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A Study on Concentration and Application Time of Lithium Sulfate-Contained Polyacrylic Acid for Adequate Crystal Growth

Joung-Sub Roh[1], Sang-Cheol Kim[2], Ki-Chul Tae[3]

The purpose of this study was to compare shear bonding strengths and debonding patterns of the ceramic brackets attached on the crystal which were grown on the enamel surface of a tooth with different concentrations of lithium sulphate-contained polyacrylic acid in different application times.

Four kinds of concentrations of mixed solutions were made and applied to the enamel surface on extracted human premolars. The solutions were made by adding 0.3M or 0.6M of lithium sulfate to 50% or 65% of polyacrylic acid with 0.3M sulfuric acid. The solutions were applied for 30 or 60 seconds. After bonding, a universal testing machine was used to measure the shear bond strength, and then observations were made of debonding patterns through the stereoscope. And the enamel surface was observed through the scanning electron microscope to examine the pattern of crystal growth and debonding.

The results were as follows:

1. Shear bond strength in the enamel surface treated with 50% polyacrylic acid was higher than that with 65% polyacrylic acid.
2. There were no statistical differences in shear bond strength according to concentration of lithium sulfate and application time of solutions .
3. Enamel surface was almost free of resin debris after debonding.
4. Enamel surface treated with 50% polyacrylic acid showed higher density of crystal growth than that with 65% polyacrylic acid under scanning electron microscope.

Key Words : crystal growth, polyacrylic acid, lithium sulfate, shear bond strength

Direct bonding system introduced by Buonocore[1] to compliment the esthetical disadvantages of band. After that, the method of the appropriate bonding strength to increase bonding strength was made by studies[2-5]. One of the studies was to compliment the disadvantage[6] which happens when a microscopic impact harms the enamel surface with traditional acid etching technique that forms crystal on enamel surface[6,7].

This crystal growth method is to form crystal on

1) *Graduate student, Dept. of Orthodontics, School of Dentistry, Wonkwang Univ.*

2) *Professor, Dept. of Orthodontics, School of Dentistry, Wonkwang Univ.*

3) *Full time lecturer, Dept. of Orthodontics, School of Dentistry, Wonkwang Univ.*

enamel surface using polyacrylic acid and then attach the bracket[6]. If polyacrylic acid containing tiny sulfuric acid is applied on the enamel surface, a projecting crystal forms. It makes the bonding strength increase[7]. This phenomenon was explained by Smith and Cartz[7] first, by which calcium ions leak out from polyacrylic acid then sulfuric acid ions fill the blank and $CaSO_4$-$2H_2O$ (gypsum) is produced[7].

This study on forming crystal had been continued and made into a commercial product[8] used clinically in 1980. But, independent studies found this product not to be sufficiently robust for routine application in the clinical environment[4]. After this, people started to use ceramic bracket for esthetical reasons[10-13]. Though there was another disadvantage which was that it might fracture the enamel when removing the ceramic bracket. This study started when the advantages came to the front, they are crystal growth method does not damage the enamel a lot, they are easy to remove the bracket and resin debris[6], does not lose outer enamel surface containing a lot of fluorine, and they minimize the amount of resin debris after removing the bracket[9].

With the continuing studies, we may make better bonding strength form by adding various ions to polyacrylic acid[8,14,15]. Observing the length, structure, and density of the crystal with an electric microscope after crystal forming by adding potassium, magnesium, and lithium to polyacrylic acid containing tiny sulfuric acid, we could see the crystal forming which is longest when adding potassium, and widest when adding magnesium[8]. In the case of adding lithium, the shortest crystal formed of which density was high and bonding strength was best[8].

Polyacrylic acid of 50% and polyacrylic acid of 65% with 0.3M sulfuric acid are used to make different 4 liquids by adding 0.3M and 0.6M lithium sulfate to each. Our purposes here are comparing shear bonding strength and effect according to the structure and treatment of crystal forming solution. These liquids were applied on enamel at 30 seconds and at 60 seconds each, then we bonded the ceramic bracket after observing the surface with a scanning electron microscope. we measured shear bond strength and observed resin bonding patterns in each solution after removing the bracket and then compared the applied time in each solution.

