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Studies on Adhesion Properties of Shellac to Bovine Enamel

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Though an attempt to apply a natural resin shellac in the dental field has been made in recent years, almost no study have concerned its adhesive strength to the tooth surface or its persistency. In the present study, therefore, the adhesive strength of shellac to the enamel surface, the influence of etching treatment on the adhesive strength and possible changes in the adhesive strength following thermal loading due to thermal cycle were examined by means of compressive shear bond strength test. By using a test material composed of shellac in alcohol solution and bovine extracted tooth, the adhesive strength of shellac at varied concentrations was examined with the results as below.

The adhesive strength with no etching treatment was about 5MPa irrespective of the shellac concentration used and no significant difference was observed between the examined groups. When an etching treatment was applied, however, the adhesive strength significantly increased in almost all experimental groups with the maximum value of 13.7±1.5MPa. Though a decreased adhesive strength was observed in all groups examined after thermal loading due to thermal cycle, the rate of decrease however tended to be relatively small in experimental groups at a shellac concentration ranging 0.1 to 1%. In particular, the rate of decrease was the smallest in 0.1% shellac group (11.4%) and the adhesive strength of 10.6±1.9MPa was maintained even after thermal cycle. Based on the above evidences, an practical adhesive strength was suggested to be successfully maintained to some extent of period when it is applied to human oral cavity.

Key words : shellac, adhesive strength, thermal cycle

Introduction

The natural resinoid material known as shellac, which is secreted by the small insect Laccifer lecca, living in a certain tree in India and Thailand, in the subtropical zone, is widely used as a brightener in various manufactured products, and as a damp-proofing agent for

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foods and tablets, utilizing its properties of making a lustrous, smooth, strong, and non-poisonous[1] film, after it hardens out of its alcohol solution. Shellac is now used in wide applications[2]. In addition to its very extensive range of application even at the present status, shellac has recently been examined on its possibility as a tool to prevent adhesion of oral bacteria[3] and dental caries[4] or as a sealant' 1[5] because of its considerably smooth film with strong acid-fast property[6] and because it provides no fear of so-called environmental estrogen elution such as bisphenol A.

The majority of these studies except for those on sealant have tried to protect the tooth surface physically by coating the enamel surface with shellac, however, no study has so far been performed to examine as for whether or not an etching treatment is necessary for obtaining an improved bond strength of shellac to the enamel surface.

This study aimed to examine the change on standing of the adhesive strength of shellac on enamel and the effects of etching treatment.

Materials and Methods

1. Experimental drug solution

0.1 to 20% shellac solution was used as the experimental drug solution, after dissolving shellac in ethyl alcohol.

2. Product of test piece of bovine enamel

Bovine mandibular anterior tooth was extracted soon after slaughter, and the crown was separated from the root part by being horizontally cut off by a diamond disc, and after filling Glass Ionomer Cement into the coronal pulp cavity, the whole crown was embedded into resin (No. 105 Marumoto Astrues, Tokyo). The surface of enamel was exposed by polishing after curing, and the bovine enamel testing piece (test piece) was used for experimentation after enamel by waterproof polishing paper (#600).

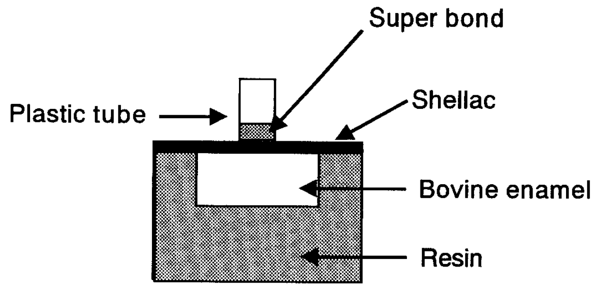


Fig. 1 Test piece of bovine enamel

3. Adhesive strength of bovine enamel

The test piece was washed and dried after etching the surface of enamel in 40% phosphoric acid solution for 15 seconds, and the test piece and its tubes were bonded (Super Bond, Sun Medical, Shiga) on the coated surface of enamels (Fig. 1). The test piece was immersed in a distilled water at 37℃ for 24 hours after curing the coated surface of enamels, the test piece was tried the adhesive strength, using a universal testing machine (1310DW, Aicho Engineering, Tokyo) at a cross head speed of 0.5 mm/min. Moreover, to study of effects of etching treatment on adhesive strength, the enamel test piece with etching no-treatment was tried the adhesive strength as following same method.

