Effects of opacity and oxygen inhibition of coating resin composites on bond strength to enamel

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The purpose of this *in vitro* investigation was to study the effects on bond strength to primed human enamel stemming from opacity and polymerization inhibition by oxygen due to two coating resins. The coating resins and primers used were White Coat and an experimental material, SIR. The bond strengths on fine-ground enamel were evaluated for three shades of each of these coating resins after 24-hour storage in water. In addition, their degrees of opacity and oxygen inhibition depths were measured. The mild self-etch primer solutions produced very shallow but distinct etching patterns for micromechanical retention of the coating resin. Significant linear relationships between bond strength on the one hand and opacity and oxygen inhibition depth on the other were found for the three shades of each coating resin. Generally, the bond strength mediated on enamel is sufficiently high when these resins are combined with their proprietary adhesives. Therefore, the decrease in bond strength with increasing opacity of the coating resin shades has to be taken into account during application and light-curing.

Keywords: Enamel bond strength, Opacity, Inhibition of polymerization

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INTRODUCTION

Recently in Japan, so-called coating resin composite materials have been introduced. These materials function mainly as tooth manicure, where instantaneous esthetic improvement of teeth is a priority or when definitive treatment measures can or must be postponed. These resin composites are commonly applied on non-instrumented pumiced enamel. Therefore, enamel etching is an integral part of the treatment.

Phosphoric acid etching is a proven method to create the micromorphological pattern needed for mechanical bonding of the composite to the tooth surface. However, enamel etching with phosphoric acid of more than 30% concentration creates deeply etched enamel which is therefore not favored for temporary retention of coating resins. To overcome this problem, manufacturers of coating resins have since delivered and recommended self-etching adhesive primers as a package component. Such primers with a pH commonly around 2 are less acidic than phosphoric acid and have the advantage that they etch and prime the target enamel simultaneously. These coupling agents are thus considered less invasive than conventional phosphoric acid etchants. Moreover, recent products are reportedly adequately effective in bonding restorative resins to enamel and dentin^{1,2)}.

With regard to bonding performance, the adhesion of a commercial coating resin — combined with the proprietary self-etching primer — to intact (cleaned with non-fluoridated paste) and ground enamel (wet 600-grit SiC paper) was evaluated recently³⁾. The micro-shear bond strengths obtained proved that the

depth and pattern of enamel demineralization were apparently suitable to retain the coating resin effectively. No differences in bond strength were noted between the intact and instrumented enamel. However, the bond strength to intact enamel decreased significantly from an average of 28 MPa throughout the first three months of water storage to 20 MPa after six months, presumably due to plasticization of the resin arising from long-term water contact. Nevertheless, these results might justify the acceptable use of this commercial coating resin on a temporary basis.

Further on bonding performance, it was also previously reported that an insufficient degree of resin cure at the interface might result in poor adhesion to tooth structure⁴⁾. A number of reasons might be responsible for the varying degrees of cure, such as the resin and filler compositions, the initiating system, filler loading, shade and translucency, type and intensity of the curing light, and irradiation duration.

On the purpose and function of coating resins, they are created to hide discolored tooth surfaces. For this reason, they commonly exhibit high opacity. However, the effects of highly opaque coating resins on the degree of conversion and bond strength to enamel is not clear — even when it is applied in thin layers on discolored enamel only. It is reasonable to speculate a relationship between resin opacity and bond strength, as high opacity might prevent sufficient curing light transmission to the bonding interface. By the same token, high resin opacity might also be related with oxygen inhibition upon polymerization.

The purpose of this *in vitro* investigation was to study the effects of two coating resins, in terms of opacity and polymerization inhibition by oxygen, on

bond strength to primed human enamel. The null hypothesis to be tested was that the bond strength of coating resins on enamel would be independent of resin composite shade, opacity, and oxygen inhibition tendency.

MATERIALS AND METHODS

Materials used

Table 1 shows the two polymer-based coating materials investigated in this study, together with their proprietary priming solutions. The three shades of each resin coating material selected for this study and the compositions of all the materials used are also listed.

Shear bond strength (SBS)

Human maxillary incisor teeth stored for a maximum of 6 months after extraction in 1% chloramine solution were used for this investigation. The roots of the teeth were cut off with a diamond blade, and the crowns were placed with the facial surface on the bottom of 20-mm-wide rubber molds for embedding in a slow-curing epoxy resin. Following overnight curing at ambient laboratory atmosphere, the tooth specimens were removed from the rubber molds. The bottom surfaces were slightly ground on wet SiC paper, grit numbers 320 through 1000, to expose peripheral enamel areas large enough for placement of resin composite cylinders which were of 2.3 mm diameter. Eight teeth were randomly allocated to each of the six resin coating materials to be tested (three shades for each resin coating material).