MATERIALS AND METHODS

1. Materials

Forty eight upper and lower premolars extracted for the purpose of orthodontic treatment, which didn't have caries or filling, healthy crowns were used[16]. Standard edgewise type ceramic brackets for premolars were used. The width of bracket's bonding surface was $8.86mm^2$.

Ortho-one(BISCO Inc, Itasca, USA) no mix self curing resin was used.

Four kinds of concentration of mixed solutions were made and applied to the enamel surface of extracted human premolars. The solutions were made by adding 0.3M or 0.6M of lithium sulfate(SIGMA Chemical Co. USA) to 50% of polyacrylic acid(5000 molecular weight: Aldrich Chemical Co. USA) or 65% of polyacrylic acid(2000 molecular weight: Aldrich Chemical Co.) with 0.3M sulfuric acid(98% SIGMA Chemical Co. USA)(table. 1).

2. The making of the specimen.

The extracted premolars were cleaned with flowing water and it were kept in normal saline before experimenting. The teeth were fixed on the block[18] of the acrylic resin(30×10×20×mm) to exposed bucal surface were kept in tap water. And then, specimen for scanning electron microscope(20×5×15mm) was made to the size of parenthesis of the microscope in order to observe through. The observed teeth were washed and dried for ten seconds after removing alien substances by ten seconds of polishing. And then, by using resin, a ceramic bracket was attached after enamel surface handling in crystal growth solution for 30 or 60 seconds. When the solution was applied, the repeat application was not used because it caused the loss of crystal forming[9]. In handling the ceramic bracket not to be polluted coated bonding side with silane layer, the bracked was bonded to the surface of teeth to be

Table 1. Groups of solutions

Solution \ Content	polyacrylic acid concentration(%)	sulfuric acid concentration(M)	lithium sulfate concentration(M)
Solution 1	50	0.3	0.3
Solution 2	50	0.3	0.6
Solution 3	65	0.3	0.3
Solution 4	65	0.3	0.6

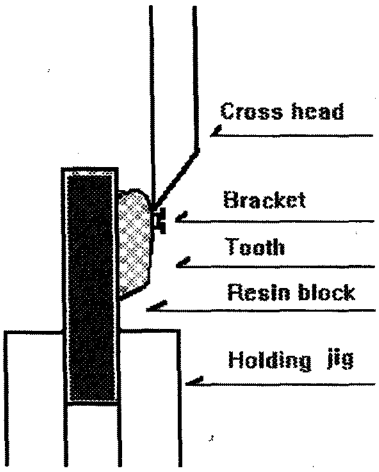

Fig. 1. Specimen mounted in the jig subjected to shear stress.

pressured uniformly 15 seconds. After the teeth bonded brackets were kept at room temperature for 15 minutes. Later, they were kept in tap water[14]. According to this experiment eight groups were formed by four kinds of mixed solutions and two types of application time.

3. The measure of shear bond strength.

After the teeth finished bracket bonding were kept in tap water, for 24 hours the shear bond strength was measured. The universal testing machine(Zwick z020) attached jig subjected to shear stress was forced vertically by 1mm/min speed. When the bracket was debonded, the maximal load was regarded as the measure of shear bond strength(Fig. 1).

4. The observation of fracture pattern.

After measuring shear bond strength, a stereoscope (Stereo Star: American optical Co.) was used to observe the fracture patten of bracket bonding side and the surface of teeth by 20 magnification. The fracture pattern was classfied four types. Debonding between enamel and resin(E/R) : The two-thirds of resin is on the bracket. Debonding inter resin (R/R) : the fracture side was only in the resin. Debonding between resin and bracket (R/B) : two-thirds of resin remained on the tooth surface. COMB fracture : resin remained on the tooth surface and bracket's bonding surface in similar amounts[18].

5. The observation of crystal pattern.

The aspect of crystal before attaching the bracket and on the pattern of enamel surface after removing the bracket was observed through the scanning electron microscope. The prepared specimen painted in silver paste was coated 30nm of gold by using ion coater(Giko Engineering) and observed by 20kv, 500 and 1500 of magnification through scanning electron microscope (HITACHI X-650: Japan).

6. Statistcal managenent.

The mean and the standard deviation of shear bond strength was output about each group. Student's t-test and one way ANOVA was used to inspect the differences between each group. The inspection was enforced at 5% of level of at statistical significance.