4. Fluctuations of adhesive strength at continuous changes of water temperature

To estimate the change on standing of adhesive strength in the practical oral cavity, the test piece was tried the stress test of temperatures by thermal cycle apparatus. And then, the test piece bonded with the plastic tube was immersed in a distilled water at 37℃ for 24 hours, and the test piece-bonded plastic tube was tried the stress test of temperatures (one cycle of this test was seconds immersed in cold water bath at 4℃, and a hot water bath at 60℃ alternately) at 3000 times of the thermal cycle, and the compressive shear test was carried out using the former method.

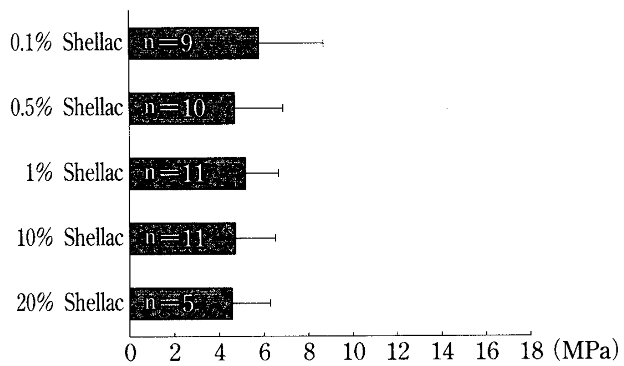


Fig. 2 Adhesive strength without etching treatment to enamel
(Enamel with immersing in the thermostat at 37 ℃ for 24 hours. n= 5 ~11)

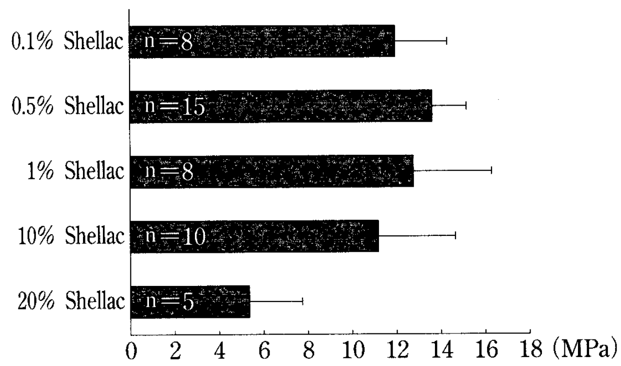


Fig. 3 Adhesive strength with etching treatment to enamel
(Enamel with immersing in the thermostat at 37 ℃ for 24 hours. n= 5 ~15)

5. Observation of the broken out section with a scanning electron microscope and a stereoscopic microscope

After carrying out the compressive shear test, in order to observe the broken-out section, the surface of enamel was examined with a scanning electron microscope (SEM, SEMEDX S-3500N, Hitachi, Tokyo) and a stereoscopic microscope (SMZ-2T, Nikon, Tokyo).

6. Statistical analysis

Comparison of no-paired two groups was carried out using Student's t-test, and comparison of multiple groups was carried out using analysis of variance (ANOVA), and then multiple comparisons were performed by Fisher's PLSD method, using statistical analyses software (Stat View Ver.4, Hulinks, U.S.A.).