Following careful rinsing with deionized water and air-drying, the respective primer solutions were applied. Using a microbrush, the White Coat Primer (Kuraray Medical Inc., Tokyo, Japan) was applied in one layer with 60-second agitated dwell time, prior to gentle but thorough air-drying. For the Shofu Primer (Shofu Inc. Kyoto, Japan), components A and B were dispensed at equal volumes, mixed with a disposable

sponge, and applied to the enamel target area for 3 seconds, followed by gentle drying with compressed air.

The primed specimens were clamped in an Ultradent bonding jig under a 2.3-mm-wide, cylindrical plastic mold. The resin coating material was inserted to a height of 1 mm and light-cured for 40 seconds with a tungsten-halogen curing unit, Translux Energy (Heraeus Kulzer GmbH, Hanau, Germany; output: approximately 800 mW/cm²). Distance between the light-exit window and resin composite surface was 5 mm.

Immediately after curing, the plastic molds were removed and the specimens were immersed in 37°C water for 24 hours. After water storage, shear bond strength test was conducted using the Ultradent notched steel rod, parallel and close to the enamel surface with a shear rate of 1 mm/minute, until failure occurred. Shear bond strength (SBS) was expressed in MPa units, as derived from dividing the imposed force in N at the time of fracture by the bond area in mm².

For each shade of the resin coating material, eight specimens were tested. One-way ANOVA and Duncan's multiple comparison test were used to analyze the SBS data statistically at a significance level of $p=0.05$.

Morphological SEM analysis of etching pattern

To visualize the morphologies of the etched enamel surfaces with different primer treatments, the labial sides of extracted upper central incisor crowns were manually abraded — but very gently — with wet 1000-grit SiC papers. After thorough rinsing with water, the ground surfaces were dried with compressed air. Two specimens were used for each treatment with the White Coat or Shofu primer, as described above. At the end of the manufacturer-specified dwell time, the priming solution was carefully washed off with a copious amount of acetone before ultrasonic cleaning in distilled water.

To visualize the detailed reproduction of the resin coating material on primed enamel surface, two specimens for each primer treatment were produced as

Table 1 Resin coating materials investigated in this study

Brand	Component	Batch/Expiry	Manufacturer	Composition
White Coat*	Primer	00009E 2009-10	Kuraray Medical, Tokyo, Japan	HEMA, MDP, water, photoinitiator
	Base-coat	00052D 2010-08		UDMA, HEMA, micro silica filler, photoinitiator
SI-R20209 (exp.)**	Primer A	010701 2010-01	Shofu Inc., Kyoto Japan	water, organic solvent, initiator
	Primer B			phosphonic acid monomer, solvent, pigments, others
	Resin	020702 2010-02		Bis-GMA, TEGDMA, S-PRG filler, glass filler, nanofiller, photoinitiator

* Shades: A1, OA3, OB0.

** Shades: BW1, BW3, BWO

described above, followed by coating with a 2-mm-thick layer of coating resin (shades OA3 and BW3). The coating resins were then light-cured with Translux Energy for 40 seconds. After 24-hour storage in 37°C water, the specimens were immersed in 6 mol/L hydrochloric acid to remove mineralized tooth substance from the resin. The resin replicas were finally cleaned ultrasonically in distilled water and air-dried.

For morphological SEM analysis, the etched teeth and resin replicas were mounted on aluminum stubs and sputter-coated with Pt for inspection in a scanning electron microscope at $\times 3000$ magnification.

Opacity (OCR)

To determine the opacity or contrast ratio (CR), which is defined as the ratio of the reflectance of a specimen disk when backed by a black standard to that when backed by a white standard⁵⁾, three disk-shaped specimens for each shade of the two resin coating materials were produced in cylindrical molds of 16 mm width and 1 mm height. The molds were treated with a microcrystalline wax (dissolved in toluene) to prevent adhesion between the steel sidewalls and the resin coating material. The mold was placed on a matrix strip-covered microscopic glass slide, filled with resin, covered with another matrix strip, and pressed flush. Specimens were then light-cured with Translux Energy for 60 seconds in a sweep mode with the light-exit window close to the surface.

By means of a spectrophotometer (SP64, X-Rite Incorporated, Grandville, MI, USA), opacity was determined after 24 hours of specimen storage at ambient laboratory atmosphere. Each specimen was measured three times on a black background followed by three times on a white background, and then the opacity or contrast ratio in percent was calculated automatically. Data were analyzed using one-way ANOVA and Duncan's *post hoc* test at 0.05 level of significance.

