPs solution for the second group teeth, and gold NPs solution for the third group teeth. The bonding procedures performed according to the manufacture directions. Each acrylic blocks with the bonded bracket was positioned to lower jaws of the universal testing machine (Instron, CAT, France). Orthodontic wire (0.14 inch in diameter) was wrapped close to the base of the bracket and aligned with the loading axis of the upper movable compartment of the testing machine figure 5 A shearing load with tensile mode of force was applied at a crosshead speed of 0.5 mm/min. The shear load values required to debond the brackets were measured in Newton (N). The shear strengths values in Megapascal were calculated by dividing the load value by the surface area of the bracket base.

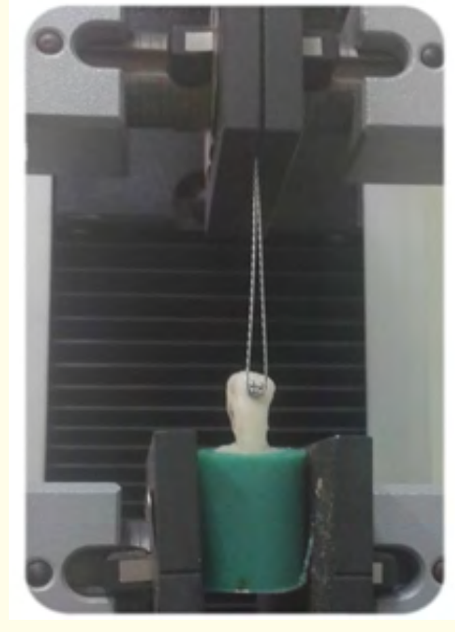


Figure 5: *The acrylic mold in the Instron machine during shear test.*

Ultra morphologic examination

Two representative samples of each group were prepared for ultra- morphologic examination of tooth-adhesive interface using Environmental Scanning Electron Microscope (ESEM).

- Upper incisors sheep's teeth were cleaned, polished with rubber cup in contra-angle hand piece, slurry of pumice and water and dried using oil free airs for 5 seconds.
- The brackets were bonded similar to those in shear bond strength test. Teeth were stored in distilled water at room temperature till the morphologic examination. Metal disc figure 6 was used for sectioning the specimen into mesial and distal halves.

Figure 6: *Metal disc used to cut the specimen for microscopic examination.*

- Finishing and polishing of the flat splitted surfaces were performed with-600, 1000, and 2000 grit abrasive paper. The specimens were prepared for ESEM examination.

To dissolve the enamel at the cut surfaces and reveal the extent of resin infiltration into etched enamel the following was carried out [27]

The surfaces were immersed in 6 mol/L hydrochloric acid for 90 seconds then rinsed with distilled water and immersed in 1% sodium hypochlorite (NaOCl) for 15 minutes to remove any organic remnants, and then rinsed again with distilled water. Finally, specimens were immersed in alcohol for 10 minutes and left to dry before examination. The dissolved enamel thickness was about 0.01mm so the resin tags were exposed and able to be examined figure 7.