Results

1. Effects of shellac at several concentrations on adhesive strength and etching treatment to bovine enamel

Figure 2 shows the adhesive force to enamel by shellac for 0.1 to 20% solutions, and Fig. 3 shows the adhesive strength to enamel with etching treatment. The adhesive strength to enamel without etching treatment showed about 5MPa at all concentrations, so there was no good correlation between shellac concentrations and adhesive strength. In addition, there was no significant difference in each group as a result of analysis of variance. In addition, the adhesive strength of each group to enamel with etching treatment significantly increased, excluding the 20% shellac group : The adhesive strength of the 0.1 shellac group was 12.0± 2.9MPa; that of the 0.5% group was 13.7± 1.5MPa; that of the 1% group was 12.8± 3.5MPa, and that of the 10% group was 11.2± 3.5MPa. In this case, there was an increasing tendency with a lower shellac concentration, but conversely, the adhesive strength decreased with decreasing till 0.1% shellac group. In this study, the 0.5% shellac group showed the most adhesive strength, and the mean of adhesive strength to enamel with etching treatment was about three-fold of that without etching treatment (4.7→13.7MPa), but there was no significant difference in the adhesive strength between the 0.1% shellac group and the 1.0% group (Table 1).

2. Changes of adhesive strength to enamel by thermal cycle test

Figure 4 shows the adhesive strength to

Table 1 Results of multiple comparisons test among each group without thermal cycle (group of etching treatment)

0.5% Shellac Group	1 % Shellac Group	10% Shellac Group	20% Shellac Group	Group
N. S.	N. S.	N. S.	※	0.1% Shellac Group
	N. S.	N. S.	※	0.5% Shellac Group
		N. S.	※	1 % Shellac Group
			※	10% Shellac Group

※$p<0.05$
N. S. : not significant

Table 2 Results of multiple comparisons test among each group with thermal cycle (group of etching treatment)

0.5% Shellac Group	1 % Shellac Group	10% Shellac Group	Group
N. S.	N. S.	※	0.1% Shellac Group
	N. S.	N. S.	0.5% Shellac Group
		N. S.	1 % Shellac Group

※$p<0.05$
N. S. : not significant

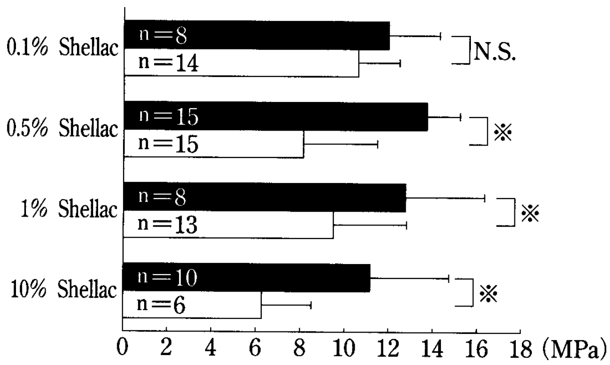
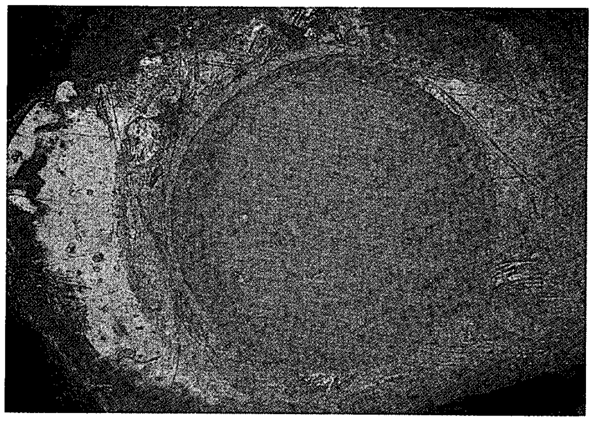
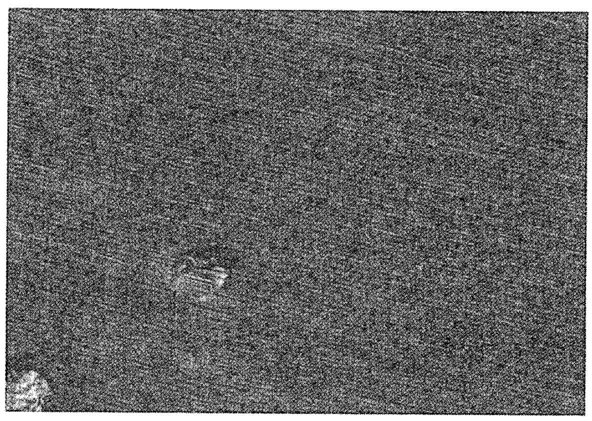


