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ORIGINAL ARTICLE

Effect of etchant variability on shear bond strength of all ceramic restorations - an in vitro study

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Abstract The present study was carried out to evaluate the effect of pre-luting surface treatments by 3 different etchant used at 3 different etching periods and their effect on shear bond strength of IPS Empress 2 luted to tooth by dual cure resin cement. Fifty samples of ceramic were divided into four groups as group I control group: No surface treatment, group II: Etched with Hydrofluoric (HF) acid (4.9%), group III: Etched with Ammonium bifluoride acid (9.4%) and group IV: Etched with Phosphoric acid (37%). Group II, III and IV were further divided into 3 Subgroups; namely A, B and C according to the etching periods (20, 60 and 120 s) respectively. The shear bond strength was determined by using a Universal testing Machine. The morphological changes of the surface treated ceramic samples prior to luting to tooth and mode of the fracture failure after shear bond test were observed by using a Scanning Electron Microscope. The mean shear bond strength was highest when IPS Empress 2 ceramic samples were surface treated using 4.9% Hydrofluoric acid gel and 9.4% Ammonium bifluoride acid for 120 s. The least mean shear bond strength was noticed in case of control group, where no surface treatment was done and samples treated by 37% Phosphoric acid. Thus it could be concluded, that Ammonium bifluoride could be an appropriate alternative to be used instead of HF acid. 120 s etching showed highest bond strength values for HF acid (4.9%) and Ammonium bifluoride (9.4%).

Keywords All ceramic restorations · Shear bond strength · Ammonium bifluoride acid · Phosphoric acid · Hydrofluoric acid

Introduction

Since the introduction of Dicor, a castable ceramic material, in 1984, a number of all ceramic restorative systems have been developed. The IPS—Empress System (Ivoclar—Vivadent Schaan Liechtenstein) glass–ceramic is made up of a lithium disilicate framework and a fluoroapatite layering ceramic. This has been successfully used for single unit restorations as well as for three unit's fixed partial dentures in the esthetic zone. It offers benefits in terms of machinability, polishability, appearance and reduced wear of opposing tooth structure [1].

Now it possible to repair the intra-oral fracture of metal ceramic restorations and luting of all-ceramic restorations, such as inlays, onlays, laminates, veneers and full crowns on to the tooth structure because of improved bonding technique and resin cements. Bonding techniques require surface treatment to increase the roughness of both the tooth and ceramic surface. Porcelain surface treatments are abrasion with aluminum oxide or roughening with a course diamond bur [2], etching with Hydrofluoric acid [3, 4] and/or silane coupling agent [5, 6]. As an alternative to Hydrofluoric acid, Ammonium bifluoride [7] Acidulated phosphate fluoride (APF) [8] and phosphoric acid [9] were investigated.

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Factors affecting bond strength are type of etchant, etching concentration and etching time used for etching ceramic materials. Till recent date IPS Empress 2 has been effectively treated with Hydrofluoric acid to create surface irregularities for better bonding, however Hydrofluoric acid has been considered a dangerous and harmful compound to be handled. Both laboratory evaluation and clinical procedures have been reported to substantiate this [10].

Thus there arises a need to try out other chemical agents which are equally effective and more bio friendly. For this reason 9.4% Ammonium bifluoride and 37% Phosphoric acid were tried out which could serve as a safe and effective substitute for Hydrofluoric acid. Also, variation in time period for etching also needed to be evaluated so as to come to a definitive conclusion as regards to ideal time required with individual etchants.

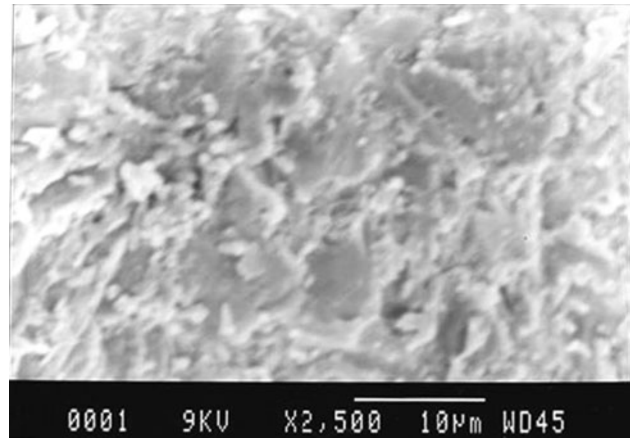

Fig. 1 Group-I: control group examined under scanning electron microscope

Method

Attempts were made to standardize the machinery and the procedures throughout the study to minimize the effect of variable factors on the observations and the final results. This standardization also helped to predict the clinical performance of the various materials used and to improve the success of this in vitro study. The various factors considered for standardization included specimens preparation, cross-sectional surface area, thickness of luting agent, storage conditions and the direction, magnitude and frequency of the applied load.

