Influence of oxygen inhibition layer on the enamel bond strength and surface free energy characteristics of adhesive systems

Hirofumi Ueta

Nihon University Graduate School of Dentistry,

Major in Operative Dentistry

(Directors: Prof. Masashi Miyazaki and Assist. Prof. Akimasa Tsujimoto)

Contents

This thesis is based on the published article listed below, with additional data.

Abstract

The polymerization reaction in adhesive systems induced by photo-curing leads to the decomposition of camphorquinone and tertiary amine, resulting in the generation of reactive free radicals, which are able to add to the double bonds of resin monomers. Oxygen leads to retardation or inhibition of the free radical polymerization reaction and consequently to the formation of an oxygen inhibition layer (OIL) on the outermost layer of photo-cured resin-based materials when these are polymerized in the presence of air. The evidence concerning the role of the OIL of adhesive systems is still inconclusive, thus further studies are necessary in order to elucidate its effects on bond durability. The influence of the OIL on the shear bond strength (SBS) to enamel and surface free energy (SFE) characteristics of adhesive systems was investigated.

The adhesive systems tested were a three-step adhesive system, Scotchbond Multipurpose (SM), a two-step self-etch primer system, Clearfil SE Bond (CS), a single-step self-etch adhesive system, Clearfil tri-S Bond (CB), and a universal adhesive system, Scotchbond Universal (SU). Resin composite was bonded to bovine enamel surfaces ground with 320-grit silicon carbide paper to determine the SBS, with and without an OIL, of adhesives. SBS measurements were performed using a notched-edge test as described by ISO 29022. The SFE of cured adhesives with and without an OIL on enamel was determined by measuring the contact angles of bromonaphthalene, diiodomethane and distilled water using the extended Fowkes equation, as developed by Kitazaki-Hata. SEM observations of enamel-resin interfaces for tested adhesive systems with and without OIL were also conducted.

Although there were no significant differences in the enamel SBSs of SM and CS with or without OIL, the SBSs of CB and SU with OIL was significantly higher than without OIL. For all adhesive systems, the SFE (γ_S), polarity force (γ_S^p), and hydrogen-bonding force (γ_S^h) of cured adhesives with OIL were significantly higher than those of cured adhesives without OIL. SEM observations of enamel-resin interfaces showed that the approximate mean thickness of the adhesive layer was 30 µm for SM and CS, and 10 µm for CB and SU, for the specimens with OIL. By contrast, for the specimens without OIL, the approximate mean thickness of the adhesive layer was around 10 µm for SM and CS, and 4 µm for CB and SU. SEM images revealed thicker OILs in SM and CS compared with CB and SU.

The results of this study indicated that the presence of an OIL enhanced the enamel SBSs of single-step self-etch and universal adhesive systems, but had no influence on the SBSs of three-step adhesive and two-step self-etch primer systems. In addition, the SFEs of cured adhesives with an OIL were significantly higher than those without an OIL. The SFE characteristics of the OIL of adhesives were different depending on the type of adhesive system. The thickness of the OIL on adhesive systems was different depending on the adhesive system, and OILs of three-step and two-step self-etch adheisves were thicker than those of single-step self-etch and universal adhesive systems.

Introduction

The polymerization reaction in adhesive systems induced by photo curing leads to the decomposition of camphorquinone and tertiary amine, resulting in the generation of reactive free radicals, which are able to add to the double bonds of resin monomers (1). However, oxygen has a greater ability to react with the propagating free radicals than the monomer molecule does, oxidizing them into peroxy radicals, which have relatively low reactivity towards the monomer, and which form peroxides, terminating polymerization, if they do react (2). This leads to retardation or inhibition of the free radical polymerization reaction (3). Consequently, an oxygen inhibition layer (OIL) will appear on the superficial surface of the cured adhesive when an adhesive is polymerized in the presence of air (4).

Some previous studies (1,5) reported that the presence of an OIL on the adhesive systems is required for bonding with resin composite. By contrast, other studies found no significant difference in bonding performance (6-8), or even a negative effect (9-11). Therefore, the role of the OIL of adhesive systems is still a controversial topic, and further work is necessary in order to determine the influence of the OIL on bonding properties.