Oxygen inhibition upon polymerization (INH)

The depths of oxygen inhibition of the resin coating materials were measured microscopically. A small droplet of the resin was placed on a microscopic glass slide between two spacer cover glasses (0.1 mm in thickness). Another cover glass was placed over the droplet and pushed in place until contact with the two supporting spacer glasses was established. The disk-shaped specimen was then light-cured with Translux Energy for 40 seconds prior to inspection in an incident light microscope at $\times 500$ magnification.

Due to the differing refractive indices of polymer and monomer, a clearly discernible line was seen. On each of the three specimens for each resin shade, the width of the outer, non-polymerized, inhibited zone was measured at four locations at 90 degrees apart. Inhibition depth was determined using an ocular screw micrometer with a reading accuracy of 0.2 μm . Data were then analyzed using one-way ANOVA and *post*

hoc multiple comparisons using the Duncan's test ($p=0.05$).

RESULTS

Figure 1 shows the box-and-whisker plots of shear bond strength to enamel according to the different resin coating materials and shades. The horizontal line inside each box represents the median, the upper and lower box borders give the interquartile distances, and the lengths of the whiskers the minimum and maximum SBS values. One-way ANOVA revealed significant differences among the six groups, whereby groups with the same lower case letter denote homogeneous data subsets that are not significantly different ($p>0.05$). The lowest mean bond strength was obtained with BW0 (11.3 MPa). BW1 showed the highest mean bond strength (21.0 MPa), but it did not differ significantly from A1.

The SEM micrographs at $\times 3000$ magnification (Fig. 2) show the etching patterns produced with the acidic Kuraray and Shofu priming solutions, as well as the resin replications of the etched enamel surfaces. Etching pattern on the enamel surface was very shallow, and that prismatic structures were hardly recognizable on both the enamel and replica surfaces. Reproduction of the etched enamel details was however satisfactory.

Table 2 shows the means and standard deviations of the opacity data together with the significant differences among the six resin shades. The highest CR value was registered for OA3 at 97% and the lowest for BW1 at 54.8%. All the six shades exhibited significantly different CR values.

Table 3 summarizes the depths of oxygen inhibition

Fig. 1 Shear bond strengths of coating resins on enamel by product and shade. Box-and-whisker plots with medians and interquartile distances. Same lower-case letters denote groups that are not statistically significantly different ($p>0.05$).

Fig. 2 SEM micrographs of etch patterns on enamel. (A) and (C) are the direct enamel patterns after treatment by Kuraray and Shofu Primers respectively. (B) and (D) show the corresponding resin replicas.

Table 2 Opacity (CR) values of coating resins (%)

Material	White Coat				SIR	
	A1	OA3	OB0	BW1	BW3	BWO
Shade	A1	OA3	OB0	BW1	BW3	BWO
Mean	81.8	97.0	86.5	54.8	72.8	95.3
± S.D.	0.3	0.2	0.3	0.4	0.2	0.6
Significance $\alpha=0.05$	c	f	d	a	b	e

Mean value and standard deviation of three specimens (five measurements each)

One-way ANOVA at $p<0.001$; Duncan ranking at $p=0.05$

Table 3 Depths of oxygen inhibition of coating resins (μm)

Material	White Coat				SIR	
	A1	OA3	OB0	BW1	BW3	BWO
Shade	A1	OA3	OB0	BW1	BW3	BWO
Mean	14.0	21.5	14.6	7.9	10.4	13.2
± S.D.	1.2	2.5	1.8	1.3	2.7	2.0
Significance $\alpha=0.05$	c	D	c	a	b	c

Mean value and standard deviation of three specimens (four measurements each)

One-way ANOVA at $p<0.001$; Duncan ranking at $p=0.05$

Fig. 3 Representative microphotographs at same magnification, illustrating two same-brand coating resin shades with significantly different depths of polymerization inhibition. The peripheral demarcated zone gives the depth of oxygen inhibition.

for each shade of the two investigated coating resins. On the overall, the inhibition depths of White Coat resin were greater than those of SIR resins. BW1 was inhibited by oxygen only to a depth of approximately 8 μm , whereas OA3 was not polymerized to a depth exceeding 20 μm . Figure 3 shows two representative microphotographs of the same magnification of resin coating disks with inhibited polymerization at the periphery, which was in contact with oxygen from the surrounding atmosphere during light-curing. BW1 exhibited an inhibition depth of approximately 8 μm , whereas that exhibited by BW3 was approximately 12 μm . Monomer and polymer were clearly distinguishable due to their differing refractive indices.