Fig. 4 Adhesive strength with thermal cycle
■ : Control (n= 5 ~15) , □ : Adhesion force with thermal cycle test (n= 6 ~15)
(all tested sample with etching treatment)
※$p<0.05$ (t-test) , N. S. : not significant

enamel at 3000 times of thermal cycle for 0.1 to 10% shellac groups. There was a significant decrease in adhesive strength to enamel with thermal cycle for each group : The 0.1% shellac group was 10.6±1.9MPa; the 0.5% group was 8.2±2.3MPa ; the 1% group was 9.5±3.3MPa, and the 10% group showed decreasing adhesive strength till 6.3±2.2MPa. Moreover, the

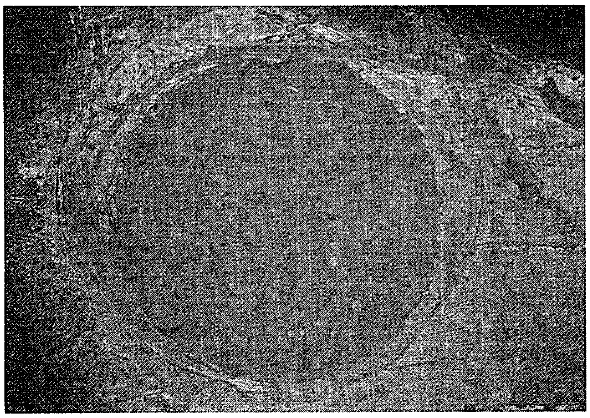


a



b

Fig. 5 Enamel surface without etching treatment
a : ×2.5 b : ×16



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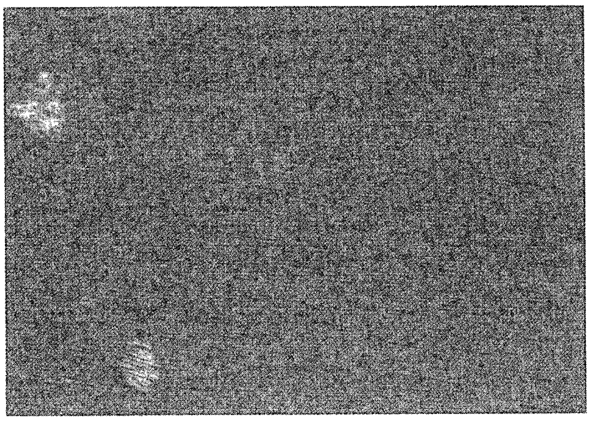
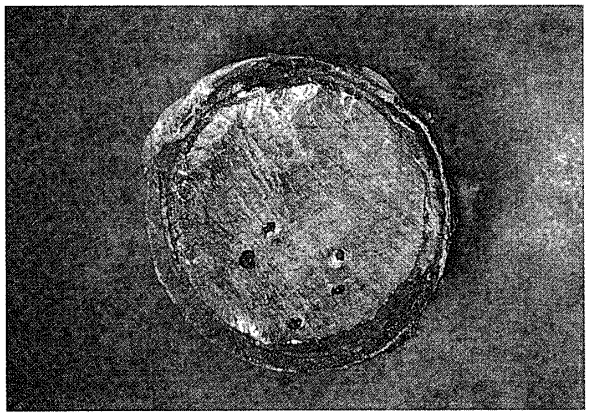