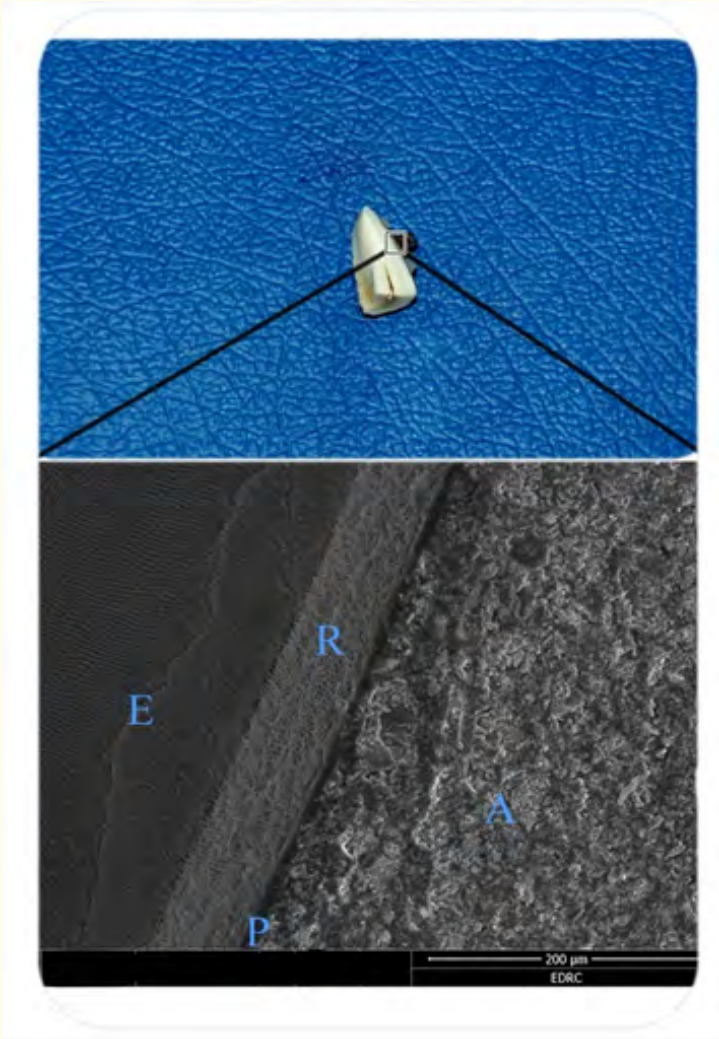


Figure 7: *Sliced tooth: the square represent the inspected area under ESEM.*

Results

Shear test

Data of shear bond strength test explored for normality using kolmogorov-smimov and Shapiro-wilk tests.

- One way ANOVA was used to study the interaction between variables followed by Tukay's post-hoc test for pairwise comparison when ANOVA is significant. The significance level was set at $p \leq 0.05$.
- Statistical analysis was performed with SPSS version 1.5 for windows.
- The highest mean bond strength was detected among the control group was (7.8 ± 2.8 MPa), while it was (7.4 ± 1.96) MPa and (7.7 ± 2.54 MPa) in silver and gold group respectively.

- The difference between the three values was statistically insignificant.
- Data were summarized in table 3 and graphically drawn in figure 8.

	N	Mean	SD	Min	Max	P-value
Control Group	12	7.8	2.8	3.98	12.6	0.908
Silver Group	12	7.4	1.96	5.06	10.8	
Gold Group	12	7.73	2.45	3.77	11.98	