Fabrication of the Wax Pattern

Fifty disc shaped wax patterns (Renfert, Germany) (8 mm diameter and 2 mm thickness) were prepared.

Fabrication of Ceramic Samples

Fifty samples of ceramic were divided into main four groups:

Group I: Control group. 5 ceramic samples, not subjected to any surface treatment.

Group II: 15 ceramic samples were treated with 4.9% Hydrofluoric acid gel. IPS ceramic Atzel (Ivoclar—Vivadent Schaan Liechtenstein).

Group III: 15 ceramic samples were treated with 9.4% Ammonium bifluoride acid. (Bombay Ammonia and chemical co, Mumbai, India).

Group IV: 15 ceramic samples were treated with 37% phosphoric acid gel. Total Etch (Ivoclar—Vivadent Schaan Liechtenstein).

Group II, III and IV were subdivided into three subgroups A, B and C each consisting of 5 ceramic specimens each to be surface treated for duration of 20, 60 and 120 s respectively.

Scanning Electron Microscope Analysis

Few ceramic samples from each group and subgroup were sputter coated with gold and observed under the Scanning Electron Microscope at ×2,500 magnification and were interpreted accordingly for the morphological changes (Figs. 1, 2, 3, 4).

Bonding of the Ceramic Specimens and Tooth

Preparation of Tooth Specimen

Sixty freshly extracted molar teeth were selected, cleaned and stored in 0.1% thymol solution at room temperature. A vertical planar bonding surface was prepared on the buccal surface of each tooth with a diamond abrasive disc. The roots of each tooth were embedded in a self-cured acrylic resin with a preformed metal mould used as a matrix. Later the exposed surface of the test specimen was wet polished with a 600 grit silicon carbide paper and etched with 37% phosphoric acid gel for 15 s and rinsed for 15 s. The dentin bonding agent Excite (Ivoclar—Vivadent Schaan Liechtenstein) was applied to the etched dentin surface for 10 s, then light cured for 20 s.

Silanisation

For the purpose of silanisation, all specimens were air-dried. Acetone based 3-methacryloxypropyl-trimethoxysilane, a silane coupling agent Monobond (Ivoclar—

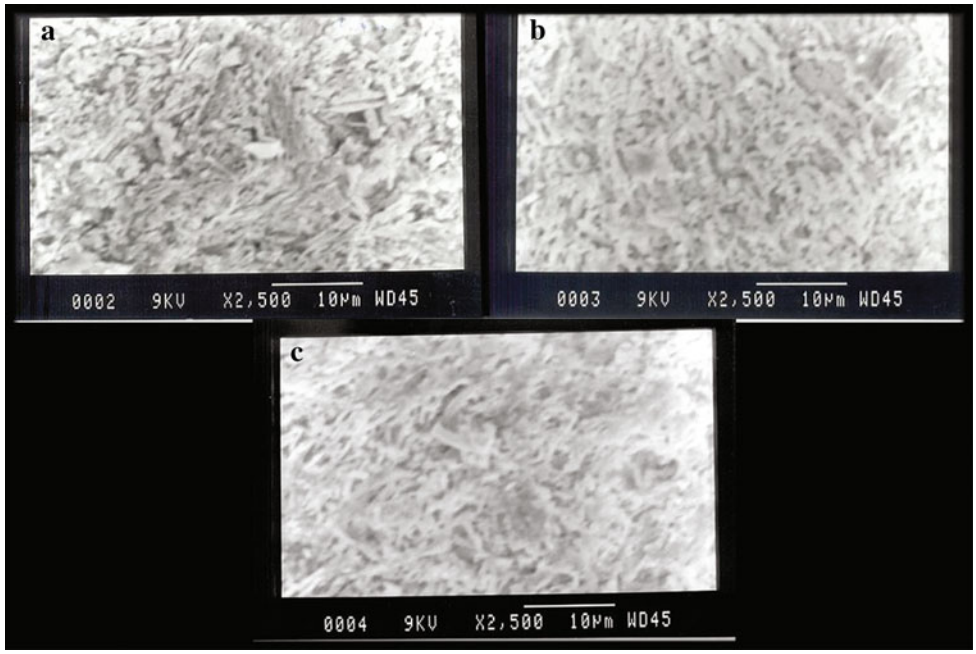

Fig. 2 Group-II: a-subgroups A, b-subgroups B and c-subgroups C specimens examined under scanning electron microscope after surface treatment