b

Fig. 6 Enamel surface with etching treatment
a : ×2.5 b : ×16



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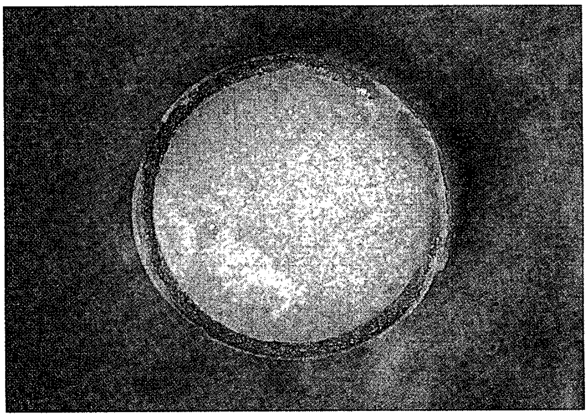

b

Fig. 7 The observed finding in the broken section of plastic tubes
a : enamel coated with shellac
b : enamel not coated with shellac
(a and b ×2.5)

decrease rates of adhesive strength were 11.4% for the 0.1% shellac group, 40.4% for the 0.5% group, 25.7% for the 1% group, and 44.3% for the 10% group, comparing adhesive strength without thermal cycle. In the above results, the 0.1% shellac group showed the strongest adhesive strength to enamel with thermal cycle, and the decrease rate of the adhesive strength, simultaneously, was the smallest of all the groups. However, there was a significant difference in the adhesive strength between the 0.1% shellac group and the 0.5% group or the 1% group (Table 2).

3. Enamel state after breakage

1) State of broken section

The state of enamel surface was observed by a stereoscopic microscope after carrying out the compressive shear test, for the 20% shellac group. Figures 5 (a and b) shows findings without etching treatment, and Figures 6 (a and b) shows findings with etching treatment. At a low magnification, an extensive luster with shellac coating was observed around the outside of adhered plastic tubes in both groups but such a luster completely disappeared from the inside of the adhered surface (Fig. 5a and Fig. 6a).