There are many kinds of adhesive systems available to the profession, and most of the adhesive systems follow either an etch-and-rinse or a self-etch approach, which differ in how the adhesive interacts with the tooth substrates (12). Total-etch adhesive systems include phosphoric acid pre-etching and subsequent application of the primer and/or adhesive (13), whereas self-etch primer systems utilize acidic functional monomers that etch and prime the tooth substrates simultaneously before application of adhesive (14). The current trend in adhesive systems is to reduce technique sensitivity and the number of clinical application steps, and thus single-step self-etch adhesive and universal adhesive systems have been developed (15). The single-step self-

3

etch adhesive systems combine the etching, priming, and bonding procedures, and simultaneously both form a continuous layer through surface demineralization by acidic functional monomers and allow penetration of resin monomers into the tooth substrates (16). Universal adhesive systems can be used with total-etch, self-etch or selective-etch modes (17), and can also be used to bond to a variety of substrates, including tooth, resin composites, glass ceramics, zirconia, and alloys (18). Thus, adhesive sytems differ in composition depending on the type of adhesive and also differ in how they interact with the tooth substrates.

Previous studies have found that the OIL thickness of photo-cured resin-based materials ranges from 4 to 40 μm (19-21). The thickness and characteristics of the OIL in resin-based materials depend on several factors, including monomer chemistry (3,20), filler morphology (22, 23), radical concentration (2), and the rate of oxygen consumption (3). Therefore, the characteristics of OILs of adhesive systems might differ depending on the type of adhesive system. To test this hypothesis, it is necessary to measure both the bond strength and the surface properties of adhesive systems, with and without an OIL. The surface properties of adhesives can be measured in terms of surface free energy (SFE) characteristics (24), and the data play an important role in determining the strength of the bond across the interface (16). Thus, analysis of the relationship between bond strength and SFE characteristics may provide insights into the effect of OIL on adhesives for bonding with resin composite.

This study investigated the influence of OIL on the enamel bond strength and SFE characteristics of adhesives. The null hypotheses to be tested were: (i) there would be no differences in enamel shear bond strength (SBS) of dental adhesives with and without OIL, and (ii) the SFE characteristics of OIL would not be influenced by the type of adhesive system.

4

Materials and Methods

1. Materials used

The adhesive systems used were: a three-step adhesive system, Scotchbond Multipurpose (SM, 3M ESPE, St Paul, MN, USA), a two-step self-etch primer system, Clearfil SE Bond (CS, Kuraray Noritake Dental Inc., Tokyo, Japan), a single-step self-etch system, Clearfil tri-S Bond (CB, Kuraray Noritake Dental Inc.), and a universal adhesive system, Scotchbond Universal (SU, 3M ESPE). Clearfil AP-X (Kuraray Noritake Dental Inc.) was used as the resin composite for the bonding procedures. The lot numbers and compositions of the materials used are listed in Table 1.

2. Specimen preparation

The shear bond strength (SBS) of the adhesive systems to enamel with and without OIL was measured by a notched-edge test as described in International Organization for Standardization (ISO) 29022 (25). Mandibular incisors extracted from 2- to 3-year-old cattle, and stored frozen (-20°C) for up to 2 weeks, were used as a substitute for human teeth. After removing the roots using a low-speed saw with a diamond-impregnated disk (IsoMet 1000, Buehler, Lake Bluff, IL, USA), the pulps were removed, and the pulp chamber of each tooth was filled with cotton to avoid penetration of the embedding media. The labial surfaces were wet ground with 240-grit silicon carbide (SiC) paper (Struers, Cleveland, OH, USA) to create a flat enamel surface. After ultrasonic cleaning for 30 s in distilled water to remove excess debris, the surfaces were washed and dried using a dental three-way syringe at a distance of 5 cm above the surface at an air pressure of 0.37 MPa. Each tooth was then mounted in self-curing acrylic resin (Tray Resin II, Shofu Inc., Kyoto, Japan) and placed under water to limit the temperature rise caused by the exothermic polymerization of the acrylic resin. The dentin bonding surfaces were

ground flat using a grinder-polisher (Ecomet 4, Buehler) and a sequence of SiC papers of grit sizes of #180 and #320, as specified by ISO 29022. These surfaces were then washed and dried using a dental three-way syringe. The specimens were prepared under ambient conditions of $23 \pm 2°C$ and $50 \pm 10\%$ relative humidity.