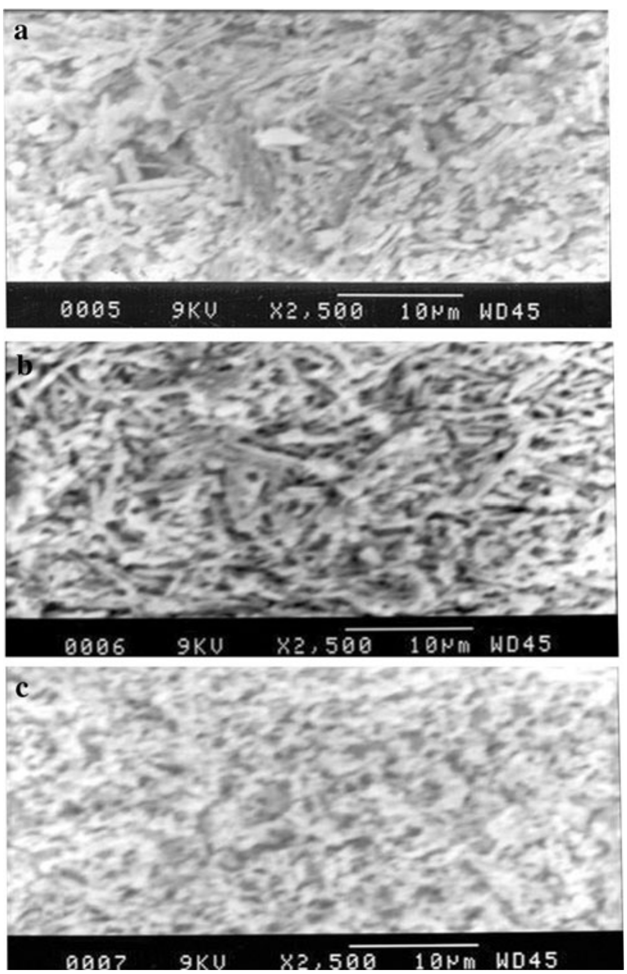

Fig. 3 Group-III: **a** subgroups A, **b** subgroups B and **c** subgroups C specimens examined under scanning electron microscope after surface treatment

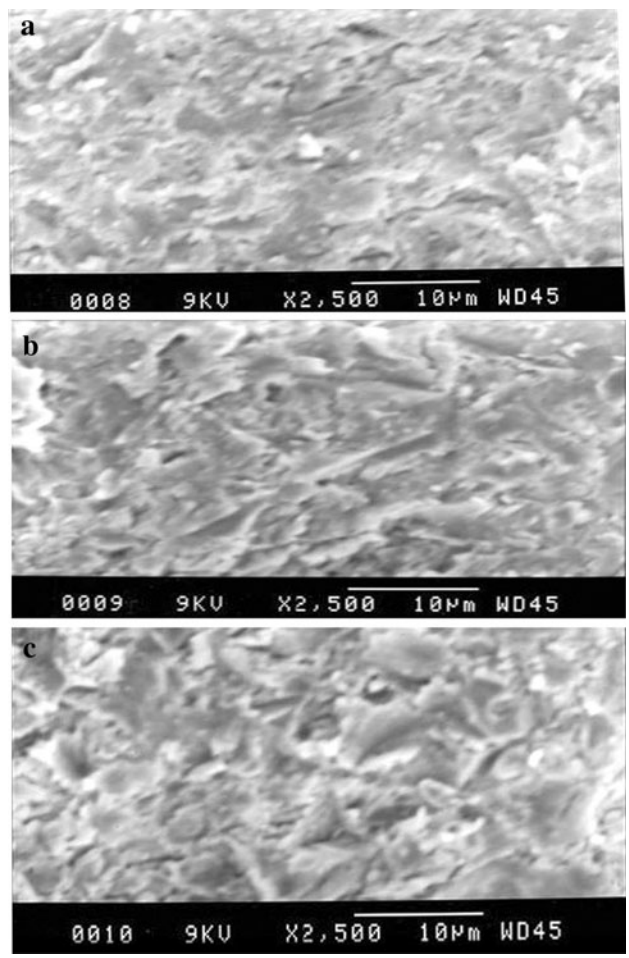

Fig. 4 Group-IV: **a** subgroups A, **b** subgroups B and **c** subgroups C specimens examined under scanning electron microscope after surface treatment

Vivadent Schaan Liechtenstein) was then applied evenly with the brush on the surface of all the ceramic samples for 60 s and samples were allowed to dry for 2 min.