Table 3: *Data of shear bond strength test of the three groups.*

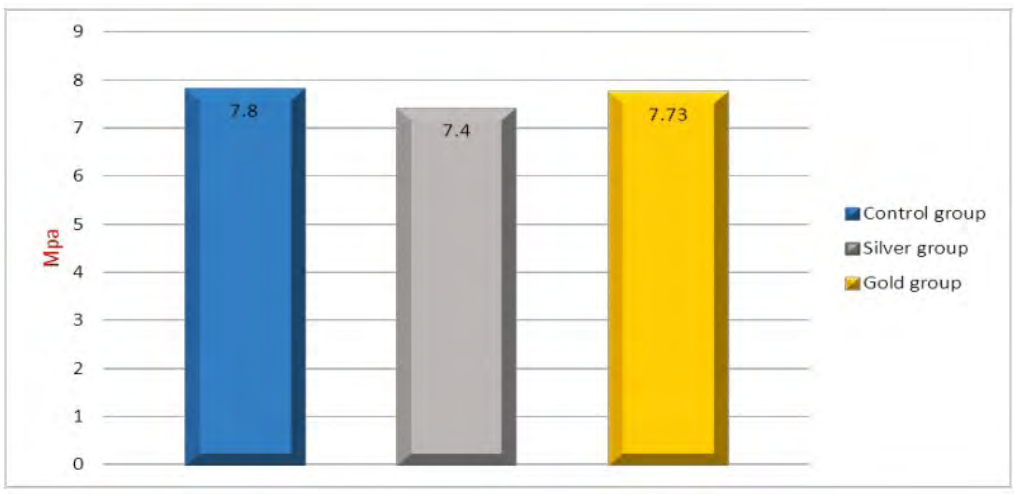
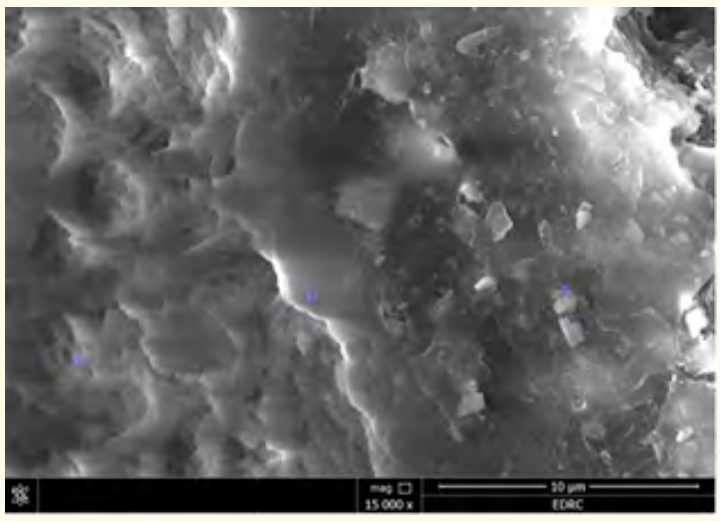


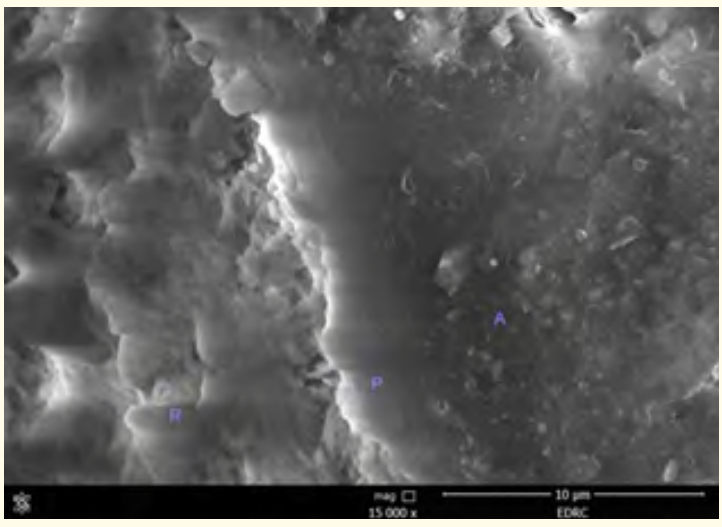
Figure 8: *The mean values of the three groups.*

Ultra-morphologic examination

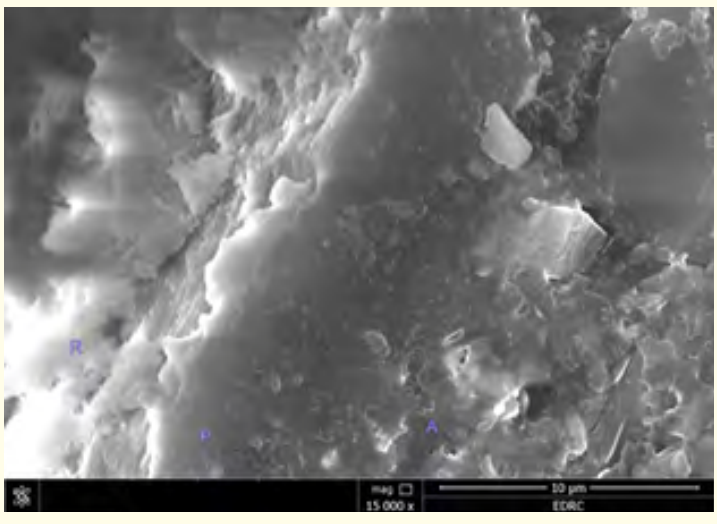
Photomicrographs of the three groups clarifying the presence of the three layers figure 9:



(A)



(B)



(C)

Figure 9: *Representative SEM micrographs of enamel-adhesive interfaces of control (A), silver(B) and gold (C) groups at magnification X15000.*

1. The adhesive layer (A).
2. The primer layer (P).
3. The resin tags (R).

The primer layer was thin and non-uniform. The surface of the primer appears smoother than the adhesive layer with no distinct border.