3. SBS test

Fifteen specimens per test group were used for each of the four adhesive systems. A Shear Bond Test Kit (Ultradent Product Inc., South Jordan, UT, USA) was used for determining SBS. The adhesives were applied to the enamel surfaces according to the manufacturers' instructions. To produce specimens without an OIL, the top surface of the adhesive was removed with an ethanol impregnated cotton pellet. Following application of the adhesive systems to the adherend surface, the resin composite cylinders were formed on the enamel surfaces by clamping plastic molds (Bonding Mold Insert, Ultradent Product Inc.) in a fixture (Bonding Clamp, Ultradent Product Inc.) against the surface. The resin composite (Clearfil AP-X; Kuraray Noritake Dental Inc.) was placed into the mold using a condenser and then photo cured for 30 s with a quartz-tungsten halogen unit (Optilux 501; Kerr, Orange, CA, USA) from a standardized distance of 1 mm. The power density (>800 mW/cm^2) of the curing unit was checked using a dental radiometer (model 100, Kerr) before preparing the specimens. The plastic molds were then removed, and the finished specimens were transferred to distilled water at a temperature of 37°C and stored for 24 h before use for SBS measurements.

SBS was determined using a universal testing machine (Type 5500R, Instron, Norwood, MA, USA), equipped with an shearing fixture (Crosshead Assembly, Ultradent Product Inc.), at a crosshead speed of 1.0 mm/min. The SBS (MPa) was calculated from the peak load at failure divided by the bonding area. After testing, the specimens were examined under an optical

microscope (SZH-131, Olympus Corp., Tokyo, Japan), at a magnification of $\times 10$ to determine the type of failure. The proportions of the resin composite surface with adherent enamel and visible remnants were estimated and used to classify the failure as follows: adhesive failure; cohesive failure in the enamel; cohesive failure in the resin composite; and mixed failure (a combination of adhesive and cohesive failure).

4. SFE measurements

Bovine mandibular incisors were prepared as described for SBS measurements. The adhesive system was applied to the enamel surfaces according to the manufacturers' instructions, followed by photo curing for 10 s. To produce specimens without an OIL, the top surface of the adhesive was removed with an ethanol-impregnated cotton pellet. The specimens were then used for contact angle measurements to analyse the SFE characteristics of the adhesives in the presence or absence of the OIL.

The SFE characteristics of specimens were determined by measuring the contact angle formed with the surface by three test liquids: bromonaphthalene, diiodomethane and distilled water, each of which has known SFE parameters. For each test liquid, the equilibrium contact angle (θ) was measured by the sessile drop method under ambient conditions of $23 \pm 2°C$ and $50 \pm 10\%$ relative humidity using a contact angle measurement apparatus (DM 500, Kyowa Interface Science Corp., Saitama, Japan) for 10 specimens per group. The apparatus was fitted with a charge-coupled device camera to enable automatic measurement. A standardized 3.0 μL drop of each test liquid was placed on the cured adhesive surfaces, and a profile image was captured after 500 ms using the apparatus. Contact angles were then calculated by $\theta/2$ method using the built in interface measurement and analysis system (FAMAS, Kyowa Interface Science Corp.).

7

The SFE parameters of the solids were then calculated based on the fundamental concepts of wetting. The Young-Dupré equation describes the work of adhesion (W) between a solid (S) and a liquid (L) in contact as follows:

$$W_{SL} = \gamma_L + \gamma_S - \gamma_{SL} = \gamma_L (1 + \cos\theta)$$

here, γ_{SL} is the interfacial free energy between the solid and liquid, γ_L is the SFE of the liquid, and γ_S is the total SFE of the solid. By extending the Fowkes equation, as developed by Kitazaki-Hata, γ_{SL} can be expressed as follows (26):

$$\gamma_{SL} = \gamma_L + \gamma_S - 2 (\gamma_L^d \gamma_S^d)^{1/2} - 2 (\gamma_L^p \gamma_S^p)^{1/2} - 2(\gamma_L^h \gamma_S^h)^{1/2}$$

$$\gamma_L = \gamma_L^d + \gamma_L^p + \gamma_L^h, \ \gamma_S = \gamma_S^d + \gamma_S^p + \gamma_S^h$$

where γ_L^d, γ_L^p, and γ_L^h are components of the SFE arising from the dispersion force, the polar force, and the hydrogen-bonding force, respectively. The γ_S, γ_L^d, γ_L^p, and γ_L^h were calculated based on these equations, using the built-in software.