Luting the Ceramic Specimens to Tooth

The Bis-GMA dual-cure resin cement Variolink II (Ivoclar—Vivadent Schaan Liechtenstein) was mixed according to manufacturers instructions and placed on the surface treated IPS Empress 2 ceramic sample and positioned on the treated tooth specimens with the help of alignment blocks under static load of 300 g to get uniform film thickness [11]. A visible light unit was used with the light beam directed approximately 45° at the intersection of the porcelain bonding sites to the dentin. Four, 20 s polymerization sequences divided equally around the circumference of the ceramic cylinder. The total polymerization time for each specimen was 80 s. The samples were ready for shear test.

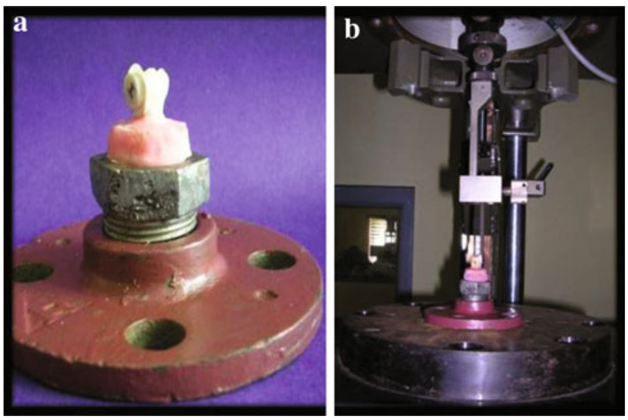

Fig. 5 Ceramic sample luted to tooth with holding device during testing shear strength

Testing the Shear Bond Strength

The samples were subjected to shear load with the help of prepared shear jig using Universal testing machine (Fig. 5) at the cross-head speed of 0.5 mm/min.

Examination of the nature of bond failure under scanning electron microscope:

Few ceramic samples from each group and subgroup after a shear test were observed under the Scanning Electron Microscope at ×2,500 magnification and were interpreted accordingly for the morphological changes (Fig. 6).

The bond failure was classified as: [12].

Adhesive, when the fracture occurred at the ceramic and cement interface.