On the other hand, in the observation of the

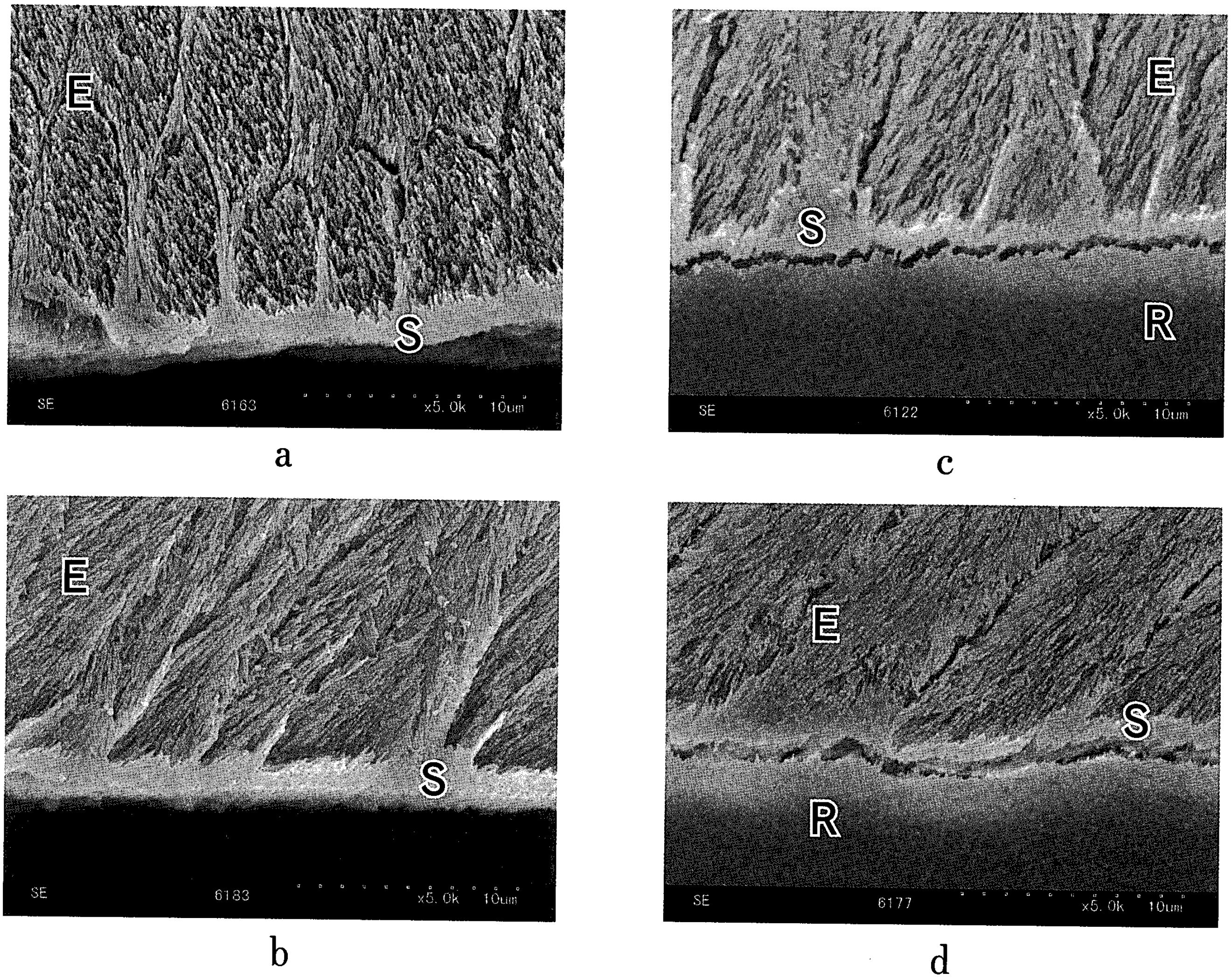

Fig. 8 The state outer of layers of enamel by SEM
a : 0.1%, b : 0.5%
c : 1%, d : 10%
(E : Enamel, S : Shellac, R : Resin)

broken enamel section by high magnification, the sample of enamel without etching treatment had many micro-flaws due to polishing of the enamel sample, while those with etching treatment had no micro-flaws, showing very lustered, smooth enamel section (Fig. 5b and Fig. 6b).

The observed findings in the broken section of plastic tubes, after the compressive shear test, for the 20% shellac group, are shown in Figure 7a, and the observed findings in enamel not coated with shellac, after the shear test, are shown in Figure 7b, as a control group.