5. Scanning electron microscopy (SEM)

The enamel-resin interface ultrastructure was examined by SEM. Bonded specimens of each group (n = 5) were stored in distilled water at 37°C for 24 h, embedded in self-curing epoxy resin (Epon 812, Nisshin EM Corp., Tokyo, Japan), and stored at 37°C for a further 12 h. Embedded specimens were sectioned perpendicularly, and then the surfaces of the cut halves were polished with an Ecomet 4/Automet 2 (Buehler), using SiC papers of successive grit sizes of #180, #320, #600, #1,200, #2,000 and #4,000. The surface was finally polished with a soft cloth using diamond paste (Buehler) with a grit size of 1.0 μm. SEM specimens were dehydrated in ascending concentrations of tert-butanol (50% for 20 min, 75% for 20 min, 95% for 20 min, and 100% for 2 h), and then transferred to a critical-point dryer for 30 min. These polished surfaces were etched for 30 s using an argon ion-beam (Type EIS-200ER, Elionix Inc., Tokyo,

Japan) directed perpendicularly to the surface at an accelerating voltage of 1.0 kV and an ion current density of 0.4 mA/cm^2. The surfaces were coated with a thin film of gold in a vacuum evaporator (Quick Coater Type SC-701, Sanyu Electron Corp., Tokyo, Japan) and analysed using a SEM (ERA 8800FE, Elionix Inc.) with an operating voltage of 10 kV.

6. Statistical analysis

A two-way ANOVA and Tukey's post hoc test were used for analysis of SBS data, and Fisher's exact test was used to statistically analyse the failure mode. A one-way ANOVA and Tukey's post hoc test were used for SFE and contact angle data. All statistical analyses were conducted using a commercial statistical software package (SPSS Statistics Base, International Business Machines, Armonk, NY, USA) at a significance level of 0.05.

Results

1. SBS measurements

The enamel SBS of the adhesive systems with and without OIL are shown in Table 2. There were no significant differences in the SBSs of SM and CS with or without OIL. However, the SBSs of CB and SU with OIL were significantly higher than those without OIL.

2. Failure mode analysis of the de-bonded specimens

The failure type after SBS tests of the four adhesive systems with and without an OIL are shown in Table 2. Fisher's exact test did not show statistically significant differences in failure mode depending on the type of adhesive, or presence or absence of OIL, and the predominant failure mode in all groups was adhesive failure.

3. SFE measurements

The SFE characteristics for the cured adhesives with and without OIL are shown in Table 3. The SFE (γ_S), polarity force (γ_S^p), and hydrogen-bonding force (γ_S^h) of cured adhesive with OIL were significantly higher than those of cured adhesives without OIL. In addition, the γ_S, γ_S^p, and γ_S^h of SM and CS with OIL were significantly higher than those of CB and SU with OIL.

4. SEM observations

SEM observations of the enamel-resin interfaces are shown in Fig. 1. The enamel-resin interfaces of all adhesive systems showed excellent adaptation to surface structure, regardless of the presence of an OIL. For the specimens with OIL, the approximate mean thickness of the adhesive layer was 30 μm for SM and CS, and 10 μm for CB and SU. By contrast, for the specimens without OIL, the approximate mean thickness of the adhesive layer was around 10 μm for SM and CS, and 4 μm for CB and SU.

Discussion

The present study indicates that the enamel SBSs of SM and CS was not significantly different in the presence and absence of OIL. However, the SBSs of CB and SU with OIL were significantly higher than those without an OIL. Therefore, the null hypothesis that there would be no differences in enamel SBS of adhesive systems with and without OIL should be rejected. The single-step self-etch adhesive system (CB) and universal adhesive system (SU) showed stronger bonds with OIL. In contrast, the presence of OIL had no effect on the enamel SBS of a three-step adhesive system (SM) or the two-step self-etch primer adhesive system (CS). The degree and depth of oxygen inhibition of light-cured resin-based materials are influenced by multiple factors (2,3,19-23). Unlike SM and CS, CB and SU contain water to ensure ionization of the acidic

functional monomers. Therefore, the SBSs obtained in the current study might have been influenced by the chemical characteristics of the OIL formed by different adhesive systems.