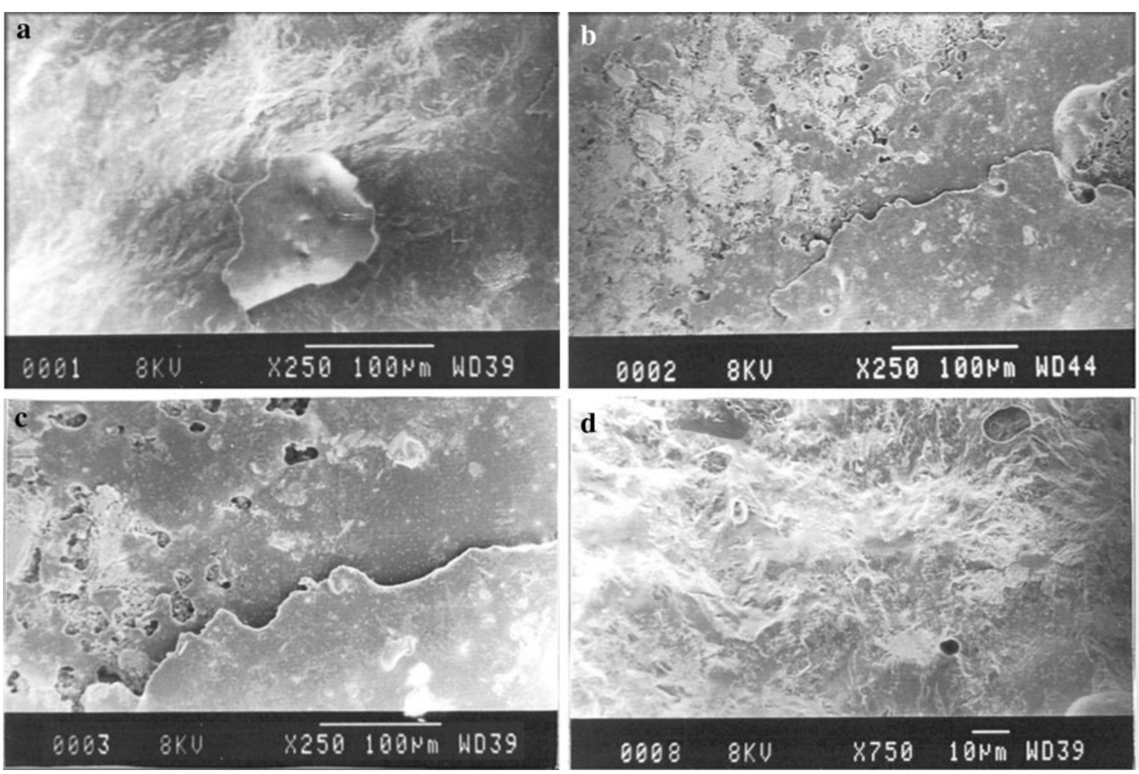

Fig. 6 Fractured specimens examined under scanning electron microscope after testing shear bond strength (**a** group I, **b** group II, **c** group III, **d** group IV)

Cohesive, when the fracture occurred in the resin cement.

Mixed, when the combination of adhesive and cohesive bond failure occurred.

Results

The load at which ceramic samples debonded was recorded in Newton. Shear bond strength (MPa) was calculated by using the formula as given below:

Shear bond strength = force/area in N/m [2].

Table 1 provides the shear bond strength values for various etchants used at different etching periods. Statistical analysis, using the unpaired '*t*'—test was done. The calculated mean, standard deviation and '*t*' test comparison of different groups and sub-groups are given in Tables 2, 3, 4, 5, 6, and 7.

On the basis of the observations, the following results were obtained.

Etching with 4.9% HF acid for 120 s (group I, sub-group C) had highest bond strength values followed by 9.4% Ammonium bifluoride acid for 120 s (group II, sub-group C). 37% Phosphoric acid (group IV) had the lowest bond strength values among the three different etchants used (Fig. 7).

Bond failure was observed to be cohesive in nature for the samples treated by 4.9% HF acid (group II) and 9.4% Ammonium bifluoride acid (group III). Control group and (group IV) i.e. etching with 37% Phosphoric acid showed bond failure to be mixed in nature.

Table 1 Shear bond strength values of various group and sub group in MPa

Sr. no.	Group	Sub group (A) (20 s)	Sub group (B) (60 s)	Sub group (C) (120 s)
1	Group I	4.88	4.88	4.88
2	Group I	4.69	4.69	4.69
3	Group I	4.87	4.87	4.87
4	Group I	4.13	4.13	4.13
5	Group I	4.28	4.28	4.28
1	Group II	9.88	13.91	15.89
2	Group II	9.05	12.07	14.38
3	Group II	9.23	11.71	15.06
4	Group II	9.81	12.63	14.48
5	Group II	10.33	12.12	15.33
1	Group III	9.04	13.15	15.02
2	Group III	7.91	11.81	14.15
3	Group III	9.3	11.67	14.38
4	Group III	7.56	12.11	14.13
5	Group III	9.44	12.44	14.4
1	Group IV	4.68	5.03	5.19
2	Group IV	4.54	4.81	4.85
3	Group IV	4.73	4.5	4.55
4	Group IV	4.38	5.05	4.67
5	Group IV	4.97	4.57	4.27

Discussions

Bonding of composite to ceramic material has played an important role in dentistry. The ceramic bonding systems are based on the mechano-chemical bonding between the luting materials and ceramic restorations. Various methods have been introduced to improve bond between the luting materials and ceramic restorations. Though HF acid is reported to provide good bond strength, it is one of the most harmful compounds to handle for clinical as well as for laboratory use. HF acid is corrosive and readily destroys tissue in contact like eyes, skin. Inhaling HF vapors can seriously damage the lungs, eyes. The mechanisms that cause tissue damage are corrosive burn from the free hydrogen ions and chemical burn from tissue penetration of the fluoride ions [10]. The hypothesis for this present study was whether 9.4% Ammonium bifluoride acid and 37% phosphoric acid could be a substitute for HF acid for preluting surface treatment of IPS Empress—2 ceramic as these are relatively less harmful than HF acid.