The resin tags represented the infiltration pattern of the primer into the enamel pores.

Discussion

This study attempts to produce adhesive system with nano sized fillers (Polymer matrix-metallic fillers Nanocomposite system) by adding gold and silver in nano scale to an experimental adhesive. The bond strength was then evaluated.

Improvement of the bond strength of filled adhesive depends on the size, shape, concentration, distribution content of the fillers particles and surface properties of fillers [24]. It was found that the materials with nanometer-sized counterpart yield superior mechanical properties compared to their micron-sized counterparts [26].

The need for increasing bond strength with available, antibacterial and biocompatible materials was the goal of the present study.

Many studies attempted to add NPs of different types to the adhesive solution. The silver NPs and gold NPs were chosen in this study due to their availability, chemical stability [10,11], compatibility and antibacterial effect [5,7]. In this study silver NPs and gold NPs were prepared by reduction method using microwave mediated synthesis because it is an alternate method to synthesize metallic NPs at relatively short times, allowing a good control of size distribution by simple equipment [25,12].

Liu., *et al*. [18] concluded that the critical concentration for dispersion of silver NPs into the cured nanocomposite is 15 ppm, beyond these concentrations, aggregation of silver NPs could occur, which led to deterioration of the positive effect. In this study, the silver NPs concentration in the cured primer was (10ppm) considering the density of the polymer is 1.1 g/ml.

Sokołowski., *et al*. [30] prepared gold NPs solution of 50 ppm concentration, and diluted 5 µL into 2g composite, which means 12,5 ppm gold concentration in the modified composite. Accordingly, the same level of gold NPs concentration was chosen in this study which is 100 µg/ml or 90 ppm considering the density of the polymer is 1.1 g/ml.

Uniform dispersion of the NPs is the first step in the processing of nanocomposite, and the agglomeration (clustering) considered as a major problem in this process. Agglomeration affects the optimal and uniform prosperity of the nanocomposite, agglomerated particles could actually act as the mechanical weak points (structural defects) [29,31]. It interferes with the curing of the material and decreases mechanical properties [1]. It might reduce the primer penetration into the etched enamel pores. Such phenomenon could be observed when small solid particle dispersed in liquid phase without any proper surfactant treatment [16].

The microwave-assisted method for silver NPs synthesis and gold NPs is applicable to gold NPs and other noble metals also. Using ethanol as a reducing agent give a good stabilization for NPs leads to formation of highly monodispersed spherical silver nanoparticles which means a little nanoparticles agglomeration [25].

In this study absence of filler material in the primer would permit more homogenous dispersion of the NPs into the solution, this dispersion was done using a micropipette then further mixing was done by vortex. However the primer viscosity and manual way of mixing may prevent complete dispersion.

It should be noted that the EDX analysis confirmed the presence of the gold and silver on the surface of the cured examined samples. It was proved to be difficult to form uniform and stable dispersion of NPs in polymer [14].

The permanent sheep's was used as substitute for human teeth in bonding test in many studies without significantly affecting the results [23]. They are available with no sophisticated ethical protocols. Central Incisors were used due their flat buccal surface which provides a uniform thickness of the adhesive layer.

The wire loop shearing test method was performed because many studies favored it on the blade shearing test method. The wire-loop method might have more similarity to clinical loads [21]. More important the wire loop method shows a better stress distribution while the use of a knife-edge chisel causes severe stress concentration at the load application area [8]. The shear load values required to debond the brackets were measured in Newton (N). The shear strengths values in Megapascal were calculated by dividing the load value by the surface area of the bracket base.