Generally, the SFE of organic substances is defined as the sum of the dispersion force (γ_S^d), polarity force (γ_S^p) and hydrogen-bonding force (γ_S^h) in Kitazaki-Hata theory. The present study indicated that the γ_S^d of the cured adhesive surfaces remained constant (40.4 – 40.6 mN/m), regardless of the presence of OIL, and there were no significant differences seen in the γ_S^d between the different types of adhesive system. This might be attributed to the adsorption of the so-called atmospheric contamination layer. It has been reported that the γ_S^d of oxidized surfaces measured using this method were approximately 40 mN/m, whereas those of surfaces coated with polytetrafluoroethylene were approximately 20 mN/m (27). The present study indicated that the γ_S, γ_S^p, and γ_S^h of cured adhesives with OIL were significantly higher than those without OIL. The γ_S^p, which reflects polar interactions, and the γ_S^h, which relates to water and hydroxyl components, together measure hydrophilic interactions (18). Monomers in adhesives can be categorized as either cross-linking or functional monomers (28). The latter contain at least one polymerizable group plus the functional group. Functional monomers can serve additional purposes compared with cross-linking monomers, such as wetting and demineralizing tooth substrate (29), and have the potential for chemical bonding to hydroxyapatite (30). The different chemical groups of the monomer greatly influence polarity and hydrophilicity. It is reported that functional monomers of adhesives show greater hydrophilicity than cross-linking monomers (31). It is thought that these hydrophilic functional monomers interact with tooth substrates and form intermonomer bonds with crosslinking monomers, increasing the hydrophobicity of the cured adhesive after optimal polymerization. Therefore, if the reaction of monomers in adhesive systems with the substrates and polymerization both progress to completion, there should be few

hydrophilic monomers remaining in the cured adhesive. Accordingly, the hydrophilicity of adhesive without OIL should decrease, as seen in the results of the present study. Conversely, incomplete polymerization may lead to residual functional monomers within the adhesive. Therefore, oxygen in air impaired the cross-linking within the OIL of cured adhesives, and this led to the higher γ_S, γ_S^p, and γ_S^h.

The γ_S, γ_S^p, and γ_S^h of SM and CS with an OIL were significantly higher than those of CB and SU with an OIL. This may be attributed to differences in the degree of polymerization of OIL among adhesives. Furthermore, SEM images revealed thicker OILs in SM and CS compared with CB and SU, suggesting that the depth of oxygen inhibition also depends on the type of adhesive. Taken together, these results suggested that the cured adhesive in single-step self-etch and universal adhesive systems exhibited higher hydrophobicity than did three-step and two-step self-etch primer systems. According to the results of this study, the other null hypothesis, that the SFE characteristics of the OIL were not influenced by the type of adhesive system, can also be rejected.

The results of this study indicated that the presence of an OIL enhanced the enamel SBS of single-step self-etch and universal adhesive systems, but had no influence on the SBS of three-step adhesive and two-step self-etch primer systems. In addition, the SFEs of cured adhesives with an OIL were significantly higher than those without an OIL. The SFE characteristics of the OIL of adhesives were different depending on the type of adhesive. Further research is needed to determine the properties of OILs produced by various adhesives and to assess whether these differences affect clinical performance.

Conclusion

1. The presence of an OIL enhanced the enamel SBS of single-step self-etch and universal adhesive systems, but had no influence on the SBS of three-step and two-step self-etch adhesive sytems.

2. The SFEs of cured adhesives with an OIL were significantly higher than those without an OIL. The SFE characteristics of the OIL of adhesives were different depending on the type of adhesive.

3. The thickness of the OIL on adhesive systems was different depending on the adhesive system, and the OILs of three-step adhesive and two-step self-etch primer systmes were thicker than those of single-step self-etch and universal adhesive systems.

References

1. Van Landuyt KL, Cardoso MV, De Munck J, Peumans M, Mine A, Lambrechts P, Van Meerbeek B (2009) Optimization of the concentration of photo-initiator in a one-step self-etch adhesive. Dent Mater 25, 982-988.

2. Aadrzehewska E (2001) Polymerization kinetics of multifunctional monomers. Prog Polym Sci 26, 605-665.

3. Lee TY, Guymon CA, Jönsson ES, Hoyle CE (2004) The effect of monomer structure on oxygen inhibition of (meth) acrylates photopolymerization. Polymer 45, 6155-6162.

4. Kim JS, Choi YH, Cho BH, Son HH, Lee IB, Um CM, Kim CK (2006) Effect of light-cure time of adhesive resin on the thickness of the oxygen-inhibited layer and the microtensile bond strength to dentin. J Biomed Mater Res B Appl Biomater 78, 115-123.

5. Dall'oca S, Pappacchini F, Goracci C, Cury AH, Suh BI, Tay FR, Polimeni A, Ferrari M (2007) Effect of oxygen inhibition on composite repair strength over time. J Biomed Mater Res B Appl Biomater 81, 493-498.