Retief et al. [13], in 1990 have suggested that the use of human teeth to be preferable for the study. The selected teeth were preserved in distilled water with 0.1% thymol to avoid any changes in the tooth tissues throughout the study

Table 2 Comparison of bond strength between control group and group II

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Control		Group II				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	4.57	0.34	9.66	0.52	−18.23	8.43E−08	Significant
B (60 s)	4.57	0.34	12.49	0.86	−19.081	5.89E−08	Significant
C (120 s)	4.57	0.34	15.03	0.62	−32.814	8.11E−10	Significant

Table 3 Comparison of bond strength between control group and group III

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Control		Group III				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	4.57	0.34	8.65	0.85	−9.89	9.17E−06	Significant
B (60 s)	4.57	0.34	12.23	0.59	−24.97	7.07E−09	Significant
C (120 s)	4.57	0.34	14.41	0.36	−44.07	7.74E−11	Significant

Table 4 Comparison of bond strength between control group and group IV

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Control		Group IV				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	4.57	0.34	4.66	0.22	−0.48	0.64	Not significant
B (60 s)	4.57	0.34	4.79	0.25	−1.13	0.28	Not significant
C (120 s)	4.57	0.34	4.79	0.25	−1.13	0.28	Not significant

Table 5 Comparison of bond strength between group II and group III

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Group II		Group III				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	9.66	0.52	8.65	0.85	2.25	0.054	Not significant
B (60 s)	12.49	0.86	12.23	0.59	0.54	0.603	Not significant
C (120 s)	15.03	0.62	14.41	0.36	1.89	0.095	Not significant

Table 6 Comparison of bond strength between group II and group IV

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Group II		Group IV				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	9.66	0.52	4.66	0.22	19.77	4.45E−08	Significant
B (60 s)	12.49	0.86	4.79	0.25	19.15	5.71E−08	Significant
C (120 s)	15.03	0.62	4.71	0.34	32.42	8.93E−10	Significant

Table 7 Comparison of bond strength between group III and group IV

Shear bond strength (MPa)	Group				Unpaired *t* test applied		
	Group III		Group IV				
	Mean	SD	Mean	SD	*t* Value	*P* value	Significance
A (20 s)	8.65	0.85	4.66	0.22	10.1	7.83E−06	Significant
B (60 s)	12.23	0.59	4.79	0.25	25.76	5.52E−09	Significant
C(120 s)	14.41	0.36	4.71	0.34	43.55	8.51E−11	Significant

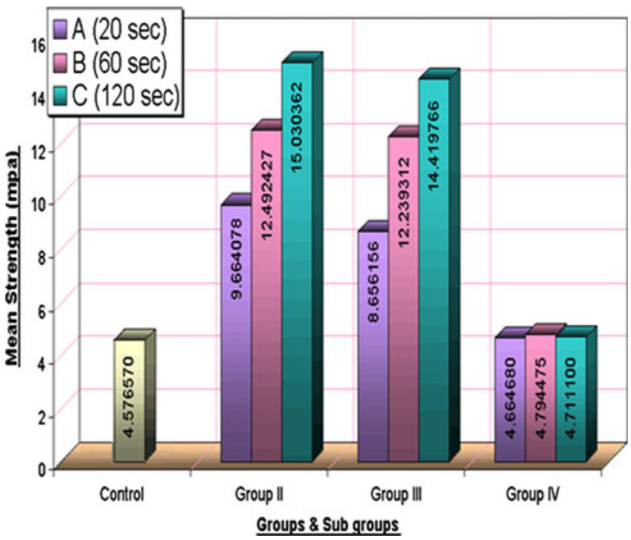

Fig. 7 Graph: comparison of shear bond strength among various groups and subgroups

[14]. It has been stated that the best substrate for dentin adhesive testing is the human dentin [14].Therefore human extracted teeth were used for the study. The teeth selected for the study were flattened till superficial dentin was exposed. It was reported that superficial dentin has composite dentin bond strength higher than that of deeper dentin [14]. The specimen teeth were attached with sticky wax to a pin fixator to the vertically prepared surface, to maintain a plane between the bonding surface and the shear loading axis of the Universal Testing Machine.