In this study, the nature of particles, size, shape, and size distribution needed to be detected, as it is critical to correlate between these filler characteristics and their effect on physical polymer properties. So transmission electronic microscope examination was performed.

Particles found in the silver primer sample were spherical, approximately 2 to 5 nm in diameter figure 1. The small size of AgNPs could allow them to flow with the primer [9]. These small sizes showed more antibacterial activity than larger particles [10]. Agglomeration was not observed in the examined sample which means that silver particles were well-dispersed in the resin [9].

Particles found in the gold primer sample were spherical, approximately 9 to 22 nm in diameter figure 2. Using such small sizes would maximize the antimicrobial effect of the gold NPs [20]. Relative to silver more tendencies toward agglomeration were observed.

Data from the shear bond strength results reveled no statistical significant difference between the control group and the gold group or silver group. This means that the addition of silver NPs or gold NPs at specific concentrations 10.7 μg/ml and 100 μg/ml respectively did not have any effect on the physical properties of the tested materials.

For silver sample results were in agreement with Ahn., *et a*l. [1], Mary., *et al*. [19], Blöcher., *et al*. [7] who found that adding nano silver in small amounts and this was used in this study, maintains the bond strength of the adhesive. Also this result were in agreement the work of Akhavan., *et al*. [2] who concluded that incorporation of 5% and 1% nanosilver /nanohydroxyapatite nanoparticles into primer solution maintains and increases the orthodontic shear bond strength of orthodontic adhesives, respectively, whereas increasing the amount of particles to 10% has an undesirable effect on shear bond strength when compared to the control group.

Blöcher., *et al*. [7] suggested that these levels of concentration do not interfere with the matrix of the primer or the adhesive. According to Akhavan., *et al*. [2] the agglomeration does not occur to level that affect the curing process nor creates defect points.

For the gold sample results were in agreement with Sokolowski., *et al*. [30] who found that the dental composite modified by small concentration of gold NPs exhibit the same mechanical properties comparing to non-modified control composite.

Scanning electron microscopy (SEM) is usually used to study the changes in polymer after modification. This technique was used to study the surface characteristics of the hybrid polymer materials comparing it to that of the unmodified primer [19].

Environmental scanning electronic microscope ESEM was used in this study since no special preparation for samples is needed which reduce the possibility of introducing artifacts [43]. ESEM has been confirmed to be of value in the investigation of the process of enamel surface [18], by this machine all morphologic features appear clearly at very high magnification with better images quality. No complicated or expensive preparation of the dental sample is needed prior to the examination.

The photomicrographs revealed same patterns of the primer infiltrated into pores created on the enamel surfaces or formation of tiny resin tags, without noticeable difference between the three groups at magnifications 26000 and 15000. This infiltration is the best achievable bond to the dental substrate [8] and an indicator for the ability of the modified primer to flow and wet the enamel surface.

Same works performed by Mary., *et al*. [19], cheng., *et al* [9]. Both latters considered this similarity between groups, along with the shear bond results, an indicator that incorporating NPs did not affect dentin bonding.

Nanocomposite appeared similar to primer control, with smooth surface. There was no obvious change in the surfaces. The NPs were not seen in both samples, and this is in agreement with the work of Mary., *et al*. [19], Cheng., *et al*. [9], Sadat-Shojai., *et al.* [29]. They performed ultra-morphologic examination using electronic microscope to the modified material but the silver NPs were not seen. But amorphous calcium phosphate could be seen on the surface of the modified adhesive. Gold NPs in the dentinal tubule were appeared in other study [4]. It could be related to the higher concentration that probably was used in this study or the larger size of gold NPs (120 nm) compared to the size used in this study, or due to more surface area were investigated by SEM.

Conclusion

Incorporating gold and silver particles in nano size scale into enamel bonding system at concentration 100 µg/ml and 10 µg/ml respectively has no effect on bond strength or the ability of the primer to wet the enamel surface.

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Volume 11 Issue 4 June 2017