6. Kupiec KA, Barkmeier WW (1996) Laboratory evaluation of surface treatments for composite repair. Oper Dent 21, 59-62.

7. Suh BI (2004) Oxygen-inhibited layer in adhesion dentistry. J Esthet Restor Dent 16, 316-323.

8. Endo T, Osada T, Finger WJ, Hoffmann M, Kanehira M, Komatsu M (2007) Effect of oxygen inhibition of self-etching adhesives on enamel-dentin polymer bond. J Adhes Dent 9, 33-38.

9. Li J (1997) Effects of surface properties on bond strength between layers of newly cured dental composites. J Oral Rehabil 24, 358-360.

10. Endo T, Finger WJ, Hoffmann M, Kanehira M, Komatsu M (2007) The role of oxygen inhibition of a self-cure resin composite bonding. Am J Dent 20, 157-160.

11. Hashimoto M, Fujita S, Endo K, Ohno H (2009) In vitro degradation of resin-dentin bonds with one-bottle self-etching adhesives. Eur J Oral Sci 117, 611-617.

12. Miyazaki M, Tsujimoto A, Tsubota K, Takamizawa T, Kurokawa H, Platt JA (2014) Important compositional characteristics in the clinical use of adhesive systems. J Oral Sci 56, 1-9.

13. Pashley DH, Tay FR, Breschi L, Tjäderhane L, Carvalho RM, Carrilho M, Tezvergil-Mutlay A (2011) State of the art etch-and-rinse adhesives. Dent Mater 27, 1-16.

14. Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, De Munck J, Van Landuyt KL (2011) State of the art of self-etch adhesives. Dent Mater 27, 17-28.

15. Cardoso MV, De Almeida Neves A, Mine A, Coutinho E, Van Landuyt K, De Munck J, Van Meerbeek B (2011) Current aspect on bonding effectiveness and stability in adhesive dentistry. Aust Dent J 56, 31-44.

16. Tsujimoto A, Iwasa M, Shimamura Y, Murayama R, Takamizawa T, Miyazaki M (2010) Enamel bonding of single-step self-etch adhesives: influence of surface free energy characteristics. J Dent 38, 123-130.

17. Tsujimoto A, Fischer N, Barkmeier W, Baruth A, Takamizawa T, Latta M, Miyazaki M (2017) Effect of reduced phosphoric acid pre-etching times on enamel surface characteristics and shear fatigue strength using universal adhesives. J Adhes Dent 19, 267-275.

18. Tsujimoto A, Barkmeier WW, Takamizawa T, Wilwerding TM, Latta MA, Miyazaki M (2017) Interfacial characteristics and bond durability of universal adhesive to various substrates. Oper Dent 42, e59-e70.

19. Rueggeberg FA, Margeson DH (1990) The effect of oxygen inhibition on an unfilled/filled composite system. J Dent Res 69, 1652-1658.

20. Finger WJ, Lee KS, Podszun W (1996) Monomers with low oxygen inhibition as enamel/dentin adhesives. Dent Mater 12, 256-261.

21. Shawkat ES, Shortall AC, Addison O, Palibn WM (2009) Oxygen inhibition and incremental layer bond strengths of resin composites. Dent Mater 25, 1338-1346.

22. Burtscher P (1993) Stability of radicals in cured composite materials. Dent Mater 9, 218-221.

23. Gauthier MA, Stangel I, Ellis TH (2005) Oxygen inhibition in dental resins. J Dent Res 84, 725-729.

24. Asumussen E, Peutzfeldt A (1998) Surface free energy characteristics of adhesive monomer. Dent Mater 14, 21-28.

25. International Organazation for Standardization (2013) Dentistry － Adhesion － Notched-edge shear bond strength test. ISO 29022; 2013, Geneva.

26. Hata T, Kitazaki Y, Saito T (1987) Estimation of the surface energy of polymer solids. J Adhes 21, 177-194.

27. Nojiri K, Tsujimoto A, Suzuki T, Shibasaki S, Matsuyoshi S, Takamizawa T, Miyazaki M (2015) Influence of light intensity on surface-free energy and dentin bond strength of single-step self-etch adhesives. Dent Mater J 34, 611-617.

28. Van Landuyt KL, Yoshida Y, Hirata I, Snauwaert J, De Munck J, Okazaki M, Suzuki K, Lambrechts P, Van Meerbeek B (2008) Influence of chemical structure of functional mono-mers on their adhesive performance. J Dent Res 87, 757-761.

29. Van Landuyt KL, Snauwaert J, Peumans M, De Munck J, Lambrechts P, Van Meerbeek B (2008) The role of HEMA in one-step self-etch adhesives. Dent Mater 24, 1421-1429.