However because all-ceramic IPS Empress 2 ceramic restorations are utilized in esthetic zone, dual cure resin cement is advocated for luting this ceramic for better esthetics and better bonding. The main advantage of this type of cement is the control of the working and setting times. In this study, only one cement was chosen otherwise too many variability would alter the study. Also too many cements could not be used in this sample size so as to get definitive data.

A piece of tape with a circular hole 5 mm in diameter was positioned on the 8 mm diameter porcelain specimen to define the area of the bond and a consistent 50 μm thickness of luting agent. Also 300 g standard weight was applied during luting the ceramic to the tooth with the help of alignment block [11].

Studies have concluded that application of the silane coupling agent significantly improved the bond strength of ceramic and resin. Jardel et al. [15] stated that because of its high wettability and chemical contribution to adhesion, the silane agent substantially increased the reliability of the bonded ceramic joint. In the present study from four groups, each ceramic sample was silanised using an acetone based silane coupling agent—Monobond S for 60 s and then dried. It enabled the bonding of the resin matrix to glass filler particles (chemical bond). This coupling agent consists of a methacrylate group, which is capable of bonding to the resin, and the other end is silanol, which is capable of bonding to ceramic surface.

Kato et al. [9] in their study showed that thermocycling the resin-porcelain bonded specimens weaken the resin bond strength significantly. They also found that the bond strength after thermocycling more closely matched that in the oral environment. Therefore in the present study, after luting the ceramic samples to the teeth by the dual cure resin, all the samples were stored in distilled water for 24 h at room temperature of 37°C. They were then thermocycled at 5 and 55°C for 500 cycles with a dwelling time in each bath for 30 s.

As most clinical failure of ceramic restorations result from shear stresses, the bond strength test employed here was a shear test. Watanabe and Nakabayashi [16] have stated that shear test was easiest to perform. The advantage of this method was that measuring equipment was easy to construct and there were only minor influences from variations in loading directions. The specimen preparation was easier than for tensile measurement. The ISO has recommended that in shear bond strength (SBS) tests, the load should be applied with a cross-head speed of within 0.45 and 1.05 mm/min (ISO-TR 11405) as relatively high cross-head speed may develop abnormal stress distribution during shear test. According to Hara et al. [17] cross-head speeds of 0.50 and 0.75 mm/min are preferable in shear bond strength tests.

It was important to visualize the morphology of the treated ceramic surface and to observe the effect of surface treatment carried out by three different etchants, at three different etching periods. This was observed by a Scanning Electron Microscope Study. The result of this SEM Study showed that the hydrofluoric acid (4.9%) and Ammonium bifluoride acid (9.4%) attacked the residual glass leaving behind a surface of rod shaped crystals, which enhanced the degree of mechanical interlocking possible. For both etchants, the surfaces etched for 120 s were rougher than those etched for 20 and 60 s. This surface treatment significantly changed the surface morphology increasing the surface area, which favored infiltration and retention of adhesive materials and made the ceramic surface more retentive. Phosphoric acid, on the other hand did not produce a good a retentive surface as the one obtained by etching with hydrofluoric acid and Ammonium bifluoride acid. No significant difference was found between control group samples and samples treated by phosphoric acid.

The results of this study showed that mean shear bond strength was highest when IPS Empress 2 ceramic samples were surface treated using 4.9% Hydrofluoric acid gel and 9.4% Ammonium bifluoride acid. The least mean shear bond strength was noticed in case of control group, where no surface treatment was done and samples treated by 37% Phosphoric acid. No significant differences for the samples etched with phosphoric acid were noticed with different etching periods. The etching time and concentration of the acidic medium were also observed as important prognostic variates.

On scanning electron microscopic examination of the fractured specimens, the bond failures appeared to be cohesive in nature for the samples etched with 4.9% Hydrofluoric acid and 9.4% Ammonium bifluoride. Application of silane agent to etched samples which improves the bond strength may also explain the occurrence of cohesive failure in the resin cement.

After relating all the data inferred, the results of this study indicate that the Ammonium bifluoride acid could be a substitute for HF acid as a preluting surface etchant to obtain comparable bond strength of IPS Empress-2 restorations to tooth structure. This study was conducted in vitro trying to simulate the oral conditions however the effects on cyclic loading which occurs naturally could not be evaluated. Whether such long etching periods need to be advocated could not also be ascertained and what effect it leads on the material properties needs to be studied further.

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