Table 2. Comparison of shear bond strength depending solutions and application time. (Newton)

	50% polyacrylic acid	65% polyacrylic acid	Significance in t-test
Lithium sulfate 0.3M,30sec	78.89 ± 8.98	45.76 ± 5.91	* * *
Lithium sulfate 0.3M,60sec	90.58 ± 5.84	39.14 ± 3.36	* * *
Lithium sulfate 0.6M,30sec	77.28 ± 6.76	42.36 ± 5.28	* * *
Lithium sulfate 0.6M,60sec	81.24 ± 10.78	48.77 ± 9.53	* * *
Significance in ANOVA	NS	NS	

(significance of difference: *** ; P<0.001, NS; Not significant)

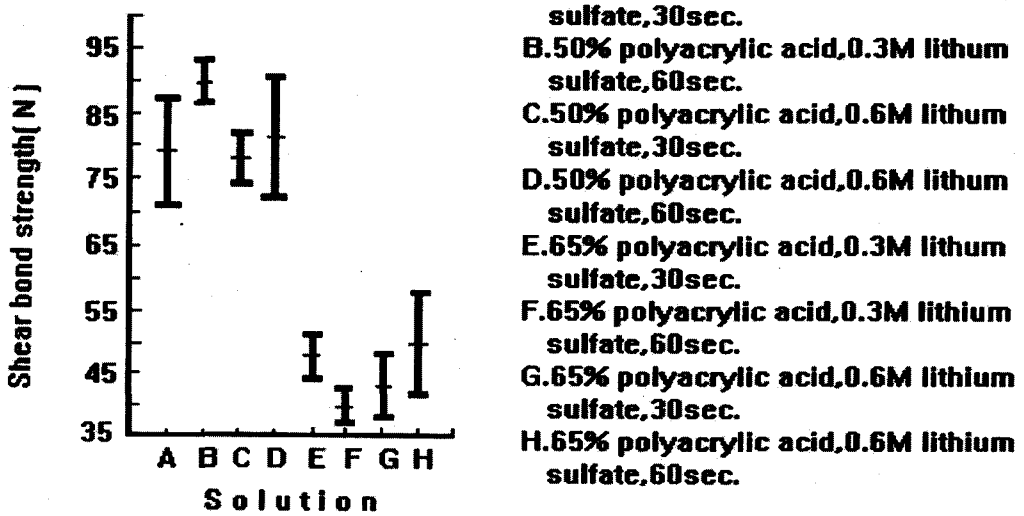

Fig. 2. Comparison of shear bond strength depending solutions and application time.

RESULT

1. Comparison of shear bond strength.

The mean and the standard deviation of shear bond strength depending the concentration of solution about each test group and application time were showed in table 2 and Figure 2.

In the case of 0.3M of sulfuric acid and lithum sulfate put into the 50% of polyacrylic acid for 60 seconds, the bond strength was the highest(90.58±5.84 Newton). Generally, enamel surface treated with 50% polyacrylic acid showed higher bonding strength than with 65% polyacrylic acid.

There were no statistical differences in shear bond strength according to the concentration of lithum sulfate and application time of solutions.

2. The comparison of fracture pattern.

The patterns of the enamel surface after removing the brackets were shown in table 3. Among forty specimens, debonding between enamel and resin(E/R) was twenty- two(55%), debonding inter resin(R/R) was three(7.5%), debonding between resin and bracket(R/B) was four(10%), mixed fracture(COMB) was eleven (27.5%).

Table 3. Debonding patterns

	Applied for 30 seconds				Applied for 60 seconds			
	E/R	R/R	R/B	COMB	E/R	R/R	R/B	COMB
50% polyacrylic acid, 0.3M lithium sulfate	3		1	1	3	1		1
50% polyacrylic acid, 0.6M lithium sulfate	2	1	1	1	1	1	2	1
65% polyacrylic acid, 0.3M lithium sulfate	4			1	4			1
65% polyacrylic acid, 0.6M lithium sulfate	2			3	3			2

E/R : debonding between enamel and resin , R/R : debonding inter resin,
R/B : debonding between resin and bracket , COMB : combination

Fig. 3. Crystal growth on the surface of the enamel treated with 50% polyacrylic acid with 0.3M lithium sulfate and 0.3M sulfuric acid for 60 seconds. (SEM X 1500).