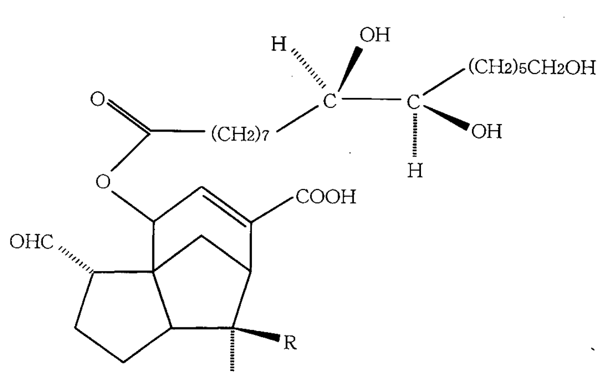

Fig. 9 Chemical structure of soft resin
R = CHO

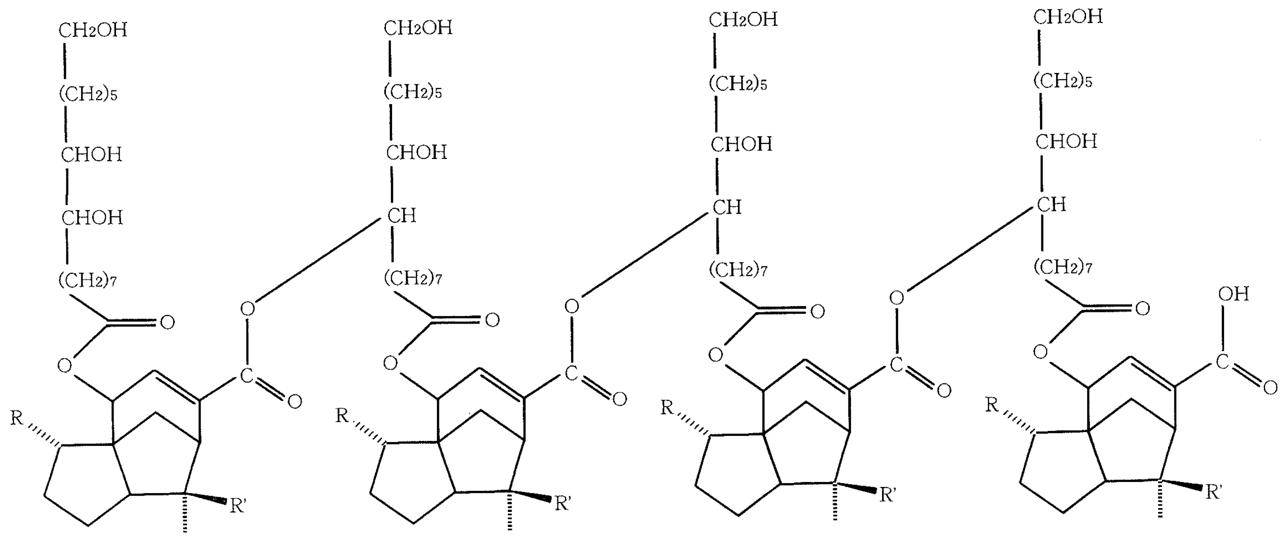

Fig.10 Chemical structure of hard resin
R =CHO/COOH, R' =CH_2OH/CH_3

The broken section of plastic tubes from the 20% shellac group showed luster and silver tone in photographs, but the tone of sample that adhered directly to enamel not coated with shellac, showed milky white.

2) Observation of SEM

The state of outer layers of enamel after conducting the compressive shear test for 0.1-10% shellac groups is shown in Figures 8a-d. The outer layer which was extensively covered with an adhered material probably being remained shellac of several micrometers in thickness was observed irrespective of the shellac concentration used for coating. Though a part of adhered material entered into the interprismatic space in some cases depending on its type of sample used, the thickness of the outer layer was almost constant in all experimental groups.

Discussion

1. Chemical structure of shellac and application to dentistry

Shellac is a mixture compound of many resin acids, and all of its chemical structures have not yet been elucidated. Its secretion elements of Laccifer lecca seem to be resins, coloring matters, and waxes. Resins elements of secretion are ester compounds of many resins acids and resin alcohols, and the main elements seem to be respective esters of aleuritic acid and jaralic acids, or laccijaralic acid. These are isolated as soft resins (Fig. 9) ; hard resins (Fig. 10) seem to be formed by ester combination among two to four or moleculars of soft resins[7~12].

An alcohol solution of these resins shows high luster, and a smooth, strong film after drying. Shellac has been recently applied to the dental field, for trial. Most applications are used to prevent the adhesion of oral bacteria to teeth, or to prevent dental caries. However, studies of the adhesive strength of shellac on enamel scarcely examine the changes on standing of adhesive strength in the practical oral cavity, and this information remains unknown. And some studies tried to examine the adhesive strength of shellac on enamel.

2. Adhesion properties on enamel

The adhesive strength of shellac on tooth surface without etching treatment was about 5MPa at most of the concentrations of shellac tested, and showed comparatively lower adhesive strength (Fig. 2). On the other hand, the adhesive strength on tooth surface with etching treatment increased remarkably (Fig. 3). The purpose of etching the tooth surface is generally to increase the inserting strength of dental adhesive materials by making a rough enamel surface. The adhesive strength of shellac seemed to be increased because the shellac had adhesivity, and shellac solution flowed into microgaps produced by etching treatment. Therefore, to produce a large adhesive strength, it seems the shellac solution must fully flow into interprismatic gaps of enamel, and the fluidity of shellac solution is increased as much as possible. Shellac of concentrations of 0.1 to 1.0% showed comparatively greater adhesive strength in the samples that received etching treatment, and the adhesive strength tended to lower for shellac concentrations above 1.0%. Shellac alcohol solution seems to have greater adhesion as the shellac concentration increases, because of increased film thickness after curing. The adhesive strength of the 0.5% shellac group was the highest value in this study; however, there was not a significant difference among the 0.1 to 1.0 % groups, including the 0.5% group, in significant statistical terms (Table 1). Therefore, it is suggested that the optimum concentrations of shellac are approximately 0.1 to 1.0%.