Linear relationships were found between opacity (CR) and depth of oxygen inhibition, for the three resin shades of White Coat ($y=1.82x + 58.08$; $r^2=0.95$) and for the three resin shades of SIR ($y=7.65x - 6.04$; $r^2=0.99$). Similarly, SBS data were linearly correlated with opacity (CR) for White Coat ($r^2=0.96$) and SIR ($r^2=0.98$), and with the depth of oxygen inhibition for White Coat ($r^2=0.82$) and SIR ($r^2=0.98$).

DISCUSSION

The present *in vitro* study has shown that the bond strength to enamel obtained after priming with the respective self-etching primer solution depended on the shade and opacity of the coating resin applied. Therefore, the null hypothesis that the bond strength of coating resins on enamel would be independent of resin composite shade, opacity, and oxygen inhibition tendency was rejected.

The two self-etching primer solutions produced a

shallow, yet clearly visible, etch pattern on the ground enamel. In the present study, the enamel surface was instrumented with 1000-grit SiC paper. However, according to a study by Imamiya *et al.*³⁾, the end result would be tantamount to priming intact enamel with non-fluoridated paste. The same authors³⁾ also reported that the etching effect of White Coat Primer (pH 2.1) was similar to acid etching with 10% phosphoric acid, which meant a sufficiently pronounced etch pattern for adequate microretention of the resin composite^{6,7)}. Moisture on the etched enamel surface was not a concern, as the primer resin film was thoroughly air-dried before the resin composite was applied on it. Thorough air-drying for volatilization of the primer solvent is mandatory to avoid or minimize water crossing through the polymerized primer layer. The latter phenomenon is caused by difference in osmotic pressure even on enamel, which might then result in high mechanical resistance against the cured primer layer⁸⁻¹²⁾.

The height of the resin composite cylinders polymerized on the primer-treated enamel was 1 mm, a thickness that might simulate the common thickness of coating resin layers applied *in vivo*. An otherwise thinner layer of coating resin might not be able to hide the often severely stained underlying enamel, despite the commonly high opacity of coating resins¹³⁾. For a resin coating layer of 1 mm thickness, light-curing for 60 seconds using a high-output tungsten-halogen curing unit was considered to be adequate for in-depth polymerization. Nevertheless, significant differences in shear bond strength for the different resin shades were found¹⁴⁾. It was therefore reasonable and necessary to determine the opacities of the resin composites, since

highly opaque materials were suspected to hinder light transmission to the bonding interface. However, as the two coating resins were of different brands and had different compositions, the relationship between shear bond strength and opacity had to be evaluated separately for these two materials so that variables which might influence the analysis were soundly excluded. Highly significant ($p < 0.01$) linear relationships were found between shear bond strength and opacity for both resin coating materials.

The degree of polymerization of the coating resins at the bonding site, expressed as bond strength, was also correlated with the oxygen inhibition tendency of the respective resins^{15,16}. The method used to determine the inhibition depth was an easy microscopic technique, based on the discernible characteristics of monomer and polymer by their refractive indices^{15,17}. However, it must be pointed out that the distinguishable borderline seen in the microphotographs did not hence mean that it was central portion of the fully polymerized resin layer. Most probably, the outermost part of the polymer at the border to the monomer portion mainly consisted of oligomers and that the maximum degree of conversion first occurred at a depth of several hundreds of millimeters or perhaps deeper. Nonetheless, the strong correlation between opacity and inhibition depth established a straight-line relationship between bond strength and inhibition depth.

In light of the direct and highly correlated relationships between opacity and inhibition depth on the one hand and these parameters with shear bond strength on the other hand, it might be advisable to seal the surfaces of opaque coating resins with a transparent top coat material, as supplied by Kuraray as part of the coating resin system. The purpose of which is to protect the oral surface of the resin from early degradation and stain adsorption.

The decrease in bond strength reported by Imamiya *et al.*³ after 6 months' storage of the bonded specimens in water might be related to water crossing through the cured primer layer. Osmotic effects, even on specimens bonded to enamel, have been reported previously¹⁸. In contrast, water absorption by the resin composite could be excluded as the cause for reduced bond strength since saturation of the resin polymer with water was already established at an earlier time.

CONCLUSIONS

Based on the findings of this study, the clinically relevant conclusions and implications were:

1. Coating resins, when conditioned with the proprietary self-etching primer solutions, achieved clinically adequate bond strength to enamel with the initial 24 hours of storage time.
2. Thickness of the applied coating resin layer should be kept to a minimum. In particular,

dark opaque shades require special attention. Eventually, separate light-curing of thin consecutive layers is required.

3. For light-curing, it is advisable to always follow the manufacturer's instruction to use a curing unit with high output energy.

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