Fig. 4. Crystal growth on the surface of the enamel treated with 65% polyacrylic acid with 0.6M lithium sulfate and 0.3M sulfuric acid for 60 seconds. (SEM X 1500).

3. The observation of crystal pattern with scanning electron microscope.

Like Smith's report[7], the long crystal formed by application of the solution on enamel surface was observed through the scanning electronic microscope of 500 and 1500 magnifications(Fig. 3, 4). In the specimen treated with 50% of polyacrylic acid, the density of crystal was higher than 65% of polyacrylic acid. The crystal growth on the surface of the enamel treated with 50% polyacrylic acid for 30 seconds was smaller and shorter then for 60 seconds. The crystal growth on the surface of the enamel treated with 65% polyacrylic acid for 60 seconds became longer and 50% polyacrylic acid for

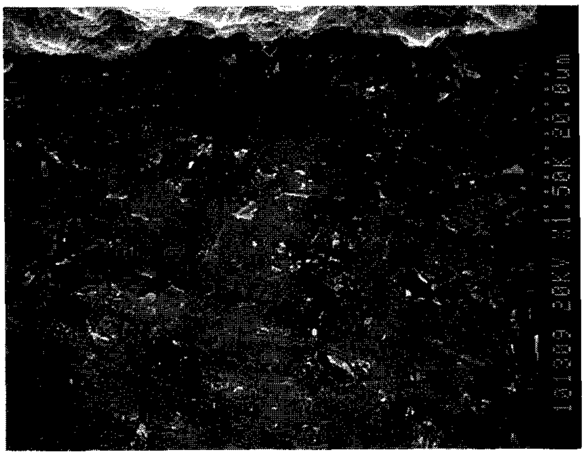

Fig. 5. Photography of the enamel surface after debonding bracket (SEM X 1500).

same time can find 10㎛ equally(Fig. 3, 4). This result was like Kim's study[28]. In more then half the specimens (55%) remaining resin was not seen on the surface of the enamel after removing the bracket. Almost all crystal debonded with resin(Fig. 5).

DISCUSSION

The premolars used in the experiment were extracted frequently in orthodontic treatment were chosen as test samples. The anatomyially abnormal teeth or those that had cracks and fillings were excepted[17]. The same kinds of bracket were used to give uniform bonding condition and the writer bonded each bracket himself.

The crystal growth solution for handling the surface of enamel was used same with Smith and Cartz[7] reported the first polyacyclic acid contained sulfuric ion to improve chemical action[8]. 50% or 65% of two types basic solutions were used to study the interrelation between density and bonding strength[6]. Lithium sulfate added in the basic solution was to promote the formative density of the crystal[8]. The additional volume of lithium sulfate was decided in the ground of the study to find bonding intensity[16]. The mixed solution was applied by the consideration of the aplication time on clinic[17].

The higher the concentration of polyacrylic acid was, the less the volum of soluability of sulfuric acid and lithium sulfate was. It was caused by the increasing viscosity of solution. After all, when the concentration of polyacrylic acid became higher, the formative crystal growth less and the density lower. This result had a point of agreement with Smith's report[14]. According to observations through the scanning electron microscope, the teeth applied for 30 seconds in the solution had very small under growth crystal. Therefore, the application time, 60 seconds, was very appropriate.

The minimal bond strength had many different causes, in orthodontic treatment such as bonding materials, bracket position, the kinds and direction of force, and design of the base of the bracket, etc. Keizer's study[25] indicated that the bond strength necessary for orthodontic attachments to clinically withstand both physiologic and mechanical forces are in the order of 28kg/cm^2. Reynolds has reported that successful clinical bonding has been achieved by means of an adhesive that is produced an in vitro tensile bond strength of 50kg/cm^2. Still others believe that 60 to 80kg/cm^2 is a more reasonable and reliable bond strength for clinical situations[9]. Also McCarthy and Hondrum[26] reported 7MPa was proper. The result of this study, when the 50% of polyacrylic acid basic solution with a mixed solution was applied for 60 seconds, shear bond strength was 9.2MPa which was enough indensity in clinic. But this was different from that presented by a senior[24-27] because of materials and methods applied differently.