30. Yaguchi T (2017) Layering mechanism of MDP-Ca salt produced in demineralization of enamel and dentin apatite. Dent Mater 33, 23-32.

31. Feitosa VP, Ogliari FA, Van Meerbeek B, Watson TF, Yoshihara K, Ogliari AO, Shinhoreti MA, Correr AB, Cama G, Sauro S (2014) Can the hydrophilicity of functional monomers affect chemical interaction?. J Dent Res 93, 201-206.

Tables and Figures

Table 1: Adhesive systems used in this study			
Adhesive system (Code)	**Type of adhesive**	**Material (Lot No.)**	**Main conponents**
Scotchbond Multipurpose (SM)	Three-step adhesive system	Etchant (N511786)	35% H_3PO_4
		Primer (N547824)	HEMA, polyalkenoic acid polymer, water
		Adhesive (N494505)	Bis-GMA, HEMA, tertiary amines, photoinitiator
Clearfil SE Bond (CS)	Two-step self-etch primer system	Primer (5L0092)	MDP, HEMA, hydrophilic aliphatic dimethacrylate, water, initiator, N,N-diethanol-p-toluidine
		Adhesive (5K0146)	MDP, HEMA, Bis-GMA, hydrophobic aliphatic dimethacrylate, initiator, accelerators, silica, N,N-diethanol-p-toluidine
Clearfil tri-S Bond (CB)	Single-step self-etch adhesive system	Adhesive (00038B)	MDP, Bis-GMA, HEMA, ethanol, water, initiator, silanated colloidal silica
Scotchbond Universal Adhesive (SU)	Universal adhesive system	Adhesive (41254)	Bis-GMA, HEMA, MDP, ethyl methacrylate, methyl-reaction products with decanediol and phosphorous oxide, propenoic acid, copolymer of acrylic and itaconic acid, dimethylaminobenzoate, methyl ethyl ketone, ethanol, water, camphorquinone, silane treated silica
HEMA, 2-hydroxyethyl methacrylate; Bis-GMA, 2,2-bis[p-(2-hydroxy-3-methacryloxy propoxy)phenyl]propane; MDP, 10-methacryloyloxydecyl dihydrogen phosphate.			

Table 2: Enamel shear bond strength of different adhesives with or without an oxygen inhibition layer			
Code	Oxygen inhibition layer	Shear bond strength (MPa)	Failure mode
SM	with	38.8 (5.3)[a]	[13/2/0/0][a]
SM	without	35.8 (5.8)[a]	[12/1/2/0][a]
CS	with	34.3 (4.7)[a]	[13/0/2/0][a]
CS	without	33.2 (5.4)[a]	[13/1/1/0][a]
CB	with	22.1 (4.5)[b]	[15/0/0/0][a]
CB	without	17.2 (4.8)[c]	[15/0/0/0][a]
SU	with	25.4 (2.7)[b]	[14/1/0/0][a]
SU	without	19.8 (2.8)[c]	[15/0/0/0][a]

Values are given as mean (SD), in MPa (n = 15). The same lowercase letter in same column indicates no significant difference ($p > 0.05$). Values in square brackets indicate failure mode [adhesive failure/cohesive failure in enamel/cohesive failure in resin/mixed failure].

Table 3: Surface free energy characteristics of different adhesives with or without an oxygen inhibition layer					
Code	**Oxygen inhibition layer**	γ_S	γ_S^d	γ_S^p	γ_S^h
SM	with	64.4 (1.9)[a]	40.3 (0.2)[a]	9.9 (0.8)[a]	14.2 (1.2)[a]
	without	52.9 (1.4)[b]	40.4 (0.2)[a]	6.0 (0.5)[b]	6.5 (0.9)[b]
CS	with	63.3 (1.8)[a]	40.4 (0.2)[a]	9.8 (0.7)[a]	13.1(1.3)[a]
	without	52.4 (1.4)[b]	40.4 (0.2)[a]	5.8 (0.5)[b]	6.2 (1.0)[b]
CB	with	59.6 (2.0)[c]	40.5 (0.2)[a]	8.0 (0.5)[c]	11.1 (1.1)[c]
	without	56.6 (2.1)[d]	40.6 (0.2)[a]	7.3 (0.4)[d]	9.7 (1.0)[d]
SU	with	60.1 (1.6)[c]	40.6 (0.2)[a]	8.1 (0.6)[c]	11.4 (1.0)[c]
	without	55.2 (2.1)[d]	40.6 (0.3)[a]	6.8 (0.4)[d]	7.8 (0.9)[d]