3. Change in adhesive strength over time

The thermal cycle test is a durability test that models the environment in the mouth, and it is a general test system because it can relatively evaluate test[13] results in the same condition.

The thermal cycle test was used to examine how the shellac adhesive strength to enamel changes in the mouth over time. The test condition[14,15] was set to dip a sample into a cold water bath at 4℃, and then into a hot water bath at 60 ℃, alternately, for 30 seconds for each dip, and for 3000 repetitions of this thermal cycle.

Compared with a control group before the thermal cycle, all test groups showed a significant decrease in adhesive strength, and a comparatively lowconcentration shellac showed a greater adhesive strength, as described above ; for example, the 0.1% shellac group showed an average adhesive strength of 10.6MPa. Retief[16] reported an increased possibility of destroying the tooth surface during removal when an adhesive object is bonded to enamel at an adhesive strength exceeding 9.7MPa. This report reveals that the 0.1 to 1.0% shellac groups, of 8.2 to 10.6MPa, on average, in adhesive strength, can be practically used.

The thermal load due to thermal cycle is a severe test for a sample, degrading the physical properties of dental materials. A sample with a thinner film as used in the present study seemed not to be affected by these factors. It is thus estimated that a sample covered with a thicker film may be affected more easily. In fact, the smallest lowering rate of adhesive strength was observed in the 0.1% shellac group in the present test, and there was no significant difference compared with the control value of the test group without the thermal cycle (Fig. 4).

4. Enamel surface after shear test

When the enamel surface after shear test was observed in the 20% shellac group by a stereoscopic microscope, luster of exposed shellac remained on the outside of a part bonded to the plastic tube, but it was not observed in just place bonded to the plastic tube, regardless of etching treatment (Figs. 5 and 6). Figure 7a shows the finding of adhesive surface on the plastic tube side at that time. Its color showed lustrous silver compared with that of the control group (Fig. 7b), which may suggest, including the above findings, that the shellac is peeled off from the enamel surface during shearing.

Chiba *et al.*[4] reported that the thickness of a film that was formed on the enamel surface through shellac coating was about 550 μm with 40% shellac, and about 370 μm with 20% shellac. The concentrations of shellac used in the current SEM observation are 0.1 to 10%, so the above findings are not substantially comparable with those of Chiba et al. Assuming that the shellac remained on the tooth surface, it is supposed that a film thickness of several hundred micrometers would be found in the 10% shellac group, and film thickness of several micrometers, or several tens of micrometers, would also found in the other test group. As shown in Figures. 8a-8d, however, no structure with such a thickness was observed on the enamel surface and it seems reasonable to consider that most of shellac applied was peeled off during shearing treatment.

Conclusions

The present study artificially examined the adhesive strength of shellac to enamel, as well as the change in adhesive strength over time in the mouth, and the following findings were obtained.

1. The adhesive strength of shellac to the untreated enamel surface was around 5MPa irrespective of the concentration of used shellac.
2. The adhesive strength tended to increase through etching treatment to the maximum level of 13.7MPa (0.5% shellac group).
3. Although a decreased adhesive strength due to thermal cycle was evident in all examined groups, a practical adhesive strength was kept at shellac concentrations of 0.1 to 1% (0.1% shellac group : 10.6Mpa ; 0.5% group : 8.2Mpa ; 1% group: 9.5MPa).
4. It was suggested that the optimal concentration of shellac with the maximum adhesive strength is around 0.1 to 1%.

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