The observation through the scanning electronic microscope found that resin was penerated through the formed crystals to make the crystal maintain. When the bracket was removed, crystals were broken and fallen with resin. So, almost all the crystals remained on the bonding surface of the bracket. Only small and short crystals remaind on enamel. These crystals which combined condition chemically on the enamel were fractured toward the direction of length. The remaining crystals were cleaned by a rubber cup which applied polishing paste easily. And then, if a little resin was left or resin debris was never remained, the surface of the enamel could be kept clean. This fact was reported by Smith, Cartz[7] and Farquhar[19].

According to the report of Farquhar[19], the resin on the surface of the enamel and crystal through the scanning electronic microphotograph was cleaned perfectly. In the case of the method by phosphoric acid etch was used, 25~180㎛[19-23] of resin debris was penetrated into the enamel. And at this time, the bonding by crystal growth, resin was not found in enamel but only around crystal. These facts were certified through scanning eletronic microphotograph which was used for this study.

The mixed solution made by the basic solution with 50% of polyacrylic acid handled the surface of enamel and the specimen attached bracket showed the high bonding strength. This could be applied in clinic, even if it were so. And the continuation of the study for the mixed solution which has high bonding strength is demanded.

CONCLUSION

Crystal growth technique has many advantages compared with acid etching technique. Four kinds of concentrations of mixed solutions were made and applied to the enamel surface on 48 extracted human premolars. The solutions were made by adding 0.3M or 0.6M of lithium sulfate to 50% or 65% of polyacrylic acid with 0.3M sulfuric acid. The solutions were applied for 30 or 60 seconds. After bonding, a universal testing machine was used to measure the shear bond strength, and then observations were made of debonding patterns through the stereoscope. And the enamel surface was observed through the scanning electron microscope to examine the pattern of crystal growth and debonding. Then we can get the following results.

1. Shear bond strength in the enamel surface treated with 50% polyacrylic acid was higher than with 65% polyacrylic acid.
2. There were no statistical differences in shear bond strength according to the concentration of lithium sulfate and application time of solutions.
3. Enamel surface was almost free of resin debris after debonding.
4. Enamel surface treated with 50% polyacrylic acid showed higher density of crystal growth than with 65% polyacrylic acid under the scanning electron microscope.

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국문초록

법랑질 표면에 크리스탈을 형성시키기 위해 사용한 황산리튬이 함유된 폴리아크릴산의 농도와 적용시간에 관한 연구

원광대학교 치과대학 교정학교실

노정섭 · 태기출 · 김상철

본 연구는 각각 다른 농도의 황산리튬을 함유한 폴리아크릴산을 적용시간을 변화시켜 치아의 법랑질 표면에 도포하여 크리스탈을 형성하고 그 위에 도제브라켓을 부착한후 전단결합강도와 파절양상을 비교하기 위하여 시행하였다.

농도가 서로다른 혼합용액 4종류를 교정치료를 위해 발거된 건전한 소구치 48개의 법랑질 표면에 적용시켰다. 실험용액들은 50%의 폴리아크릴산과 65%의 폴리아크릴산을 기본 용액으로 하여 0.3M의 황산을 공통으로 첨가하고 각각 0.3M 이나 0.6M의 황산리튬을 첨가하여 만들었다. 30초나 60초 동안 준비된 용액을 법랑질 표면에 적용한 후 브라켓을 부착시켜 전단결합강도를 측정하였다. 또한 브라켓 부착 전과 부착 후의 크리스탈 형성 양상을 주사전자현미경을 통하여 관찰하였다.치아 표면의 잔여 레진 양을 입체현미경을 통하여 관찰하고 분류하여 다음과 같은 결과를 얻었다.

1. 50% 폴리아크릴산으로 처리하였을 때의 전단결합강도가 65% 폴리아크릴산에 비해 높았다.
2. 황산리튬의 농도나 적용시간에 따른 전단결합강도의 차이는 인정되지 않았다.
3. 브라켓 제거 후 법랑질 표면에서 레진이 거의 관찰되지 않았다.
4. 50% 폴리아크릴산으로 처리하였을 때의 크리스탈 형성 밀도가 65% 폴리아크릴산의 경우 보다 높았다.

주요 단어 : 크리스탈 형성, 폴리아크릴산, 황산리튬, 전단결합강도