γ_S, SFE of the solid; γ_S^d, dispersion force of the solid; γ_S^h, hydrogen bonding force of the solid, γ_S^p, polarity of the solid. Values are given as mean (SD), in mN m^{-1} (n = 10). Same superscript lower-case letter in same column indicates no significant difference ($p > 0.05$).
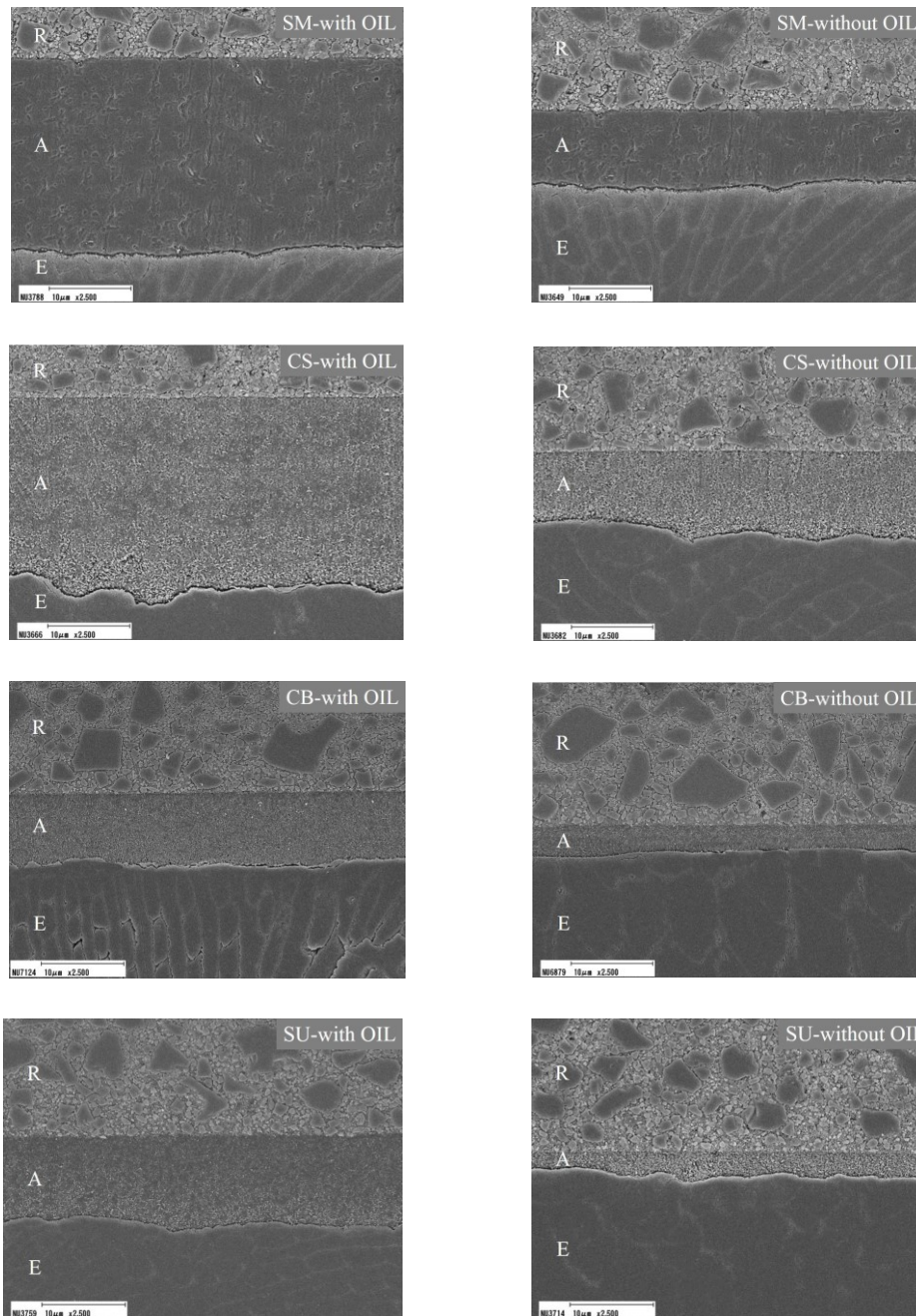
Fig. 1: Representative SEM images of the enamel-resin interface (original magnification, ×2,500). A, adhesive; E, enamel; R, resin composite.